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INDICATORS AND TEST-PAPERS

THEIR SOURCE, PREPARATION, APPLICATION, AND TESTS FOR SENSITIVENESS

A Résumé of the Current Facts regarding the Action and Application of the Indicators and Test-papers which have been Proposed from Time to Time, and are in Present Use in Chemical Manipulations

WITH A

TABULAR SUMMARY OF THE APPLICATION OF INDICATORS

DESIGNED FOR THE USE OF CHEMISTS,
PHARMACISTS, AND STUDENTS

BY

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PREFACE

MUCH has been written on indicators within the last twenty years in the various journals, etc., devoted to chemistry and pharmacy. No systematic arrangement, however, appears to have been made of the facts recorded by a host of observers, which would present the busy worker with the widely scattered information in the form of a succinct yet comprehensive compilation.

The purpose of this work is, hence, to present an up-to-date résumé of the knowledge regarding the various substances which have been proposed for use from time to time as indicators, so far as their preparation, properties, application, etc., are concerned. Such a résumé appears all the more desirable, because of the increasing value of titrimetric methods, in consequence of their ease and rapidity of application, and more particularly because, with the increase of knowledge regarding the action of the various acids, alkalies, and reaction-products on indicators, arises the recognition of the necessity for a correct choice of the indicator most suitable for a given case.

The subject-matter has been largely compiled from the files of the various chemical journals, reports of the meetings of chemical and pharmaceutical societies, and works on chemistry, in the English, French, German, Spanish, and Italian languages; and it has been arranged in the form believed to best meet the requirements of the chemist, pharmacist, and student.

In the section devoted to Indicators only those substances have been discussed which are used purely and simply as such; under Test-papers, however, it has been deemed desirable to include all regarding which any reference could be found.

ALFRED I. COHN

NEW YORK, July, 1899

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GENERAL CONSIDERATIONS

An indicator, in chemistry, is a substance used for the purpose of affording ocular evidence regarding the condition of acidity, alkalinity, or neutrality existing in a liquid; or of indicating the termination of a reaction, whereby the quantity of the reagent, the titrating liquid, used, enables the quantity of the reacting substance present in the liquid to be stoichiometrically determined. In titrimetric determinations the indicator effects its object when, without taking any immediate part in the reaction going on, it becomes affected the moment the liquid becomes neutral, acid, or alkaline, and indicates this moment by a change of color or the formation of a precipitate, because of its having also entered into a reaction with the reagent, but only after that between the reagent and the substance under investigation is complete and at an end.

The value of an indicator depends on its sensitiveness to the action of acids and alkalies, and on the difference in the intensity and sharpness of change in the colors afforded by them. Many plants yield coloring-matters which are sensitive to the action of acids and alkalies, and many synthetically produced dyes are similarly sensitive. The number of substances that may serve as indicators is, hence, a comparatively large one. Not all of them are, however, equally serviceable. Some are not sufficiently sensitive; in some the color-changes are not sufficiently pronounced; in others, the color-changes cannot be observed in colored fluids; the action of others is interfered with, or even neutralized, by products of the reaction going on, or by certain chemicals which may be present; many, again, are only applicable to special purposes, etc. To be of practical value for general use, therefore, an indicator must not only be sufficiently sensitive to sharply and decidedly show the moment when the liquid passes into a neutral, acid, or alkaline state, but the change of color must also be rapid and pronounced, the difference in the tints afforded must be as extreme as possible, and the color-changes must be as free as possible from intermediate tints, and be afforded by a minimum quantity of the indicator.

An ideal indicator that will answer for every purpose has not as yet been found. Every one so far used has some drawback, and no one can be relied on absolutely in all cases. Litmus, for instance, which may be considered as being of most general utility, may be used with organic acids or ammonia, and also for caustic alkalies in hot or cold liquids; but with carbonates or bicarbonates the titrations must be carried out in *boiling* liquids; methyl orange, on the other hand, is useful *only* in cold liquids, and when organic acids and nitrites are absent; phenolphtalein may be used in hot or cold liquids, but ammonia or ammoniacal salts must be absent; rosolic acid, again, while useful in hot or cold liquids, cannot be employed when ammonia or organic acids are present; while cochineal tincture is applicable in both hot and cold liquids, but only when acetic acid and metallic salts are absent, etc.

When the chemical characteristics of the indicators are closely studied, it soon becomes apparent that the latter possess more or less acid properties, as a rule, and fall naturally into three classes, which, though fairly distinct from each other, are not separated by decided lines of demarcation, but tend to merge, each into its next nearest neighbor. These three groups may be defined as follows:

1. *Indicators capable of forming fairly stable salts.* The members of this group are most sensitive to alkalies, and comprise such indicators as cochineal, congo-red, dimethylamidoazobenzene, iodeosine, lacmoid, methyl orange, etc.

2. *Indicators possessing very faint acid properties, and yielding salts which are very unstable, and which are, readily decomposed by the hydrolytic action of*

water. The individuals of this class are particularly sensitive to acids, and comprise such indicators as curcuma, flavescin, phenolphtalein, etc.

3. *Indicators occupying a place midway between the other two classes.* The indicators of this class are somewhat stronger acids than those of the second class, and are fairly sensitive to both acids and alkalies. The class comprises such indicators as fluorescein, gallein, hematoxylin, litmus, phenolphtalein, rosolic acid, etc.

CORRECT CHOICE OF INDICATORS

THE division into groups, or classes, enables a correct judgment, which is of great importance, to be formed with facility regarding the proper choice of the indicator most suitable for the work in hand, according to the acid or basic radical to be determined. For instance, for titrating weak acids, a glance at the various classes will show that the individuals of the second class are best adapted for this purpose; again, weak bases, it will be seen, would be best titrated by the indicators of the first class; whereas strongly acid or basic substances would be titratable by means of any of the indicators.

The majority of the indicators are, chemically considered, either weak acids or salts of weak acids, the remainder being more or less basic. In some the free acid is colorless, whereas the salt is colored, as, for instance, in phenolphtaleïn; in some the color of the salt lacks intensity to such an extent as to be comparatively inappreciable in the dilution in which titrations are ordinarily effected, whereas the free base is very highly colored, as, for instance, in methyl orange; in others, again, both the free acid and free base have high tinctorial power and decided, but different, colors, as, for instance, litmus or lacmoid.

The reasons governing the selection of an indicator may be found in the statements just made. For instance, the indicators of class 1, which form quite stable compounds, require strong acids to decompose these compounds, i.e., to replace the rather strong acids combined with the bases. For example, methyl orange, which is, chemically, the sodium salt of dimethylamidoazobenzene-sulphonic acid, is quite stable, and the fairly strong acid radical can only be partially replaced by organic acids, like acetic, tartaric, lactic, etc., whereas still weaker acids, like carbonic, boric, oleic, hydrocyanic, etc., are entirely unable to replace it. It is for this reason that the basic radicals of salts of the latter acids can be readily titrated just as though only bases were present; salts of the former acids could not, however, be titrated at all, for, since their acid radicals can only partially replace the acid radical of the indicator, the end reaction will be indefinite because of a mixture of colors.

On the other hand, the indicators of the second class, which possess but feeble acid properties, and whose salts, as already stated, are very unstable, are decomposed by almost all acids, even the weakest. Hence, phenolphtalein, a representative of this class, would be serviceable for many alkaloids, such as quinine, brucine, cocaine, cinchonine, and quinidine, and bases like aniline and pyridine, because, as these do not yield a red color with phenolphtalein, any acid combined with the alkaloids or bases may be titrated directly with alkali, just as if no alkaloid or base were present, but only free acid.

It will thus be seen that the correct choice of an indicator is of some importance.

APPLICATION OF INDICATORS

In employing an indicator, care should be exercised that a minimum quantity of the indicator be used consistent with the production of a decided color and sharp change of tint. It is needful, however, that not too little be taken for the volume of liquid to be titrated, because in too great dilutions a decided difference will be observed in the readings, due to the dissociation in the liquid of the compound formed between the indicator and the titrating acid or alkali. This dissociation will occasion intermediate tints, and more acid or alkali than is normally necessary will have to be added in order to secure a pure monotint.

On the other hand, an excess of the indicator must also be avoided, because then the sensitiveness is lessened. If too much is present, more acid or alkali must be added than would be otherwise necessary, because a minimum would not convert all of the indicator into a salt, or liberate its free base, and in such a case intermediate tints would also be produced; and could only be overcome by adding more titrating fluid, thus again rendering the readings inaccurate in very fine work.

In titrimetric operations, therefore, definite quantities of indicator and titrated solution should be employed; moreover, at least three blank experiments should be made to determine the quantities of acid or alkali, or even of both, required to effect the color-changes. The mean of the readings so obtained should be noted on the labels of the bottles holding the indicator-solutions, and should be deducted from the readings obtained in practice. New blank determinations should be made with every fresh lot of indicator-solution prepared, because in many cases considerable variation exists between different lots of indicators. It is advisable also to test from time to time the sensitiveness of the indicator-solutions, because some are prone to deteriorate on keeping for a length of time. By attention to these details greater accuracy is attained, and the errors due to personal equation are largely minimized.

In performing titrations, shallow porcelain dishes will be found most generally useful in practice. In these the color-reactions are most clearly observed, and the end of the reactions most readily determined. The close of the reaction may be considered to be reached when the color occasioned by a drop of the acid- or alkali solution, as it falls into the liquid being titrated, no longer changes, but remains permanent, and can no longer be distinguished from that of the liquid in general.

Glass beakers may also be used, but they should be placed on a white sheet of paper, and a similar sheet placed behind, in order to facilitate the observation of the color-changes. The beakers have the advantage in cases where fluorescent indicators are used; i.e., where the fluorescence is made use of in determining the end of the reaction. On the other hand, where it is necessary to boil the titrated liquid to expel carbon dioxide or hydrogen sulphide, the porcelain dishes are most suitable (although the beakers are used by many), because they are less likely to break, and, which is more important, are far less likely to yield traces of alkali to the boiling liquid, as many kinds of glass are very prone to do and thereby introduce a source of error in the readings. It is, hence, very important that this point be not forgotten or overlooked when titrating boiling liquids.

The color-changes of indicators are generally best observed by daylight. There are cases, however, when artificial light is the more suitable for use, as, for instance, with cochineal, of which the change of color from a yellowish-red to a violet-red is most clearly observed by gaslight or the sodium flame (see page 53).

Another point to which due regard should be paid is the sensitiveness of the operator to certain colors. It is often found that in the case of some operators their eyes become much more rapidly fatigued by one color than by another. Hence an indicator should be chosen, so far as is consistent with the work to be done, which the operator is best able to see well without undue fatigue. Where an extended series of titrations is being carried out it is even advisable to change the indicator from time to time in order that the eye should not lose its sensitiveness to the color-changes.

ACTION OF INDICATORS IN OTHER THAN AQUEOUS LIQUIDS

ALL the foregoing considerations have been based on the employment of aqueous fluids for obtaining the various color-reactions. Different phenomena are observed, however, when other fluids are used. It had long ago been observed that when highly alcoholic fluids were used great discrepancies were noted between the readings afforded in these and in aqueous liquids. It has been found, in fact, that the influence exerted by alcohol is sufficient to be the cause of serious errors in volumetric work, unless due attention be given to the variation in the readings caused by it. The variation increases practically uniformly with the increase in alcoholic strength, being greatest in strongly alcoholic liquids, and smallest in liquids containing but a little alcohol.

The variation in the readings may be readily proved. For instance, when cochineal, brazilin, hematoxylin, lacmoid, or litmus are used with alcohol, an increased quantity of alkali is required beyond what would ordinarily suffice to afford the change in color; i.e., alcohol appears to act the part of an acid. On the other hand, with methyl orange, dimethylamidoazobenzene, and the various tropæolins, a large excess of acid is required above what usually suffices to yield the color-changes; i.e., toward these indicators the alcohol appears to act like so much alkali.

These phenomena have been recently studied by John Waddell, who showed also that the addition of ether, benzene, or chloroform, and in some cases of acetone and alcohol, to aqueous or alcoholic solutions in which fluorescein, phenacetolin, cyanine, phenolphtalein, paranitrophenol, methyl orange, turmeric, lacmoid, and corallin were present in the form of their salts, caused a change in color to that of the free acid or base. This change of color was shown to take place more readily when the indicator was present in the form of its acetate than when in that of its hydrochlorate; and when in the form of its ammonium salt than when in that of its potassium salt.

For instance, a concentrated acetone solution of phenolphtalein is scarcely colored by a large excess of strong ammonia water; but the addition of water immediately determines the appearance of the intense red characteristic of alkaline solutions.

Methyl orange dissolved in acetic acid affords a red solution, the color of which is changed to yellow on the addition of alcohol or acetone, and restored to red again on adding water.

Cyanine yields a colorless aqueous solution, but its acetic-acid solution is changed to blue on the addition of alcohol or acetone, and the color is discharged on adding water.

The other indicators were found to yield similar reactions. The probable reason of these color-changes is to be found in the assumption that the very weak acids and bases, of which indicators are constituted, are very much less dissociated in organic solvents than in water, and that their salts become almost entirely hydrolyzed when these organic solvents are added to aqueous solutions of the salts, in spite of the fact that the concentration of the ions of the water is also reduced somewhat. Hence when these solvents are added they liberate the free indicator-acid or base, which exhibits its usual color; and they will the more readily liberate the indicator-acid or base if these are combined with a weak base or acid. By observing whether the change of color occurred on adding the solvents to the acid or to the alkaline solution of the indicator, or to both solutions, it was possible to determine whether the indicator acts as an acid or base, or if as both. From the observations made, it was determined that phenolphtalein, paranitrophenol, and turmeric act like acids; that cyanine, methyl orange, and lacmoid act like bases; and that fluorescein, phenacetolin, and corallin act both as acids and bases.

However this may be, it more clearly shows that an intelligent choice of an indicator for the work in hand, and in relation to the character of the fluid employed and the salts formed during the titration, is exceedingly important, and is not to be underrated.

THEORY OF THE ACTION OF INDICATORS

THE theory of how the color-changes are produced in indicators has been the subject of considerable study by a number of observers, chief among whom may be mentioned Nernst and Ostwald. These color-changes are ascribed to the dissociation and regeneration consequent on the addition of some foreign substance to the indicator. It has been shown that in very dilute solution, compounds undergo dissociation, or ionization, into their constituent radicals, or ions, as they are called. Compounds yielding hydrogen ions are termed acids; those yielding hydroxyl (OH) ions are designated as bases; and it is the color-reactions which these hydrogen or hydroxyl ions afford with certain dyes which are utilized, and which render the latter of service as indicators.

Any compound is suitable for use as an indicator, provided it possesses acid or basic properties, and provided that when dissociated, or ionized, its negative ion, or anion, has a color different from that which it has when in a non-dissociated state. The compound must not, however, be a strong acid or base, because these are ionizable while in a free state, in which condition no change of color occurs on neutralization. On the other hand, again, a very weak acid or base is more or less undissociated when in solution, and is ionized only after conversion into a neutral salt by neutralization. For instance, paranitrophenol, which is an acid indicator, exists in solution in the form of undissociated, colorless molecules, yet the anion is intensely yellow in color. Paranitrophenol is, however, subject to a slight dissociation in dilute solution, but this is entirely overcome when a trace of a stronger acid is present, when the solution remains colorless. If a base is now added, however, a highly ionizable salt of paranitrophenol is formed, and the solution will then exhibit the intense yellow color of the ion. Cyanine, on the other hand, is a basic indicator, the ions of which are colorless, whereas the non-dissociated salt has a color—exactly the reverse as with paranitrophenol. Other indicators, again, as lacmoid or litmus, exhibit a color both in the ionized and non-ionized state, but the colors in both conditions are different.

It may be readily conceived that the smaller the quantity of hydrogen ions or hydroxyl ions required to effect a change of color, and the greater the difference in the colors produced, the more sensitive and useful will the substance be for the purposes of an indicator. In addition, its value will also be dependent on its dissociability. For instance, supposing the indicator to be a very weak acid, it will be easily understood that another acid of moderate, or even small, ionization will readily yield up hydrogen to it, and so afford the color-change on its passage from the ionized to the non-ionized state. Such a weakly acid indicator could, therefore, be expected to be particularly useful for titrating weak acids, like acetic, tartaric, etc., but, on the other hand, be suitable for strong bases only, because with weak ones it would form weak salts readily dissociable by the hydrolytic action of the solvent. This dissociation would thus yield mixed colors which would tend to render the final color-change difficult of accurate determination.

As an example take phenolphtalein, which is a weakly acid indicator, and which is non-dissociated and colorless when in the acid state. Its alkali salt is, however, immediately ionized as soon as it is formed, the red color of the ion then becoming apparent, only again to disappear on the addition of the slightest excess of an acid because of the liberation of the phenolphtalein. Now, while the fixed alkalies readily yield ionizable salts with phenolphtalein, ammonia does not, because it is too weak a base *per se* to yield with the indicator a salt which is stable in very dilute solutions, and moreover a considerable excess would be required, in consequence, to overcome the hydrolytic action of the water. Thus is accounted the imperfect and incomplete change of color of phenolphtalein when ammonia or ammoniacal salts are present, and why the color is in fact only visible when a considerable excess of the base is added.

Methyl orange, on the other hand, is a moderately strong acid indicator, and its ion is yellow, whereas the non-ionized indicator is red. Methyl orange dissociates very readily in dilute solutions, and is hence prone to yield a mixed color, between red and yellow. The addition of a trace of a stronger acid than it, lessens the ionization, and restores the red color; a trace of alkali, again, yields a highly ionizable salt, when the yellow color of the ion is at once seen. When a weak and but slightly ionizable acid is added to the methyl-orange solution, the hydrogen ions of the acid given up in excess of what is required for neutralization are insufficient to yield enough of a non-ionized salt to afford a decided red color; hence, unless an excess of such a weak acid is added, a decided reaction is unobtainable. This explains why methyl orange is unserviceable for titrating weak organic or other acids. With bases, however, the case is different, as with these the indicator yields definite salts, even with weak bases. These salts are but little prone to be hydrolyzed, and are, hence, capable of yielding sharp end-reactions.

Precisely similar considerations also apply to basic indicators; i.e., for titrating weak acids a highly ionized indicator is most serviceable, whereas weak bases require an indicator which is as weakly basic as possible.

The characteristic action of the acids and alkalies on plant pigments and dyes has also been explained by F. Mohr by the mechanical theory of affinity. According to the theory, the acids have a molecular oscillation different from that of the alkalies; the oscillations of the former are few in number and of considerable amplitude, whereas those of the latter are many and narrow. Mohr assumes that the acid and alkali impart each its own motion to the sensitive pigment. Since it is assumed that the colors also only exist on the theory of molecular vibration, the final color is directly referable, hence, to these vibrations. It has been shown that in the spectrum the greatest number of the oscillations of color-waves are found at the red end, and beyond it. Since it may be optically shown that the red rays oscillate less rapidly than do the violet ones, the amplitude of their vibrations must be greater, in order to account for the excess of heat evolved by them. From this it follows, then, that those substances which change the colors to red (acids) have similarly few vibrations but of considerable amplitude, and those which restore the colors (alkalies) numerous vibrations of small amplitude. The neutralization is the act wherein the dissimilar vibrations are made uniform in number and in amplitude; at the same time the vibrations are in part converted into heat which is given off during neutralization.

PART II

INDICATORS

ALIZARIN

$C_6H_4.2(CO).C_6H_2(OH)_2$

ALKALIES = Purplish-red ACIDS = Yellow

Synonyms: Dioxyanthraquinone; Dihydroxanthraquinone; Schaal's Indicator.

Source: Alizarin was first found in the roots of *Rubia tinctorum* Lin., madder, a herbaceous perennial indigenous to the Levant and Southern Europe, and cultivated in France, Holland, and Asia Minor. It was first isolated and named by Robiquet and Colin in 1826, although Kuhlmann in 1823 showed the existence of a crystalline coloring-matter in madder.

Alizarin does not exist in the roots as such, but in the form of ruberythrinic acid (Rochleder's), a glucoside which, on boiling with acids, yields alizarin and a glucose, as follows:

$$\underset{\text{ruberythrinic acid}}{C_{20}H_{22}O_{11}} = \underset{\text{alizarin}}{C_{14}H_8O_4} + \underset{\text{glucose}}{C_6H_{12}O_6} + H_2O$$

In 1847 Schunck isolated from madder a bitter principle which he named rubian, but which Rochleder considered to be an impure ruberythrinic acid having the formula $C_{16}H_{18}O_9$. This substance was also shown to be a glucoside which, on boiling with acids or alkalies, yielded alizarin and a glucose, presumably as follows:

$$\underset{\text{rubian}}{2C_{16}H_{18}O_9} + 6H_2O = \underset{\text{alizarin}}{C_{14}H_8O_4} + \underset{\text{glucose}}{3C_6H_{12}O_6}$$

Alizarin was also obtained synthetically by Gräbe and Liebermann in 1868 from anthracene, by first converting this substance into anthraquinone, and the latter then into anthraquinone dibromide (or dichloride), and finally heating the dibromide (or dichloride) with concentrated potassa-lye; the alizarin-potassa formed was then dissolved in water, and the alizarin precipitated by adding an acid.

More recently it has been shown that alizarin is also formed on heating phtalic anhydride with pyrocatechin and sulphuric acid to a temperature of 150° C. The reaction is expressed as follows:

$$\underset{\text{phtalic anhydride}}{C_6H_4(CO)_2O} + \underset{\text{pyrocatechin}}{H_2C_6H_2(OH)_2} = \underset{\text{alizarin}}{C_6H_4(CO)_2.C_6H_2(OH)_2} + H_2O$$

Preparation: The process generally employed for making alizarin is that patented in 1869 by Perkin, simultaneously with, yet independently of, Gräbe, Liebermann, and Caro. This process depends upon the conversion of pure anthraquinone into anthraquinone monosulphonate, this latter being then converted into a sodium salt. One part of this salt is then mixed with 3 parts of sodium hydrate, a little water and potassium chlorate added, and the mixture then heated for several days at a temperature of from 180° to 200° C. in closed vessels under pressure. The mass is then dissolved in water and decomposed by hydrochloric acid, the precipitated alizarin being finally well washed with distilled water.

It had been the accepted view for a long time that it was the anthraquinone disulphonate which, on fusion with the potassa, yielded the alizarin. It was pointed out by Perkin, however, in 1876, that this view was erroneous, and that the disulphonate was converted into isopurpurin and flavopurpurin, but that it was the monosulphonate which yielded the alizarin. On fusing the anthraquinone monosulphonate with potassa, the sulpho group is replaced by hydroxyl, oxyanthraquinone being formed. This latter, however, in the strongly alkaline mass, is rapidly oxidized to alizarin, small quantities of oxyanthraquinone-sulphonic acid and alizarin-sulphonic acid being simultaneously formed.

Rochleder obtained the alizarin by preparing an aqueous extract of madder, and precipitating with lead acetate. The lead precipitate, containing alizarin, purpurin, fat, and lead salts of other acids present in madder, is suspended in water and decomposed by a current of hydrogen sulphide. The precipitate, now containing, besides lead sulphide, only the alizarin, purpurin, and fat, is filtered off and boiled with alcohol. Water is then added to the alcoholic solution, and precipitates a yellow, gelatinous mass which soon becomes crystalline flocks consisting of alizarin and the fat, the purpurin remaining in solution. The fat is next removed by washing with cold ether, and the alizarin is finally recrystallized from hot ether.

L. Vilmorin obtained alizarin by heating garancin (obtained by the action of hot sulphuric acid on ruberythric acid) two or three times with an aqueous solution of pure ammonia alum, evaporating to dryness the filtered orange-red extract, and powdering the dry residue. This is then boiled with absolute alcohol or carbon disulphide, and the alizarin crystallized from the hot, filtered liquid.

Properties: Alizarin crystallizes from alcohol in the form of long, transparent, brilliant, reddish-yellow or orange-colored prisms with 3 molecules of water of crystallization. The crystals have a bitter taste, and are difficultly soluble in water, more so in boiling water; soluble in alcohol, ether, carbon disulphide, volatile and fatty oils, and in benzene, with yellow color. At 100° C. the crystals lose their water of crystallization; they melt at about 215° C., and solidify on cooling to a solid, reddish-brown crystalline mass; they sublime at from 215° to 225° C. as golden-yellow, shining prisms having a reddish reflection. With concentrated sulphuric acid alizarin yields a dark, yellowish-brown solution, precipitated by water. Boiled with dilute nitric acid it is converted into oxalic and phtalic acids, as follows:

$$\underset{\text{alizarin}}{C_{14}H_8O_4} + 2H_2O + O_{16} = \underset{\text{phtalic acid}}{C_8H_6O_4} + \underset{\text{oxalic acid}}{3C_2H_2O_4}$$

On boiling with ferric nitrate or chloride, only phtalic acid is formed.

Alizarin is colored violet in ammoniacal vapors, and dissolves in solutions of ammonia or of alkali carbonates with a violet-purple color. Alizarin dissolved in aqueous solutions of an alkali affords a solution which, at certain concentrations, possesses a deep purple color by transmitted light, and a pure blue by reflected light. When greatly diluted, the color of the solution is uniformly violet, and on adding an acid the alizarin is precipitated as orange-colored flocks.

Alizarin is soluble in a hot solution of alum, but precipitates again on cooling. With alumina and zinc oxide it yields handsome, red, insoluble lakes; with ferric oxide it gives a violet or black lake, and with red acetate a bright purple one. Its alcoholic solution yields with ferric acetate a dark purple, with cupric acetate a light purple, and with stannous chloride and ammonia a bright red, precipitate.

Application: Alizarin solution, for use as an indicator, is prepared by boiling an excess of alizarin in potassa solution, with a drop of carbolic acid added, and filtering off the excess of alizarin. Alkaline solutions are colored red, acid solutions yellow.

In using this indicator it is found best in practice to supersaturate the acid with standard alkali and titrate back with acid.

ALKANIN

$C_{15}H_{14}O_4$

ALKALIES = Blue   ACIDS = Red

Synonyms: Anchusin; Alkannin; Pseudalkannin; Alkanna Red; Anchusic Acid.

Source: Alkanin was first obtained by Pelletier, in 1818, from the bark of the root of *Anchusa tinctoria* L. (dyer's alkanet), one of the Boraginaceæ found growing in the Grecian Archipelago and in Southern Europe. Pelletier obtained it in an impure state, however, and named it "anchusin"; he calculated its formula to be $C_{17}H_{20}O_4$. Later on it received the name "anchusic acid," because of its acid-like properties, as it was found to yield neutral compounds with alkalies and alkaline earths, blue in color and soluble in alcohol and in ether.

Preparation: Bolley and Wydler were the first to obtain alkanin in a pure condition, in 1847. They obtained it as a dark-red, amorphous, resinous, brittle mass, by exhausting finely comminuted alkanet root with alcohol after previous treatment with water and drying. The alcoholic extract was acidulated with hydrochloric acid, the alcohol then evaporated, and the residue exhausted with ether; the ethereal solution was then washed by shaking with water, and the ether finally evaporated. They assigned to it the formula $C_{35}H_{40}O_8$. These observers were unable to confirm the statements previously made regarding the acid-like properties of alkanin, and hence simply named it "alkanna red."

Carnelutti and Nasini, however, appear to have shown that alkanin does possess the properties of a weak acid. They obtained the coloring-matter by exhausting commercial alkanin with petroleum ether, treating the latter with weak potassa lye, repeatedly shaking the indigo-blue solution with ether, which removes an onion-red substance, and finally precipitating the pure alkanin by a current of carbon dioxide. The precipitated alkanin was then dried in a vacuum, dissolved in ether, and the solution filtered and evaporated. Alkanin so obtained was found to possess the formula $C_{15}H_{14}O_4$, which is the one now generally accepted.

Commercially, alkanin is obtained by exhausting the dried, coarsely ground root-bark by percolation with benzin, evaporating the percolate to a small bulk on a water-bath at a temperature of from 60°

to 80° C., and spreading the residue on glass plates to dry.

Lepage obtained the alkanin by exhausting the alkanet-root bark with carbon disulphide, evaporating the solvent, and treating the residue with a 2-per-cent. sodium-hydrate solution at a temperature of 100° C. From the filtered indigo-blue solution so obtained the alkanin is precipitated by hydrochloric acid in slight excess, and, after standing for about 24 hours, is filtered off, washed with distilled water, and dried.

When using alcohol for extracting the alkanin it is necessary to slightly acidulate it with hydrochloric acid before evaporating the solvent, because, although the alcoholic solution of alkanin does not change color on heating, the alcoholic extract of the alkanet root does, and, on evaporation, yields a blackish-green residue which partially dissolves in water with a brown color, and leaves an insoluble portion which yields to ether a substance to which the name of "alkanna green" has been given, and which, according to Bolley and Wydler, is formed from alkanin by the replacement of one molecule of carbon dioxide in the latter by one molecule of water.

Properties: Alkanin occurs as a dark-red, amorphous, resinous powder, or amorphous masses of metallic luster. C. J. S. Thompson obtained from 5.25% to 6.02% from the root-bark.

Alkanin is insoluble in water, but is soluble in alcohol, ether, ligroin, chloroform, benzin, benzene, carbon disulphide, acetic acid, and in oils generally, yielding solutions having a handsome red color changed to blue by alkalies. It is also soluble with a blue color in solutions of the alkalies, from which it is precipitated by acids in the form of brownish-red flocks. Concentrated sulphuric acid dissolves it with a blue color; nitric acid oxidizes it to oxalic and succinic acids, and so does also a solution of bromine in alkalies. Alkanin melts at 60° C., and sublimes when carefully heated, yielding violet fumes which condense to form light flocks.

With alkalies and alkaline earths, alkanin yields blue compounds soluble in alcohol and in ether; its alcoholic solution yields with lead subacetate a grayish-blue precipitate; with stannous chloride, a carmine-red one; and with mercuric chloride a flesh-colored precipitate, whereas that obtained with stannic chloride is violet in color. Concentrated ammonia converts alkanin into alkanna green.

Application: Alkanin is used principally in the form of test-paper, a red and a blue being made.

These are described under Test-Papers.

ALPHA-NAPHTOLBENZEÏN

$2(C_6H_5.C)O.4(C_{10}H_6.OH)$

ALKALIES = Green ACIDS = Reddish-yellow

Preparation: Alpha-naptholbenzeïn is obtained by the interaction of 2 molecular weights of alpha-naphtol and 1 molecular weight of benzotrichloride. In practice it is found advisable to add sufficient benzene to moderate the reaction, which begins at the ordinary temperature, and may even become violent. The addition of the benzene also enables a much purer product to be obtained. After standing for 24 hours, the reaction is brought to a close by warming the mixture to 30° to 40° C.; the benzene and excess of benzotrichloride (if any) are then removed by a current of steam. The residue is purified by repeatedly dissolving it in soda-lye and precipitating with hydrochloric acid; the product is finally washed with distilled water and dried.

Properties: Alpha-naphtolbenzeïn occurs as a brown powder, insoluble in water, but soluble in alcohol. Its formula is as follows:

$$2(C_6H_5.C)O.4(C_{10}H_6.OH).$$

With alkalies it yields a green, with acids a reddish-yellow color.

Application: Alpha-naphtolbenzeïn was proposed by Zaloziecki as an indicator.

It is exceedingly sensitive to **carbonic acid,** and is, hence, inapplicable for **carbonates**; otherwise, it is equal to phenolphtalein in sensitiveness, and resembles the latter in action excepting that, on adding an acid to a carbonate, the change of color occurs before the acid salt is formed.

It acts with **mineral acids, hydrogen sulphide, sulphurous acids,** and **organic acids** like phenolphtalein.

Alpha-naphtolbenzeïn is much more sensitive to **acids** than to **alkalies,** hence it is best to always add an excess of alkali and titrate back with decinormal acid. One drop of a decinormal acid or alkali suffices to effect a distinct change from green to orange with acid, or orange to green with alkali.

For use a 1-per cent alcoholic solution is made; of this from 10 to 20 drops are added to 100 Cc. of the liquid to be titrated.

AZOLITMIN

$C_7H_7NO_4$

ALKALIES = Blue ACIDS = Red

Source: Azolitmin is the chief coloring-matter of litmus (which see). It was first described by Kane in 1841, who found it in litmus besides earthy matter and three other coloring matters—erythrolein, a purplish-red fatty matter soluble in ether and yielding a purple-colored solution with ammonia; erythrolitmin, a red, crystalline substance insoluble in ether, but soluble in alcohol, the color of the solution being changed to blue by alkalies; and spaniolitmin, a light-red substance soluble in water, and present in but very small quantity.

Azolitmin does not exist ready-formed in the lichens from which litmus is prepared, but is believed to result from the oxidation of orcin, $C_7H_8O_2$, a colorless principle isolated by Robiquet in 1829 from various species of lichens. Orcin, in the presence of dry ammoniacal air, remains unchanged, but if moisture is also present, it rapidly takes up nitrogen and oxygen, and becomes converted into orcein, $C_7H_7NO_3$, a purple pigment, while water is eliminated. The reaction which takes place is expressed as follows:

$$\underset{\text{orcin}}{C_7H_8O_2} + NH_3 + O_3 = \underset{\text{orcein}}{C_7H_7NO_3} + 2H_2O$$

When, however, besides ammonia, potassa (or soda) is simultaneously permitted to act on the orcin, a further oxidation occurs, and the product of the reaction is no longer purple or violet in color, but blue. A potassium (or sodium) compound has been formed which, on decomposition with an acid, yields a red coloring-matter, azolitmin. The higher oxidation may be expressed as follows:

$$\underset{\text{orcin}}{C_7H_8O_2} + NH_3 + O_4 = \underset{\text{azolitmin}}{C_7H_7NO_4} + 2H_2O$$

Preparation: The process followed by Kane for obtaining azolitmin was to exhaust powdered litmus with water, and then to mix with the liquid some fine, washed sand. The mixture was then evaporated on a water-bath, sufficient hydrochloric acid added to yield a decidedly red solution after the carbon dioxide had been driven off, and the evaporation continued to dryness. The residue was then washed with water, and again dried on the water-bath. The particles of sand were then freed from their covering of pure azolitmin by treatment with a weak ammonia, and the azolitmin obtained from its solution by precipitation with sulphuric acid.

According to Wartha, litmus is macerated with 95-per cent. alcohol for two days, and then collected and dried. It is then macerated in distilled water for 24 hours, filtered, and the filtrate evaporated on a water-bath. The residue is next digested with successive portions of absolute alcohol containing 1 per cent. of acetic acid, each portion being evaporated before treatment with the next. By this means the residue is freed from all moisture, and is enabled to be more readily dried and powdered. The brown, dry powder is next exhausted with the alcohol and acetic-acid mixture, a scarlet-red pigment, yielding a purplish-red color with ammonia, being thus removed. The insoluble residue is now dissolved in water, the solution filtered and then evaporated, alcohol being added several times during the evaporation in order to remove every trace of acetic acid. The residue, azolitmin, is finally dried and powdered.

Stolba impregnates washed linen with a litmus extract, and then plunges it into a 5- or 10-per-cent. sulphuric acid, whereby the azolitmin is precipitated on the fibers. The material is then washed with pure water, and finally treated with weak ammonia, and the pure azolitmin finally obtained by neutralizing the ammoniacal solution with sulphuric acid, collecting, washing, and drying.

The quality of azolitmin present in litmus varies considerably. D. R. Brown examined 7 samples of litmus, and obtained on an average 4.6 % of azolitmin; two of the samples, however, were found to contain over 13 % of azolitmin.

Properties: Azolitmin occurs as a dark, reddish-brown, amorphous powder or as scales. It is but slightly soluble in water, and is insoluble in alcohol or ether. With alkalies it yields blue compounds readily soluble in water.

Tests: The sensitiveness of azolitmin is determined by adding 0.5 Cc. of a 1-per-cent. aqueous solution of the pigment prepared by means of a few drops of centinormal alkali, to 100 Cc. of distilled water, and observing how much centinormal hydrochloric acid is required to change the color to red, and then testing again to find how much centinormal potassium-hydrate solution is required to restore the blue color. With good azolitmin, 1.2 Cc. of centinormal acid, and 3 Cc. of centinormal potassa, should more than suffice.

Application: Azolitmin is used in the form of a solution made by dissolving 1 Gm. of the pigment in 100 Cc. of water, just sufficient centinormal potassa-solution being added to effect a distinct blue color. (For details of application see Litmus).

Azolitmin Test-Paper is also prepared, and is exceedingly sensitive. (See under Test-Papers).

BENZAURIN

$C_6H_5.C.2(C_6H_4).OH.O$

ALKALIES = Violet ACIDS = Yellow

Synonym: Phenolbenzeïn.

Preparation: Benzaurin is prepared by heating 2 molecular weights of phenol with 1 molecular weight of benzotrichloride on a water-bath. After the reaction is over, the excess of phenol is removed by a current of steam, and the benzaurin purified by repeatedly treating it with warm solutions of sodium or potassium sulphite, precipitating by adding hydrochloric acid, and then collecting and drying the precipitate. The reaction is as follows:

$$\underset{\text{benzotrichloride}}{C_6H_5.CCl_3} + 2C_6H_5.OH = \underset{\text{benzaurin}}{C_6H_5.C.2(C_6H_4).OH.O} + 3HCl$$

Properties: Benzaurin occurs as hard, red crusts, presenting a metallic reflection. It is only slightly soluble in water, but readily soluble in alcohol, ether, and in glacial acetic acid, yielding yellow solutions. It is insoluble in benzene, and melts at 100° C. With alkalies, benzaurin yields a violet color, changed by acids to yellow.

By reducing-agents it is converted into dioxytriphenylmethane.

Application: Like other phenol derivatives of benzotrichloride.

BENZOPURPURINE B

$$(C_6H_3)_2.(CH_3N)_2.N_2.(C_{10}H_5)_2.(NH_2.SO_3Na)_2$$

ALKALIES = Brownish-red ACIDS = Bluish-violet

Synonym: Sodium Ortholidine-disazobinaphtylamine-sulphonate.

Source: Benzopurpurine B. is prepared by the action of 1 molecular weight of ortho-tolidine on 2 molecular weights of betanaphtylamine-sulphonic acid, and the conversion of the resulting product into the sodium salt.

Properties: Benzopurpurine B. was discovered in 1885 by Duisberg. Its formula is $(C_6H_3)_2(CH_3.N_2)_2$: $(C_{10}H_5)_2(NH_2.SO_3Na)_2$, and it occurs as a brown powder yielding an orange-red to brownish-red solution with water. The color of the solution is unchanged by alkalies, but is changed to a blue or violet by acids.

Application: Benzopurpurine B. was recommended by Storch as the most useful of the tetrazo dyes, and as being superior to Congo red as an indicator. Its aqueous solution affords an excellent reagent for **free acids**; and the solution, made violet by means of an acid, is, according to Storch, one of the most sensitive of indicators for **alkalies**, known. Even the slightest traces of **free ammonia** in the atmosphere suffice to change the color of paper impregnated with a solution of Benzopurpurine B. from bluish-violet to red. The indicator may be used for estimating **ammonia** in the presence of pyridine, as titration with hydrochloric acid will indicate the total base; a second titration with litmus or tropæolin OOO, on which pyridine has no effect, will show the ammonia present, and the difference will, hence, equal the pyridine. If very much pyridine is present, however, the indications are apt to be unreliable.

In general the indicator may be used like phenolphtalein; and it is more sensitive than litmus.

BRAZIL WOOD

ALKALIES = Purplish-red ACIDS = Yellow

Synonyms: Fernambuco; Pernambuco; Red-Wood.

Source: Brazil wood is a red dye-wood obtained from several species of *Cæsalpinia* found in South America and in the West Indies. The chief species yielding the commercial wood are *Cæsalpinia echinata* Lam. (*Guilandina echinata* Sprengel), *C. crista*, *C. brasiliensis* Lin., and *C. vesicaria*. A species of red-wood closely allied to the Brazil wood is also obtained from the *Cæsalpinia sapan* L., Sapan (or Japan) wood.

Brazil wood has been long used for dyeing purposes, and has of late years been recommended as an indicator, in the form of a decoction, or in the form of a solution of the crystalline principle, brazilin, present in the wood, and upon which the value of the wood as a dye depends (see Brazilin).

Preparation: Brazil-wood test solution may be prepared by boiling 50 Gm. of the comminuted heart-wood with 250 Cc. of water for half an hour, replacing the loss by evaporation from time to time. After the mixture has cooled, it is strained, the residue washed with water until 100 Cc. of liquid are obtained, and 25 Cc. of alcohol then added.

Properties: The color of the solution is changed to an orange-yellow by acids, and almost disappears on dilution; caustic alkalies and their carbonates produce a purplish-red color.

Stannic chloride gives with the decoction a red precipitate ; iron oxide a dirty-red to brown compound ; and chromium oxide yields a brown compound which, on the addition of potassium chromate to the decoction, is deposited as a dark precipitate. On adding alum to the decoction, the latter is colored red, but yields no precipitate until a basic alkali carbonate is added, when a red lake is deposited. A similar lake is obtained on boiling Brazil-wood decoction with aluminum acetate.

Application : Brazil-wood test solution is used like Brazilin (which see).

BRAZILIN

$C_{10}H_{14}O_5$

ALKALIES = Purplish-red ACIDS = Yellow

Synonym : Brasilin.

Source : Brazilin is obtained from several species of *Caesalpinia*, principally *C. brasiliensis* Lin. and *C. echinata* Lam., but is also found in Sapan (or Japan) wood, *C. sapan* L.

Brazilin was first isolated by Chevreul in an impure condition, and was considered by Gerhardt to be identical with hematoxylin, a view not generally accepted because of the difference in the colors exhibited by the compounds of the two substances.

Preisser, however, in 1844, succeeded in isolating, from the inner and less colored portions of the wood, the brazilin, in the form of colorless acicular crystals, the solution of which became yellow on standing and exhibited bright-red margins at the surface, and which, on boiling, became a handsome carmine-red and deposited on evaporation handsome bright-red needles, which he named brazilein; this he believed was formed from brazilin by oxidation of the latter in the presence of an alkali, as follows:

$$\underset{\text{brazilin}}{C_{10}H_{14}O_5} + O = \underset{\text{brazilein}}{C_{10}H_{12}O_5} + H_2O$$

Later investigations also seemed to make it appear probable that brazilin is formed from a glucoside contained in the wood, but this has not as yet been shown to be a fact.

Preparation: Brazilin is generally obtained during the preparation and storage of the commercial extract of Brazil wood used in dyeing, in the form of a deposit of dark, brownish-red crusts consisting of brazilin and its lime compound. These crusts are either dissolved in boiling 5- to 10-per-cent. alcohol with the addition of some hydrochloric acid and zinc dust, or they are carefully washed with a 5-per-cent. hydrochloric acid and then extracted with 12-per-cent. alcohol and the brazilin crystallized.

Properties: The appearance of brazilin varies according as it is crystallized from dilute or concentrated solutions. From the former it is obtained as compact, amber-yellow, rhombic crystals containing 1 molecule of water of crystallization; from the latter it crystallizes as white, silky, felted needles containing 1½ molecules of water of crystallization, which is driven off, however, at a temperature of 80° C.

Brazilin is soluble in alcohol, water, and in ether, has a sweetish taste, and on heating sublimes partly unchanged. On dry distillation it yields resorcin. Nitric acid converts it into trinitroresorcin. On exposure to air and light its solution rapidly becomes orange-colored.

Brazilin possesses the properties of a weak acid, and yields with alkalies soluble, purplish-red compounds affording solutions which are decolorized by zinc dust, sunlight, sulphurous acid, and by hydrogen sulphide; the color of the solutions is changed by acids to yellow.

With the earths and oxides of the heavy metals, brazilin forms insoluble compounds. Caustic alkalies and their carbonates yield a purplish-red color with brazilin solutions, and with alum a red lake is formed.

Brazilin is extremely sensitive to light and air, by which it is rapidly darkened, becoming orange-colored, or even red. It must be **preserved, hence,** in carefully stoppered, opaque vials.

Application : Brazilin and decoction of Brazil wood have been found to be among the most sensitive of indicators, and especially serviceable for titrating **alkaloids,** with which other indicators yield indistinct colors, and particularly for **quinine, atropine, brucine,** and **cocaine.**

The indicator is inapplicable where **sulphurous acid** or **hydrogen sulphide** are liberated, as these destroy the color of the solution.

A test-paper is also used, and is described under under Test-papers.

CABBAGE, RED

ALKALIES = Green ACIDS = Red

Source : The red cabbage is a variety of the *Brassica oleracea*, which has been brought under cultivation from stock originally found wild on the coast of England and the Mediterranean as well as in Continental Europe, and known as Wild Cabbage, or Sea Cabbage.

Preparation : A tincture of the leaves of the red cabbage is made by comminuting the leaves, and exhausting them with water or diluted alcohol.

Properties : The tincture of the leaves is violet in color. The color is changed to green by alkalies, and to red by acids.

Application: Tincture of red cabbage may be applied for all titrimetric processes, and is quite sensitive, even to **Ammonia.** A paper impregnated with the tincture is also quite sensitive. It is but seldom used.

CARMINE

ALKALIES = Purplish-red ACIDS = Yellowish-red

Source : Carmine is the pigment obtained from the dried female insect, *Coccus cacti*, Lin. It was first isolated (and named) by Pelletier and Caventou in 1818, by treating cochineal with boiling ether to remove the fat, then exhausting with alcohol so long as any color was extracted, distilling off the greater bulk of the alcohol, and allowing the residue to evaporate spontaneously. The impure carmine so obtained was then treated with cold alcohol, which dissolved the carmine but left the fatty matter. From its solution the carmine was then precipitated by adding an equal volume of ether. The carmine so obtained is, however, impure, and it was only in 1847 that Warren de la Rue succeeded in obtaining the pure carmine in the form of carminic acid (which see).

Preparation : Commercial carmine is generally prepared by a process similar to the following: Powdered cochineal is boiled with 40 times its weight of water for 15 minutes, and $\frac{1}{4}$ of its weight of powdered alum is added. The mixture is next boiled for 3 minutes longer, and then set aside, when the carmine precipitates, and is removed by filtration. On allowing the mother liquor to stand for several days, a second deposit of carmine is obtained, which, however, is not of as good a color as that first obtained.

The celebrated process of Madame Cenette is as follows: Powdered cochineal is boiled with 75 times its weight of water for two hours; then $\frac{1}{16}$ of its weight of potassium nitrate is added, and the whole boiled for 3 minutes longer, and finally $\frac{1}{4}$ of its weight of oxalic acid added, and the mixture boiled for another 10 minutes. The liquid is then allowed to clarify by depositing for 4 hours, when the clear liquid is decanted into shallow glass vessels and set aside for three weeks; the deposited carmine is then separated from the supernatant liquid and dried in the dark.

Properties: Carmine occurs in the form of small, bright-red lumps, soluble in ammonia water, and yielding a deep-red solution, the color of which is changed to a yellowish-red by acids. It consists chiefly of carminic acid, but contains also alumina, lime, other organic acids, and a protein compound, according to Liebermann.

Carmine solution is not decolorized by sodium sulphite; on boiling with lime-water it is colored violet.

Tests: Carmine is frequently adulterated, according to Donath, not only with starch, alumina, and brick-dust, but also with baryta, zinc, and lead lakes, and certain azodyes. The impurities are left behind on dissolving the carmine in ammonia.

Equal quantities of the sample and of a known carmine are heated in porcelain crucibles, and the odors compared: That from pure carmine resembles the odor evolved on heating proteins, while that from eosine-lake will have a distinct bromine odor, and that from pæonin-lake will smell like phenol. On incineration the adulterated preparations will also yield more ash.

Colorimetric comparisons may also be made between the sample and a known carmine, solutions of both being similarly made by the aid of a small quantity of ammonia, and compared in two similar burettes.

Application: Carmine is used in a manner similar to that of cochineal (which see).

Alkaline Carmine Solution is also used in titrimetry. It is prepared by dissolving carmine in soda lye. For use as an indicator 1 Cc. of this solution, previously decolorized by the addition of sufficient hypobromite solution, is added to the liquid to be titrated.

Alkaline carmine solution is very sensitive to atmospheric oxygen. With it, **carbonates** of the **alkalies** are best titrated in warm solutions; and

carbonic acid gas is not so disturbing as when **litmus** is used. The change is very sharp and **bright, particularly** with pure **alkalies** or **acids.**

CARMINIC ACID

$C_{17}H_{18}O_{10}$

ALKALIES = Purplish-red   ACIDS = Yellowish-red

Source: Carminic acid is the true coloring-matter of the dried female insect, *Coccus cacti* L., cochineal (which see).

Preparation: Carminic acid was first obtained by Warren de la Rue in 1847, by exhausting powdered cochineal with boiling water, and precipitating the filtered solution with lead-acetate solution acidulated with acetic acid. The precipitate was washed with water, and then decomposed by a current of hydrogen sulphide, while suspended in water. After filtering, the filtrate was again precipitated by lead-acetate solution and the precipitate decomposed by hydrogen sulphide. The filtrate now obtained was evaporated in vacuo, the residue dissolved in boiling alcohol, and a little ether added to precipitate nitrogenous matter, the solution again filtered, and finally evaporated.

Ordinarily carminic acid is obtained by first treating cochineal with ether, and then exhausting the residue with successive portions of boiling alcohol, which, on cooling, deposits a part of the acid, and yields the remainder on spontaneous evaporation. It is then freed from adhering fatty matter by dissolving in alcohol and adding an equal quantity of ether. The pure carminic acid is deposited in the course of a few days.

Properties : Carminic acid occurs as a red or brownish-red amorphous powder, or crystals, readily soluble in water and in alcohol, but difficultly soluble in ether.

Its formula is $C_{17}H_{18}O_{10}$. It is soluble in concentrated sulphuric acid and in hydrochloric acid without decomposition, but, on boiling with diluted sulphuric acid, it yields a coloring-matter, carmine red, and a sugar, according to the following reaction:

$$\underset{\text{carminic acid}}{C_{17}H_{18}O_{10}} + 2H_2O = \underset{\text{carmine red}}{C_{11}H_{12}O_7} + C_6H_{10}O_5$$

Carminic acid is hence considered to be a glucoside. It has the properties of a weak, dibasic acid, and forms easily soluble salts with the alkalies, but forms insoluble violet or purple salts with the alkali earths, earthy metals, and metals generally.

Chlorine, bromine, and iodine decompose it, and nitric acid converts it into oxalic and nitro-coccic acids. Fused with potassium hydrate it yields oxalic and succinic acids and coccicin.

The aqueous solution is faintly acid, and of a yellowish-red, the color being changed by alkalies to a purplish-red. Nascent hydrogen decolorizes the solution, but the color is restored on contact with the air.

Schützenberger believes carminic acid to be a mixture of at least two acids, one being the true carminic acid, having the formula $C_9H_8O_5$, and insoluble in a mixture of alcohol and ether; the other, oxycarminic acid, $C_9H_8O_7$, and soluble in a mixture of alcohol and ether.

Tests: 1 Gm. of carminic acid should completely dissolve in 2 Cc. of water; the addition of 20 Cc. of 95-per-cent. alcohol to the solution should cause no noticeable precipitation.

A simple method of estimating the value of carminic acid is by colorimetric comparison. This is accomplished by dissolving equal quantities of a preparation of known quality and the one to be tested, in equal volumes of water, solution being facilitated by adding a few drops of ammonia.

The sensitiveness of carminic acid is tested by adding 0.5 Cc. of a 1-per-cent. aqueous solution of carminic acid to 100 Cc. of water, and observing how much centinormal ammonia, or centinormal hydrochloric acid, is required to effect changes in color. A good preparation will not require more than 0.6 Cc. of the acid, 0.8 Cc. of the ammonia, or 2.8 Cc. of centinormal sodium hydrate.

Application: Carminic acid is used in titrimetric operations like cochineal (which see). It is now being frequently used in microscopy as a stain, although carmine is more generally used.

Carminic acid is far more sensitive to **bicarbonates** of **alkali earths** than is litmus. According to H. N. Draper it yields a reaction with **alkalies** in solutions of 1 : 1,400,000; and the reaction is only slightly influenced by **carbonic-acid** gas.

Carminic acid has also been lately recommended as a precipitant of albumins and proteoses. It is claimed to be exceedingly sensitive, 1 part of albumin in 90,000 parts of solution being readily detected.

COBALTOUS NITRATE

$Co(NO_3)_2.6H_2O$

Synonyms: Normal Cobalt Nitrate; Neutral Cobalt Nitrate.

Preparation: Cobaltous nitrate is prepared by dissolving metallic cobalt, cobalt oxide, CoO; cobalt hydrate, $Co_2(OH)_6$; or cobalt carbonate, $CoCO_3$; in nitric acid, evaporating the solution, and crystallizing from the concentrated solution on cooling.

Properties: Cobaltous nitrate occurs in the form of red prisms or monoclinic plates, which are deliquescent in moist air, but permanent in dry air, and which melt at a temperature below 100° C. At a higher temperature, cobaltous nitrate melts to form a viscid, green liquid, and on strongly heating, nitrogen monoxide, NO, is evolved, cobaltic oxide, Co_2O_3, remaining.

Application: Cobalt nitrate has been recommended by G. C. Stone as an indicator in the volumetric determination of **zinc** by titration with potassium ferrocyanide. The cobalt solution should be quite dilute, and a drop of it placed on a white porcelain plate, just touching a drop of the solution to be tested. If the drops touch but do not mix, the end-reaction is marked immediately by a greenish line at the juncture of the two drops. The best strength of the potassium-ferrocyanide solution was found to be about 3 per cent.

COCHINEAL

ALKALIES = Violet ACIDS = Yellowish-red

Source: Cochineal is the dried female insect, *Coccus cacti* Lin., one of the Hemiptera first found living on various species of cactus in Southern Mexico, Guatemala, and Honduras, and later on introduced into the West Indies, East Indies, Spain, Algiers, Teneriffe, and Malta.

The insect is gathered some time after being fecundated, and is killed by immersion in boiling water, exposure to steam, or by drying in a hot oven or on heated plates. The last-mentioned treatment is believed to yield the finest product, known as "silver cochineal" in the trade; but that obtained by the immersion process, and known as "black cochineal," may be frequently found covered with powdered talcum, calcium sulphate, lead carbonate, and even stearin, in order to simulate the grayish color of the "silver cochineal."

Besides the above impurities, barium sulphate, particles of lead, vermilion, chrome red, insects already exhausted of their coloring-matter, and grains of substances artificially prepared to imitate the dried insect, have been met with as adulterants.

The pigment upon which the value of cochineal depends, and to which is due its color, was first isolated by Pelletier and Caventou in 1818, and named by them "carmine." This was found to be impure, however, and it was only in 1847 that Warren de la Rue succeeded in obtaining the pure pigment, which he named carminic acid (q. v.).

Properties: Dried cochineal is about 2 to 5 Mm. long, nearly hemispherical, flat or slightly concave beneath, convex above, transversely wrinkled, purplish-gray or purplish-black in color, and easily pulverizable, yielding a dark-red powder. It has a faint, heavy, peculiar odor, and a slightly bitterish, acidulous taste, and swells up in water, to which it yields its coloring-matter, which is soluble also in alcohol and in ammonia, slightly soluble in ether, and insoluble in fixed and volatile oils.

According to researches by Clark, it would appear that the coloring-matter, carmine, is not present in the living insect in solution, but consists of minute, red granules surrounding a larger, colorless granule suspended in a colorless liquid.

The aqueous infusion of cochineal is of a crimson-violet color, which is deepened by alkalies and brightened by acids. With bismuth, nickel, and zinc salts, it affords lilac-colored precipitates; with iron salts a dark-purple, almost black, precipitate is had; stannic salts give a brilliant scarlet and stannous salts a red precipitate, and with alum it forms lakes.

Tests: The value of cochineal as an indicator depends on its carminic-acid content. The process followed by Penny for testing its value is as follows: 1 Gm. of the cochineal is digested with 5 Gm. of caustic potassa in 20 Cc. of distilled water for an hour, and the mixture then diluted so as to measure 100 Cc. Sufficient of a 1-per-cent. potassium-ferricyanide solution is then added to 10 Cc. of the mixture to convert the purple into a yellowish-brown color. The quantity required for this purpose is then compared with that required for a sample of cochineal known to be good.

0.5 Cc. of a 1 : 80 aqueous infusion of cochineal added to 100 Cc. of distilled water, requires 3 Cc. of centinormal hydrochloric acid, and 2.8 Cc. of centinormal sodium hydrate, to effect changes of color.

Application: Cochineal is an exceedingly valuable indicator. It is used in the form of solution generally, although a paper is also prepared (see Test-Papers).

A cochineal tincture recommended by Luckow, and which is very sensitive, is made by macerating 3 Gm. of whole cochineal in 250 Cc. of a mixture of 3 to 4 volumes of water and 1 volume of alcohol, and decanting the clear solution. The whole cochineal is directed to be used, because the liquid is difficult to filter if the powdered insect is used.

The color of these solutions is a deep, ruby-red which is changed to a violet by **alkalies, carbonates** of the **alkalies, alkaline earths, sodium phosphate, acetates** of the **alkalies,** and **salts** of the **weak acids** generally. **Acids** restore the red color.

Cochineal is very serviceable for indicating the **carbonates** of the **alkaline earths** for which litmus is inapplicable, and also for the **caustic alkalies, carbonates** and **sulphides.** Although somewhat influenced by the **carbonic-acid** gas or **hydrogen sulphide** liberated, it is far less affected by these than is litmus. It is also particularly useful for titrating the **ammonia** or the excess of **sulphuric acid** in the Kjeldahl nitrogen estimation process, in which phenolphtalein is not very serviceable.

Cochineal may be used hot or cold for titrating **carbonates** or **bicarbonates,** and also for **alkali** in **soaps.**

With **normal sulphites** 50% of the base may be titrated with a strong acid. For **organic acids** the indicator is inapplicable. With **phosphoric acid,** the reaction is neutral when a monobasic salt is formed, as **acid phosphates** are neutral to cochineal.

The indicator is excellently adapted for titrating the **alkaloids** generally, and **morphine, brucine, atropine** and **cocaine** in particular.

On account of the acid reaction of the cochineal tincture (or carminic-acid solution), no harm is done when **alkalies** are being titrated with acid. When, however, **acids** are being titrated with alkalies, the cochineal tincture must be first neutralized (colored violet by a minute quantity of ammonia); the end of the reaction is then indicated by the violet color.

Tincture of cochineal is best kept in an acid condition, because the neutral or alkaline tincture soon spoils. In use, the absence of **iron, aluminum,** or **copper** salts must be assured from the solutions to be operated on, as these salts yield a pink color, even when solutions are acid. The tincture is also particularly serviceable for titrations by **artificial light,** as the change of color is very sharply defined, and the depth of the colors enhanced. The sodium flame is very useful with this indicator.

COLEIN

$C_{10}H_{10}O_{3}$

ALKALIES = Yellow ACIDS = Red

Source: Coleïn is a resin-like substance isolated from the stems and leaves of *Coleus verschaffelti*. It was first obtained and described by A. H. Church in 1877.

Preparation: Coleïn is obtained by crushing the stems and leaves of Coleus verschaffelti with a small quantity of alcohol faintly acidulated with sulphuric acid, expressing the crimson pulp (avoiding contact with metals), shaking the liquid obtained with barium carbonate, and filtering. Most of the alcohol is then distilled off, and at a certain stage a deep-colored, resin-like substance sinks to the bottom of the vessel beneath a supernatant rich-red liquid. The precipitated matter is the coleïn, and it is purified by dissolving it in alcohol and reprecipitating it by the addition of ether or water ; the purifying process is repeated several times.

Properties: Pure coleïn is a brittle, resinous substance, having a conchoidal fracture, and yielding a reddish-purple powder verging on crimson. It is freely soluble in alcohol, very difficultly so in water, and insoluble in ether. It yields red solutions, but the alcoholic solution soon loses its color, owing, probably, to union with a portion of alcohol. The color may, however, be restored by the addition of a drop of sulphuric acid. Concentrated sulphuric acid dissolves it unchanged, but nitric acid converts it into a brown, resinous mass. Concentrated caustic alkalies (even ammonia) profoundly alter it. Its composition, from analyses made by Church, is $C_{10}H_{10}O_5$.

Application: Boettger recommended coleïn as an indicator, but it has found very little use, so far.

Coleïn Test-Paper is also used (see under Test-Papers).

CONGO RED

$(C_6H_4)_2.(N_2)_2.(C_{10}H_5)_2.(NH_2.SO_3Na)_2$

ALKALIES = Red   ACIDS = Blue

Synonyms: Sodium Tetrazodiphenyl-naphtionate; Sodium Diphenyl-diazobinaphtionate.

Preparation: Congo red was discovered by Boettger in 1884. It is the sodium salt of diphenyl-diazobinaphtionic acid, and is obtained by dissolving 28.2 parts of benzidine sulphonate in 500 parts of water, adding first 30 parts of hydrochloric acid (20° Bé.), and then 13 parts of sodium nitrite dissolved in 50 parts of water, in small portions. The solution is cooled, and to it is then added a solution of 55 parts of sodium naphtionate and 12 parts of sodium acetate in 100 parts of water.

The precipitate is collected, dissolved in a solution of sodium carbonate, and the dye salted out, and dried.

Properties: Congo red occurs as reddish-brown lumps which are readily soluble in water and in alcohol. Its solutions are very sensitive to free acids, which yield a blue color and liberate the base; alkalies restore the red color.

Application: Congo red is very useful for estimating **free acids,** more particularly as **acid salts** do not affect it. It may, therefore, be employed for estimating **sulphuric acid** in aluminum sulphate, as the alum has no action on it. Free **carbonic** or **acetic acid,** present to the extent of only 0.002%, suffices to yield the blue color. But, if a drop of ammonia water is added to the solution, a stream of carbonic-acid gas may be passed through it without the blue color being produced. **Hydrogen sulphide** also yields the blue color; nor does boiling the solution remedy the change effected by the hydrogen sulphide or carbonic-acid gas.

Congo red may be used for estimating **mineral acids** in the presence of **organic acids,** as the latter do not affect it.

Congo red is also useful for titrating **aniline** and **toluidine** in the residual liquors from aniline works. For this purpose, the liquid is diluted with water until a perfect solution is had, then an alcoholic

Congo-red solution is added, and finally sufficient sulphuric or hydrochloric acid carefully added until a decided bluish-violet color is observed (a distinct blue is seen only when a decided excess of acid is added).

Sulphates, chlorides, and **nitrates** of the alkalies seriously interfere with the end-reaction, hence their absence should be assured.

Bisulphites and **biphosphates** are neutral to Congo red. For **organic acids** the indicator is useless.

Phosphates may be titrated by means of Congo red; **sulphites,** however, cannot; and **bichromates** are neutral to the indicator, whereas the **chromates** are alkaline.

Congo-red solution for titrimetric use is made by dissolving 1 part of Congo red in 100 parts of 30-per-cent. alcohol, about 10 drops being added to 100 Cc. of the liquid to be titrated. The sensitiveness of the solution is such that 0.1 Cc. added to 100 Cc. of distilled water requires only 0.7 Cc. of centinormal hydrochloric acid, and 0.6 Cc. of centinormal ammonia, to produce the changes of color, but requires 2.5 Cc. of centinormal potassa.

Congo paper is also used as an indicator, and is treated of under Test-Papers.

CORALLIN

$C_{19}H_{14}O_3$

ALKALIES = Violet-red ACIDS = Yellow

Synonyms: Aurine; Commercial Rosolic Acid.

Preparation and **Properties**: See Rosolic Acid.

Application: Corallin test solution may be prepared by dissolving 1 Gm. of Corallin in 10 Cc. of alcohol, and adding distilled water to make up to 100 Cc. The solution is colored violet-red by alkalies, and yellow by acids. It is especially useful for titrating **free ammonia**.

CORALLIN RED

$C_{18}H_{13}O_2.NH_2$

ALKALIES = Red ACIDS = Yellow

Synonyms: Paeonin; Aurine R.; Impure Rosaniline Rosolate; Diamidotriphenylcarbidride.

Preparation: Corallin red was discovered by Marnas. It is obtained by heating one part of commercial rosolic acid (corallin; aurine) with three parts of ammonia in a closed vessel at a temperature of 140° C. The semi-liquid mass is then treated with hydrochloric acid, and the precipitate collected, washed, and finally dried.

Corallin red is believed to be most probably a product intermediate between aurine and pararosaniline, in which the hydroxyl is replaced by an amido group.

Properties: Corallin red occurs as a reddish-brown powder, which is readily soluble in alcohol, insoluble in cold water, and but slightly soluble in boiling water. Its solutions have a beautiful red color, which is changed, even by a trace of acid, to a yellow.

The formula assigned to it is $C_{19}H_{13}O_2(NH_2)$.

Application: Like Commercial Rosolic Acid (which see).

CURCUMIN

ALKALIES = Reddish-brown ACIDS = Yellow

Synonyms: Turmeric Yellow; Curcummin.

Source: Curcumin is a coloring-matter obtained from the roots of *Curcuma longa* L., one of the Zingiberaceæ, and found in the East Indies, China, and Madagascar. It was first isolated by Vogel, who also found in the root another, a brown coloring-matter.

Preparation: Curcumin is obtained by first exhausting curcuma roots with water to remove the brown matter, extractive, etc., then drying, powdering, and exhausting with alcohol, which takes up the curcumin. The alcohol is next distilled off, the dried residue treated with ether, and the filtered ethereal solution evaporated. The impure curcumin so obtained is dissolved in alcohol, precipitated by lead acetate, the precipitate collected and washed with alcohol, and decomposed by a current of hydrogen sulphide while suspended in water. This precipitate is then collected, dried, and exhausted with ether which, on evaporation, deposits pure curcumin.

Gajewski, in 1870, obtained pure curcumin by removing the fatty matter from the root with carbon disulphide, then extracting the coloring-matter with ether, and recrystallizing from ether or hot benzene. In 1873 he modified the process by washing the ethereal extract with weak ammonia, and precipitating the pure curcumin by means of a current of carbonic-acid gas.

Daube also, in 1870, obtained the curcumin by exhausting the roots with boiling benzene, and dissolving the crystals obtained on cooling, in cold alcohol, precipitating the filtrate with alcoholic lead-acetate solution, decomposing the precipitate with hydrogen sulphide, and crystallizing from alcohol.

The yield of curcumin is about 0.3 per cent.

Properties: Curcumin occurs as a cinnamon-colored, translucent, foliaceous mass which yields a yellow powder melting at 40° C., or as yellow prisms or crystalline powder melting at 178° C.

Curcumin is insoluble in water, is somewhat soluble in hot benzene, and is readily soluble in ether, alcohol, acetic acid, alkalies, fats, and in oils. On exposure to sunlight it is bleached.

Curcumin yields with alkalies intensely reddish-brown solutions; and similar solutions are afforded by the alkaline earths and borax. Acids restore the yellow color. In concentrated sulphuric acid, curcumin dissolves with a carmine color; in phosphoric and in hydrochloric acids it dissolves without decomposition, and also with a carmine color. Nitric acid decomposes it.

Boric acid added to an alcoholic solution of curcumin does not change the color of the latter, but on boiling and evaporating, a carmine-red residue remains. This compound is decomposed, according to Schlumberger, by long contact with water, yielding a resinous yellow substance, known as pseudo-curcumin, which does not yield a red color with boric or hydrochloric acid, and dissolves in alkalies with a greenish-gray color.

The curcumin-boric-acid compound yields with alkalies, reddish-violet solutions which rapidly become gray. On boiling an alcoholic solution of the compound with sulphuric acid, a dark, blood-red color is formed, and on cooling, rosocyanine is deposited.

Curcumin solutions exhibit a green fluorescence, and yield brown, insoluble lakes with lead, lime, and baryta.

Application: The sensitiveness of curcumin appears to be increased by the presence of most salts, hence the indicator is applicable to a wide variety of titrimetric determinations. It is also applicable in the presence of **ammonia,** to which it is insensitive. It is sensitive, however, to **carbonic acid,** but is neutral to **bicarbonates.**

With the **sulphates** and **sulphides** of the alkalies, the indicator shows when half of the combined alkali becomes a sulphate or sulphide; i.e., when bisulphates or bisulphides are formed. With **sulphites** and **phosphates** the end-reaction is not definite; hence, for these the indicator is useless. In **sodium silicate** only 90% of the sodium, and in **borax** only 50% of the sodium, is shown, and the end-reaction is uncertain.

Sodium thiosulphate is neutral to the indicator.

CURCUMIN W.

$CH_2.(C_6H_3.SO_3Na.N)_2O$

ALKALIES = Red ACIDS = Greenish Yellow

Synonyms: Curcumin S.; Sun Yellow; Sodium (or Ammonium) Azoxystilbene-disulphonate.

Preparation: Curcumin W. is obtained by dissolving 5 parts of sodium (or ammonium) para-nitrotoluenesulphonate in 70 parts of water, adding 3 parts of soda-lye (40° Bé.), and warming the mixture while stirring vigorously. When the color has changed from a saffron to a yellowish-red the dye is salted out and dried.

Properties: Curcumin W. forms a reddish-brown powder, soluble in water, and yielding a yellow solution, the color of which is changed to a red by **alkalies**, and restored by **acids.**

Application: Curcumin W. was recommended by Storch, who states that it is more sensitive than phenolphtaleine. Salts which ordinarily affect the sensitiveness of indicators appear to even increase that of Curcumin W. It is neutral to **bicarbonates,** and is serviceable for **ammonia. Carbonic-acid** gas affects it. The indicator may be used in those cases where other indicators, such as phenolphtaleine and curcuma, cannot be used for ammonia.

CYANINE

$C_6H_5.CH_2.C_9H_6N.C.C_9H_6NCl.$

ALKALIES = Deep Blue ACIDS = Colorless

Synonyms: Quinoline Blue; Diamylcyanine Iodide.

Preparation: Cyanine was discovered by Greville Williams in 1856. It is prepared by heating a mixture of equivalent quantities of quinoline and lepidine (*g*-methylquinoline) with amyl iodide, then heating the resulting product with potassa, and finally crystallizing.

Properties: Cyanine is obtained in the form of shining prisms or plates having a green metallic luster. The crystals are insoluble in cold water, difficultly soluble in boiling water, with which they yield a violet-blue solution having a quinoline odor, and are soluble in alcohol with deep, blue color. Acids discharge the color, which is restored by alkalies. Cyanine dissolves in concentrated sulphuric acid, and the colorless solution, on heating, yields iodine vapors.

Application: Cyanine is very sensitive to **acids,** even **carbon dioxide** sufficing to discharge the color. It is capable of but limited use, however.

DIAZO-PARANITRANILINE-GUAIACOL

$NO_2C_6H_4N:NC_6H_3(OCH_3)OH$

ALKALIES = Red ACIDS = Greenish-yellow

Synonym: Riegler's Indicator.

Preparation: The indicator is prepared by adding a solution of diazo-paranitraniline to an alkaline solution of guaiacol.

Properties: Diazo-paranitraniline forms a brown substance insoluble in water but soluble in alcohol. Its composition is represented by the formula $NO_2C_6H_4N : NC_6H_3(OCH_3)OH$.

Application: This indicator has but very recently been introduced by E. Riegler, who states that a solution of 0.2 Gm. in 100 Cc. of alcohol is much more sensitive than phenolphtalein. One or two drops of the solution added to an **alkaline** solution suffice to color the latter a very handsome red, changed by an excess of **acid** to a greenish-yellow color.

DIMETHYLAMIDOAZOBENZENE

$C_6H_5.N:C_6H_4N(CH_3)_2$

ALKALIES = Yellow ACIDS = Red

Synonyms: Butter Yellow; Aniline-azodimethylaniline; Benzene-azodimethylaniline.

Preparation: Dimethylamidoazobenzene was discovered in 1875 by O. N. Witt. The indicator is prepared by dissolving 9.3 Gm. of aniline in 30 Gm. of a 25-per-cent. hydrochloric acid, and after cooling the solution and diluting it, adding 7 Gm. of sodium nitrite previously dissolved in water, whereby the aniline hydrochloride is converted into diazobenzene chloride. The mixture is now stirred well, and poured into a solution of 12 Gm. of dimethylaniline in 15 Gm. of hydrochloric acid, 30 Gm. of sodium acetate being then added. The crystals, which soon separate, are then recrystallized from alcohol.

Properties : Dimethylamidoazobenzene crystallizes in the form of golden-yellow scales which melt at 115° C., and are soluble in alcohol, strong mineral acids, alkaline solutions and oils, but insoluble in water. In dilute solutions of dimethylamidoazobenzene, even traces of acids yield a handsome red color, which is changed to yellow by alkalies.

Application : Dimethylamidoazobenzene was recommended by B. Fischer and O. Phillip as an indicator instead of methyl orange, because the transition from the lemon-yellow to red is more easily observed than the change from orange to red exhibited by methyl orange, and also because the indicator may be readily prepared by the operator, whereby a constant and definite preparation may always be at command (which is not the case with methyl orange).

Lunge and Thompson state, however, that methyl orange is more sensitive than the dimethylamidoazobenzene, and that, in equal concentration, it will exhibit similar shades of color.

For use, a 1:200 alcoholic solution of dimethylamidoazobenzene is made, about 5 drops being added to 100 Cc. of the liquid to be titrated. The color of the liquid will be lemon yellow, and changed sharply by **acids** to a handsome carnation red. **Carbonic-acid** gas does not affect the indicator.

DIPHENYLAMINE

$(C_6H_5)_2NH$

Synonym: Phenylaniline.

Preparation: Diphenylamine is obtained by the dry distillation of triphenyl-rosaniline (aniline blue), and by heating aniline hydrochloride with aniline to 240° C.

Properties: Diphenylamine occurs as a grayish, crystalline mass, or white crystals, slightly soluble in water, easily soluble in alcohol and in ether, and fairly so in acids, with which it forms salts. It is a very weak base, however, its salts being decomposed even by water. It has a pleasant odor, melts at 54° C., and boils at 310° C. A 1-per-cent. solution in concentrated sulphuric acid, forming diphenyl-sulphonic acid, is colored intensely blue by nitric acid. It is also temporarily colored by nitrous acid, the color gradually fading to a greenish yellow; hypochlorous, permanganic, molybdic, and selenous acids likewise color it somewhat; and so do certain ferric salts, barium salts, and hydrogen dioxide. Ozone colors the alcoholic solution, or test-paper prepared from the latter, a yellow to brown.

Application: According to Longi, diphenylamine is serviceable as an indicator in the volumetric determination of **nitric acid** using a decinormal solution of stannous potassium sulphate.

Diphenylamine is principally employed for the detection of **nitrates** in potable water, or in wine or milk to which any water containing nitrates has been added. Traces of **nitric acid** in sulphuric acid may also be detected by means of it.

In testing water, wine, or milk, a few drops of diphenylamine solution are added to 1 Cc. of the liquid, and then 1 Cc. of concentrated sulphuric acid is added so as to form a lower layer. At the zone of contact a blue color develops, and is so intense that 1 part of nitric acid in 3,000,000 parts of liquid is readily detected.

EOSINE

$C_6H_4.(CO)_2.O.(C_6HBr_2.NaO)_2$

ALKALIES = Green Fluorescence ACIDS = Yellow

Synonyms: Eosine Yellowish; Bromeosine; Tetrabromeosine; Tetrabromfluoresceine; Tetrabromoresorcinphtalein.

Preparation: Eosine was discovered in 1874 by Caro. It may be obtained by the action of bromine on fluoresceine, $C_6H_4.CO_2.C.O.(C_6H_3)_2(OH)_2$, in a cold solution in glacial acetic acid, some potassium chlorate being finally added to the mixture in order to decompose the hydrobromic acid formed, whereby a saving is effected in the quantity of bromine required. Four hydrogen atoms of the fluoresceine are thus replaced by an equal number of bromine atoms, and the tetrabromfluoresceine gradually separates in the form of yellowish-red crystals, which are purified by recrystallization from alcohol, and finally converted into a potassium or sodium salt, which is the commercial form of the article.

Eosine is also obtained by heating in an enamelled steam-kettle a solution of 120 parts of soda lye (36° Bé.) and 300 parts of water, and gradually adding 64 parts of bromine. There results from the reaction sodium bromide, sodium bromate, and sodium hypobromite. The mixture is then heated for half an hour to convert the last into bromate. The solution is then cooled, and to it is added a cooled solution of 32 parts of fluoresceine, 300 parts of water, and 50 parts of soda lye (36° Bé.). The mixture is briskly stirred, and 280 parts of hydrochloric acid gradually added, the whole boiled for 5 minutes and 600 parts of cold water added. The precipitate is then collected and dried. The boiling and addition of water are usually repeated once or twice to remove all traces of hydrochloric acid. The dye is then converted into a potassium or sodium salt.

Properties : Uncombined eosine occurs as yellowish-red crystals containing some alcohol of crystallization. It is almost insoluble in water, but yields readily soluble, bibasic salts with alkalies.

The potassium salt of eosine forms bluish-red crystals, or a brownish powder. It is soluble in water and in alcohol, and yields solutions having a magnificent green fluorescence. Acids destroy the fluorescence, the solution becoming yellow. Mineral acids cause a yellowish-red precipitate in the solutions. Organic acids only partially decompose the salt. Eosine yields handsome, insoluble lakes with salts of lead and tin, and with alumina.

Application: Eosine is peculiarly applicable for use in **dark-colored solutions,** in which the ordinary color-changes can be observed only with difficulty or not at all. It is also useful for the titration of **soap,** and for **alkalies.**

For use as an indicator a 3-per cent. aqueous solution is prepared, of which about 10 drops are added to 100 Cc. of the liquid to be titrated.

EOSINE-METHYLENE BLUE

ALKALIES = Red ACIDS = Blue

Preparation: The compound is prepared by mixing stoichiometrical equivalents of basic eosine and methylene blue dissolved in alcohol.

Properties: The alcoholic solution of the compound has a bluish-violet color which is changed by organic and other acids, as well as acid compounds, to a pure blue or bluish-green; and by alkalies, and alkaline substances, to a red color. The neutrality point is always indicated by the restoration of the original bluish-violet.

Application: Eosine-methylene blue is said by H. Rosin to be exceedingly sensitive—so much so that glass, which is alkaline in spots, is colored red in those places by the solution. The solution is also applicable as a sensitive biochemical reagent, as it affords characteristic colors with pathological elements.

ETHYL ORANGE

$C_6H_4.SO_3Na.N_2.C_6H_4N(C_2H_5)_2$

ALKALIES = Yellow ACIDS = Red

Synonyms: Diethylaniline Orange; Sodium (or Ammonium) Diethylamidoazobenzene-sulphonate; Sodium (or Ammonium) Diethylaniline-azobenzene-sulphonate.

Preparation: Ethyl orange is prepared in exactly the same manner as methyl orange (which see), diethylaniline being substituted for the dimethylaniline in the formula.

Properties: Ethyl aniline occurs as an orange-yellow crystalline powder, soluble in alcohol, and almost insoluble in water.

Application: Ethyl orange has been recommended as being more delicate than methyl orange. It is sensitive to **free acids**, and is colored red even by **neutral aluminium sulphate.** It may be used like methyl orange, but is not, however, as sensitive as the latter.

A solution of 1 part in 400 parts of 30-per-cent. alcohol is used, 3 to 5 drops of which are added to 100 Cc. of the solution to be titrated. Its sensitiveness is such that 100 Cc. of distilled water to which 0.2 Cc. of the indicator-solution has been added will require 3 Cc. of decinormal hydrochloric acid (methyl orange similarly tested requires only 1 Cc. of centinormal acid).

EUPITTONIC ACID

$(C_6H_2)_3.(OCH_3)_6.OC.(OH)_2$

ALKALIES = Blue ACIDS = Carmine Red

Synonyms : Eupitton ; Pittakal ; Hexaoxymethylaurin; Hoffmann's Indicator.

Preparation : Eupittonic acid was first isolated by Liebermann from pittakal, which was discovered in 1835 by Reichenbach during the fractional distillation of beech-tar creosote on treating certain portions of the distillates with baryta and exposing to air. Later on Hoffmann demonstrated that the pittakal resulted from the oxidation of pyrogallol-dimethyl ether and the dimethyl ether of methyl-pyrogallol, the reaction occurring as follows :

$$\underset{\text{pyrogallolmethyl ether}}{C_6H_3(OCH_3)_2OH} + \underset{\text{methylpyrogallol-dimethyl ether}}{C_6H_2(CH_3).(OCH_3)_2OH} + 3O$$

$$= \underset{\text{eupittonic acid}}{C_{19}H_8(OCH_3)_6O_3} + 3H_2O$$

Eupittonic acid is prepared by dissolving 2 molecular weights of pyrogalloldimethyl ether and 1 molecular weight of methylpyrogalloldimethyl ether in alcohol, adding an excess of caustic soda, and heating the mixture on an oil-bath for half an hour to a temperature of from 200° to 220° C. The mass soon becomes greenish, then blue. It is then treated with hydrochloric acid, and the brownish-red residue crystallized by dissolving in alcohol and precipitating with ether.

Properties: Eupittonic acid occurs as orange-yellow crystals, insoluble in water, soluble in alcohol and in ether, and yielding with glacial acetic acid a brown solution. The acid is bibasic, and yields with alkalies blue compounds soluble in water, with a violet-blue color. The solutions are, however, precipitated by an excess of alkali. In ammoniacal solutions it dissolves with a reddish-blue color. Acids change the color of alkaline solutions to a carmine-red. With salts of lead, tin, and other heavy metals eupittonic acid yields blue, difficultly soluble lakes.

Application: Eupittonic acid is practically unused as an indicator. Its sensitiveness is stated to be such, however, that 0.6 Cc. of centinormal alkali suffices to afford a distinct change in 50 Cc. of solution containing the indicator.

FLAVESCIN

ALKALIES = Intense Yellow ACIDS = Colorless

Synonym: Lux's Indicator.

Source: Flavescin is a peculiar coloring-matter obtained from oak shavings.

Preparation: It is obtained by passing hot air saturated with steam through oak shavings, condensing the vapors in a cooled receiver, filtering the liquid thus obtained, and shaking it out two or three times with ether. The ethereal solution, containing the flavescin and empyreumatic acids, is evaporated, and the vessel heated to 40° or 50° C., while a current of air is passed through it until the odor of acetic acid has disappeared. The brownish residue is then digested with ten or twenty volumes of cold water; this treatment yields a concentrated solution of flavescin, which is preserved by diluting it with several volumes of alcohol.

Properties: Flavescin occurs as a brown, translucent, tenaceous mass, readily soluble in water, alcohol, and in ether. It yields colorless solutions changed to an intense yellow by alkalies. The reaction is very sharp, and is clearly seen even by artificial light. Nascent carbonic-acid gas and bicarbonates decolorize it, the coloration and decoloration being more rapid in alcoholic solution. Flavescin is decomposed by most inorganic and organic acids, the solution being decolorized. Even the fatty- and resin-acids act thus. The color is, however, restored by alkalies.

Application: Flavescin was recommended by Warder F. Lux as an indicator, and in his hands has given results closely agreeing with those of other indicators. It is not serviceable, however, for titrating small quantities of **caustic alkalies** when considerable quantities of carbonates of the alkalies are present, although it is useful for **carbonates** in the presence of bicarbonates, and also for **carbonic acid.** The reaction occurring with carbonates is due to the decomposition of the latter into a bicarbonate and a compound of flavescin. It is useful for **inorganic acids,** as well as for **organic acids.**

FLUORESCEIN

$(C_6H_3OH)_2.C.O.(C_6H_4.COO)$

ALKALIES = Green Fluorescence   ACIDS = No Fluorescence

Synonyms: Resorcin-phtalein; Diresorcin-phtalein; Tetra-oxyphtalophenone; Uranine; Krüger's Indicator.

Preparation: Fluorescein was discovered by Baeyer in 1871. It is prepared by heating an intimate mixture of 2 molecular weights of resorcin and 1 molecular weight of phtalic anhydride on an oil-bath at a temperature of from 190° to 200° C., until aqueous vapors are no longer evolved. It is important that pure materials, particularly resorcin, be used, in order to obtain a pure product. If impure materials are employed, the final purification of the fluorescein is rendered extremely difficult.

The mass obtained is then treated with boiling water, and the residue is powdered, dissolved in potassa solution, and reprecipitated by means of an acid.

Tests: The fluorescence of a solution of 0.1 Cc. of a 1:100 fluorescein-solution in 100 Cc. of distilled water is destroyed by the addition of 0.5 Cc. of decinormal hydrochloric acid.

Properties: Pure fluorescein occurs as a yellowish-red, crystalline powder, or dark-brown crystals, insoluble in water. It is but difficultly soluble in cold alcohol, more readily soluble in boiling alcohol, and quite soluble in ether and in dilute acids. With alkalies it yields solutions having a magnificent, bright-green fluorescence, permanent even in very dilute solutions; by transmitted light the solutions are red. Its formula is

$$O(C_6H_3.OH)_2.C.C_6H_4.O.CO + H_2O.$$

The sodium or potassium salt forms a yellowish-brown powder, soluble in alcohol and in water with intense green fluorescence.

Application: Fluorescein was recommended for use as an indicator by Krüger. It is very useful for titrating in **dark-colored liquids** in which color-changes are observed only with difficulty, because the fluorescence is clearly visible so long as the liquid is alkaline, but disappears the instant the liquid becomes neutral or acid. When fine white precipitates are formed in the liquid, however, the fluorescence may be masked; hence the precipitates (e.g., barium sulphate) are allowed to settle before determining the end of the reaction.

Fluorescein is serviceable in the presence of **carbonic-acid gas,** as this does not affect it. It is, however, inapplicable in the presence of **acetic acid,** as the latter dissolves the fluorescein with fluorescence, and the reading would, hence, be incorrect.

For use, a solution may be prepared by shaking together 1 Gm. of fluorescein and 100 Cc. of diluted alcohol, and then filtering. The solution has an orange-red color; it does not keep very well. From 3 to 5 drops are used.

FUCHSINE

$C_{20}H_{19}N_3HCl$

Alkalies = Crimson
Colorless in Excess
Acids = Yellow

Synonyms: Magenta; Roseine; Aniline Red; Rubin; Azaleine; Solferino; Fuchsiacine; Erythrobenzeine; Harmaline; Rubianite; Rosaniline Hydrochloride.

Preparation: Fuchsine was discovered by Natanson, of Warsaw, in 1856, by heating aniline with ethylene chloride in sealed tubes at a temperature of 200° C. In 1858 Hoffmann also obtained it by heating carbon bichloride and aniline for 30 hours at a temperature of 170° to 180° C., while looking for carbo-triphenyltriamine; he considered the red color due to an impurity. It was first made on a practical scale by Verguin, in 1859, by substituting tin bichloride for the carbon bichloride. The processes now generally followed are modifications of those patented by Hellman in 1859 and by Medlock in 1860, in which arsenic is used; and that patented by Coupier in 1866, in which nitrobenzene is employed.

Fuchsine is obtained by heating a mixture of equal molecular weights of orthotoluidin, paratoluidin, and aniline with a concentrated solution of arsenic acid at a temperature of 170° to 180° C. A part of the water distills over during the operation, which lasts from seven to eight hours. The mass is then comminuted, after cooling, and exhausted with boiling water under pressure; the arsenous and arsenic acids present are neutralized by the addition of lime. Sodium chloride is now added, and the rosaniline hydrochloride, fuchsine, obtained by crystallization; it is then recrystallized several times, but cannot be obtained entirely free from arsenic acid.

In order, however, to obtain an arsenic-free product, a mixture of aniline, nitrobenzene, nitrotoluene, iron, and hydrochloric acid is heated as in the arsenic process. The fuchsine is extracted from the fused mass, and purified as already described.

Properties: Fuchsine occurs in the form of crystals of various size having a brilliant green, metallic color. They are soluble in water and in alcohol, yielding intensely crimson solutions. The commercial preparation is most generally a mixture of pararosaniline and rosaniline hydrochlorides, the latter predominating, and is most generally found to contain arsenic, which should always be tested for; if found to be present, the preparation should be rejected.

Pure fuchsine is chemically rosaniline hydrochloride, $C_{20}H_{19}N_3HCl$.

Tests: Fuchine should be tested for arsenic by Marsh's apparatus.

Mineral impurities may be detected by incineration.

Pure fuchsine is decolorized by sulphurous acid.

Application: A solution of fuchsine in glacial acetic acid constitutes a delicate reagent for **nitrous acid** and **nitrites**, which change the color of the solution to violet first, then through blue, green, yellow, and finally into orange. **Nitric acid** does not yield the color reactions.

The crimson color of fuchsine solutions is changed by **acids** to yellow; on greatly diluting the solution, however, or on adding an **alkali**, the crimson color is restored. **Ammonia**, however, and concentrated **caustic alkalies** also destroy the color, hence fuchsine is not satisfactory for use as an indicator generally.

Fuchsine-Sulphurous Acid, prepared by passing sulphurous acid gas into a dilute solution of fuchsine until the crimson color has changed to a pale yellow, has been found to be a very delicate reagent for **aldehydes** and some of their derivatives. These all afford an intense, violet-red color with it. The solution may be preserved in well-stoppered bottles.

GALLEIN

$(C_6H_2.O.HO)_2.(CO)_2.O.C_6H_4$

ALKALIES = Bright Red   ACIDS = Pale Brown

Synonyms: Alizarin Violet; Anthracene Violet; Pyrogallol Phtalein; Dechan's Indicator.

Preparation: Gallein was discovered by Ad. Baeyer in 1870. It is prepared by heating 1 molecular weight of phtalic anhydride and 2 molecular weights of pyrogallol at a temperature of from 190° to 200° C. for several hours, dissolving the melted mass in alcohol, and precipitating by adding water. The precipitate is purified by repeated solution in alcohol, reprecipitation by water, and finally drying.

Properties: Purified gallein has the composition $C_{20}H_{10}O_7$, and forms dark-reddish crystals having a greenish reflection, or a brownish-red powder. It is almost insoluble in cold water, chloroform, or benzene, and is difficultly soluble in hot water, ether, acetone, or glacial acetic acid. It is but slightly soluble in cold alcohol, but is very readily soluble in hot alcohol, yielding a dark-red solution. It also dissolves in cold sulphuric acid unchanged, yielding a dark-red solution.

With minute quantities of alkalies, lime, or baryta, it yields salts which dissolve in water with a red color, which is changed to a blue, however, on adding an excess of alkali. Acids, even sulphurous, precipitate the gallein from the solution unchanged. Gallein also dissolves in ammonia-, lime-, or baryta-water, with a violet color; the color of the ammoniacal solution remains unchanged by heating.

With alumina and chromium oxide gallein forms grayish-violet, insoluble lakes. Reducing agents convert it into hydrogallein, and finally into gallin.

Application: Gallein was proposed by Dechan as an indicator. It is more sensitive towards **alkalies** than phenolphtalein, and may be advantageously used in titrating many **alkaloids,** such as **strychnine, morphine, quinine, inchonidine,** and **atropine.** It is practically unaffected by **carbonic-acid gas. Ammoniacal salts,** when present, do not affect it, and it is serviceable for **ammonia. Organic acids** may be titrated by means of gallein, as the indicator is sharply affected by them. **Carbonates** and **alkaloidal bases** which are neutral toward phenolphtalein yield a rose-red color with the indicator.

For use a solution of 1 : 1000 in alcohol may be made, about 10 drops being added to 100 Cc. of liquid to be titrated.

HÆMATOXYLIN

$C_{6}H_{14}O_{6} + Aq$

ALKALIES = Blue ACIDS = Red

Source: Hæmatoxylin was discovered in 1811 by Chevreul, who named it Hæmatin, in the heart wood of *Hæmatoxylon campechianum* L. (logwood; Campeachy wood), one of the Leguminosæ native to Campeachy, Yucatan, Honduras Bay, and several of the West Indies.

Preparation: Hæmatoxylin was obtained by digesting ground logwood with water at a temperature of from 50° to 55° C. for several hours, straining, evaporating the extract to dryness, and exhausting the residue with strong alcohol. The alcohol was then evaporated, the residual liquid mixed with a little water, and the whole set aside to crystallize.

Erdmann, in 1842, obtained the hæmatoxylin from the commercial extract by powdering the latter, mixing it with some sand, and exhausting with repeated portions of ether containing a slight proportion of water. The ethereal extract was then distilled off, and the remaining syrupy liquid mixed with water, loosely covered, and set aside to crystallize. The crystals separated in a few days, and were then collected, washed with cold water, and recrystallized from hot water, or from water to which a little ammonium- or sodium-sulphite had been added.

Properties: Hæmatoxylin forms colorless, or slightly yellowish, sweetish, efflorescent, shining prisms containing three molecules of water of crystallization, or occurs as rhombic crystals with one molecule of water of crystallization. The crystals have the composition $C_{16}H_{14}O_6 + Aq.$, and are soluble in ether, alcohol, and in hot water, but are only slightly soluble in cold water. They melt at from 100° to 120° C. in their water of crystallization, and char at higher temperatures. On exposure to air they are rapidly converted into hæmatein.

Hæmatoxylin is very soluble in a solution of borax; and with warm solutions of this a very concentrated, syrupy solution may be obtained, which is no longer alkaline, but neutral, or even slightly acid, has a bluish tinge, and does not deposit borax on adding alcohol or alcohol and ether, or yield hæmatoxylin crystals on evaporation. Acids do, however, precipitate the hæmatoxylin crystals with one molecule of water of crystallization; so do also certain salts, such as sodium- or ammonium-chloride, precipitate hæmatoxylin, but in an amorphous form.

Boiling hydrochloric acid or potassa lye does not decompose hæmatoxylin; nitric acid converts it into oxalic acid, and concentrated sulphuric acid dissolves it with brownish-yellow color.

With alkalies, hæmatoxylin yields solutions having a purple color changed to blue by the action of atmospheric oxygen which converts the hæmatoxylyn by oxidation into hæmatein, $C_{10}H_{12}O_6$, the color changing finally to a yellowish-brown.

On dry distillation hæmatoxylin yields pyrogallol and resorcin; on exposure to light it is colored reddish.

With baryta and with lead acetate it yields white precipitates; with copper salts, greenish-gray precipitates, which soon become blue on contact with air; and with stannous chloride a red precipitate is afforded.

Hæmatoxylin is extremely sensitive to ammonia, the most dilute solutions being rapidly affected by it. It must be kept in well-closed bottles, from air and light.

Tests: Hæmatoxylin should always be tested before use, so far as its solubility is concerned. A small quantity heated on platinum foil should leave no residue. The crystals must also be clean and not effloresced.

Application: Hæmatoxylin is not well adapted for alkalimetry or acidimetry, because, during warming with an **alkali carbonate,** it undergoes a certain change, and upon neutralization exhibits a color entirely different from what it originally had, which may, hence, be the cause of uncertainty in observation. It may be used for certain substances, such as **copper salts, alum, chalk,** etc.

Hæmatoxylin is one of the best of indicators for general use for **alkaloids,** and particularly for **atropine** and **emetine.**

Hæmatoxylin Test-paper, when recently made, is also very serviceable. (See Test-papers).

HÆMATOXYLON

ALKALIES = Blue ACIDS = Red

Synonyms: Logwood; Campeachy Wood.

Source: Hæmatoxylon is the name usually applied to the wood of *Hæmatoxylon campechianum* L., logwood, one of the Leguminosæ native to Campeachy, Yucatan, Honduras Bay, and several of the West Indies.

Properties: Hæmatoxylon is heavy, hard, and coarsely grained, brown or reddish-brown within, and blackish-red or bluish-black externally. The constituents of the wood are hæmatoxylin (upon which its colorific properties depend), a volatile oil, tannin, resinous substances, various salts of acetic acid, calcium oxalate, potassium chloride, alumina, iron and manganese oxides, and silica. The wood yields to water its coloring-matter, and affords a dark-red extract which affords blue precipitates with lead acetate, lime-water, and alkali carbonates; with alum a violet one; with nutgalls a black, and with iron and chromium salts a violet-blue to black precipitate.

Preparation: Hæmatoxylon is generally applied as an indicator in the form of a tincture or decoction, and is exceedingly sensitive. Since the wood is very easily affected by both light and air, shavings from the inner portion of a billet are used, and the tincture prepared by treating the shavings with a 45-per-cent. pure alcohol for 24 hours in a well-closed vessel in a warm place. The tincture so obtained is filtered through glass wool, carefully avoiding any exposure to ammoniacal vapors, and is preserved in small vials with closely fitting glass stoppers.

Application: A tincture so prepared is one of the most sensitive of reagents for **free alkalies** and **alkaline salts.** It is particularly sensitive to **ammonia,**

the faintest traces of which suffice to afford a blue color,—a fact that renders the application of the hæmatoxylon as an indicator somewhat unsatisfactory because of the difficulty of securing an absolutely ammonia-free atmosphere in which to operate.

A few drops of the tincture added to a solution containing **alkalies** or **alkaline earths** affords a red, violet, or blue color, according to the quantity of alkali present. One part of **ammonia** in 500,000 parts of water affords a distinct red color. Many metals, particularly **iron** and **copper,** yield blue or bluish-violet precipitates with hæmatoxylon tincture, even when other reagents fail to show the minute traces present.

An aqueous decoction of hæmatoxylon is similarly sensitive, and its color is rapidly changed to a violet even by pure **calcium carbonate, chalk,** and **marble dust.** Both the tincture and the decoction should be kept only in an acidulated condition because of their exceeding proneness, when in neutral or alkaline solution, to become colored.

A hæmatoxylin test-paper is also used at times, and is described under Test-papers.

INDIGOSULPHONIC ACID

$(C_6H_3)2.(CO)_2.C_2.(NH)_2.(HSO_3)_2$

ALKALIES = carbonates: Blue
caustic: Yellow
ACIDS = Blue

Synonyms : Sulphindigotic Acid; Indigosulphuric Acid.

Preparation : Solution of indigosulphonic acid for indicating purposes is prepared by dissolving powdered indigo in fuming sulphuric acid, then neutralizing with calcium carbonate, diluting the solution with 10 times its volume of water, and filtering the blue liquid so obtained.

Application : The blue color of the indigosulphonic-acid solution is not disturbed by **carbonates** of the **alkalies,** but **caustic alkalies** change the color to yellow, hence these latter may be determined in the presence of carbonates. For this purpose, 1 or 2 drops of the indicator solution are added to the solution to be titrated, and the acid then added. When the free alkali is neutralized, a green color forms, which gives place to a blue. With a white dish, the color-change is seen to take place very sharply, and good results may be had. The indicator was recommended for use by Engel and Ville.

INDIGO CARMINE

$(C_6H_3)_2.(CO)_2.C_2.(NH)_2.(SO_3Na)_2$

ALKALIES = Yellowish-brown ACIDS = Blue

Synonyms : Soluble Indigo; Indigo Extract; Blue Carmine; Indigotine; Sodium Indigotin-disulphonic Acid.

Source : Indigo carmine is the blue pigment prepared from indigo, an oxidation product of indigo white, or indican, a constituent of the sap of various species of the Indigoferæ, chiefly *Indigofera tinctoria* L., *I. disperma*, *I. anil* L., and *I. argentea* L., Nat. Ord. Leguminosæ. These are found in the East Indies, Africa, West Indies, Brazil, China and Hindostan.

Preparation : According to Joclét, indigo carmine is prepared by dissolving 1 part of powdered indigo in 5 parts of concentrated sulphuric acid heated to 50° C., and adding to the solution gradually 3.3 parts of sodium carbonate dissolved in 30 parts of water. The mixture is stirred, and, after 12 hours, strained through a woolen cloth, the precipitate of indigo carmine being finally washed with a very small quantity of water.

Indigo carmine is also obtained by adding 1 part of powdered and dried indigo, in two portions, to a mixture of 4.5 parts of fuming sulphuric and concentrated sulphuric acids, stirring constantly and avoiding a rise in temperature. When the mixture is homogeneous, it is kept at a temperature of 50° C. for a week, and is then poured into 10 parts of water, after which a solution of 10 parts of sodium chloride having a sp. gr. of 1.170 is next added. The precipitated indigo carmine is then collected by filtration, washed and finally dried.

Properties: Indigo carmine is the sodium salt of indigotin-disulphonic acid, and has the composition $C_{16}H_8N_2O_2(SO_3Na)_2$. It occurs both as a blue, pasty mass, and as a blue, dry powder soluble in from 140 to 150 parts of water. It yields a blue solution, the color of which is changed by caustic soda to a yellowish brown, and restored by acids.

Tests: The fitness of indigo carmine for use is recognized, according to Mierzinski, by placing a small quantity of the preparation on a piece of white filtering-paper. If the preparation is impure, a green ring soon forms around the indigo carmine. When the powdered indigo carmine is to be tested, it is first stirred with a little boiling water before placing on the filter-paper.

Application: Indigo-carmine solution is used in the estimation of **nitrites** and of **chlorine**, both of which decolorize it on boiling. It is also employed for the estimation of **oxygen** and of **tannin**, the latter particularly. For tannin, Löwenthal and Schröder recommend the following solution:

30 Gm. of indigo carmine, in dry form, are dissolved in 3 liters of diluted sulphuric acid (1 : 5 by volume), then 3 liters of distilled water added, the whole thoroughly shaken and filtered.

Care must be exercised that only a good quality of indigo carmine be used, because, when a poor quality of indigo carmine is employed when titrating with potassium permanganate solution, the end of the reaction is not clear, as the greenish tint does not change sharply to yellow, but changes through reddish and brownish tints which render it impossible to note the end of the reaction.

IODEOSINE

$C_6H_4(CO.C_6H_2I_2O)_2O$

ALKALIES = Rose-red ACIDS = Yellowish

Synonyms: Tetraiodofluoresceine; Erythrosin B.; Pyrosine B.; Dianthine B.

Preparation: Iodeosine is obtained by dissolving 6 parts of fluorescein in a hot mixture of 8 parts of soda-lye and 60 parts of water, and adding to this a solution of 24 parts of iodine in 27 parts of soda-lye mixed with 60 parts of water; to this mixture are then added 25 parts of glacial acetic acid. The whole is boiled, then neutralized with caustic soda, and 25 parts of hydrochloric acid are added.

The precipitate is then collected and purified by dissolving it in aqueous ether, shaking out with weak caustic-soda solution and reprecipitating by adding concentrated soda-lye. The brick-red precipitate is then washed with alcohol, and crystallized from hot alcohol. The pure sodium salt thus obtained is then decomposed by hydrochloric acid, and the precipitate thoroughly washed and dried at a temperature of about 120° C.

Properties: Iodeosine occurs as a brick-red powder, almost insoluble in water and in cold water, but soluble in hot alcohol and in ether.

Application: Mylius and Förster recommend iodeosine for the estimation of very minute quantities of **alkali**; for instance, such as may be dissolved out from glass on contact with water. For this purpose they recommend an ethereal solution containing 0.002 Gm. per liter (1 : 500,000).

Titration with this indicator is carried out by introducing from 50 to 100 Cc. of the liquid to be operated on into a stoppered bottle and adding from 10 to 20 Cc. of the ethereal solution. If desired, 4 or 5 drops of a 1 : 10,000 aqueous solution may be added to the liquid, and ether then added. If **free alkali** is present, even in mere traces, the aqueous layer soon acquires a rose-red tint, whereas if **acids** are added the ethereal layer becomes colored yellowish.

Iodeosine is one of the best of indicators for use in **alkaloidal** estimations, and for detecting traces of **acids** or of **acid salts** in so-called neutral chemicals.

H. A. Cripps gives the following process for using the indicator for alkaloids: 20 to 25 Mg. of alkaloid (or alkaloidal residue from a drug assay) are dissolved in 5 Cc. of *n*/20 hydrochloric acid, and the solution diluted to measure 20 Cc. with perfectly neutral water. Four drops of a 1 : 10,000 aqueous iodeosine solution are now added, and 10 Cc. of neutral ether. *n*/200 barium-hydrate solution is now added from a burette, with frequent agitation until the aqueous layer has assumed a rose color. A previous titration will have determined the value of the baryta solution; and the difference between the two titrations will indicate the alkaloid.

IODEOSINE G

$C_6H_4(CO.C_6H_2IONa)_2O$

ALKALIES = Cherry-red ACIDS = Brownish-yellow

Synonyms: Pyrosine J.; Dianthine G.; Jaune d'Orient; Erythrosine G.; Diiodofluoresceine-Sodium (or Potassium).

Preparation: Iodeosine G. is obtained by mixing solutions of 6 parts of fluoresceine and 16 parts of iodine in 20 parts of soda lye each, and precipitating with 20 parts of glacial acetic acid. The precipitated diiodofluoresceine is then converted into a sodium (or potassium) salt, which is purified by recrystallization from hot alcohol.

Properties: Iodeosine G. forms a yellowish-brown powder or plates, soluble in water, and yielding a cherry-red solution free from fluorescence. The color of the solutions is changed to a brownish-yellow by acids, and is restored to red by alkalies.

Application: Iodeosine G. or Iodeosine (which see) is particularly useful in **alkaloidal assays**, and is also serviceable for **alkalies**.

IRON AND AMMONIUM SULPHATE

Ferrous Halogen Salts = Red

Silver Salts = Red

$Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$

Synonym: Ammonio-Ferric Alum.

Preparation: 240 Gm. of solution of ferric sulphate (sp. gr. 1.43) are added to a solution of 28 Gm. of ammonium sulphate in 100 Gm. of warm water. On slowly cooling the solution crystals are obtained which are subsequently freed from the mother liquor, washed with a little water and dried.

Properties: Ammonio-ferric alum occurs as lilac or violet efflorescent crystals having a sour, styptic taste, and soluble in 3 parts of water and in 0.8 parts of boiling water. The salt is affected by light, by which it is reduced to a ferrous condition, hence it should be kept in amber bottles or in a dark place, and also from contact with air. Its formula is $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$.

Application: Ammonio-ferric alum is employed as an indicator in titrating **silver salts** by means of decinormal ammonium- or potassium-sulphocyanate solution, and similarly for titrating **ferrous halogen salts**, using silver nitrate and a sulphocyanate.

LACMOID

$C_{12}H_9NO_4$(?)

ALKALIES = Blue ACIDS = Red

Synonyms: Resorcin Blue.

Preparation: Lacmoid was first prepared by Weselsky and Benedikt, in 1880. It is obtained by heating 20 parts of resorcin, 1 part of sodium nitrite, and 1 part of distilled water on an oil-bath to 110° C., at which temperature the reaction becomes quite active. When the reaction moderates, the heat is raised to from 115° to 120° C.; ammoniacal vapors are freely disengaged and the raspberry-red mass becomes reddish-violet, bluish-violet, and finally blue. When the vapors are no longer disengaged, the mass is dissolved in a little water, and precipitated by hydrochloric acid. The precipitate is then collected, washed and dried, and constitutes the lacmoid in an impure form.

Schaerges recommends preparing the lacmoid by the reaction of resorcin on sodium nitrite without the addition of any water, and at a temperature not exceeding 110° C., dissolving the product in a little water, and removing the undecomposed resorcin still present by shaking out with ether. Schaerges claims that lacmoid so prepared is clearly soluble in all proportions in water and in dilute alcohol, but is insoluble in ether.

For obtaining a perfectly pure lacmoid, Förster recommends treating the commercial article in fine powder with boiling water, acidulating the blue solution after cooling and filtering, with hydrochloric acid, collecting the precipitate after a few hours, washing it with a little cold water, and drying it at not too high a temperature; or, dissolving it in alcohol and evaporating the solvent.

Lacmoid solutions, no matter how carefully prepared, are more or less prone to exhibit a violet tinge which may prove very deceptive to other than normal eyes. To remedy this defect, Förster recommends the addition of 5 Gm. of naphtol green (Cassella & Co.) to 3 Gm. of purified lacmoid obtained as above, and dissolving both in 700 Cc. of water and 300 Cc. of alcohol. Malachite green had formerly been proposed, but the naphtol green has been found to be more permanent, and to yield no precipitate with lacmoid (malachite green does), while it imparts a pure blue color to neutral and alkaline fluids, which is changed to an onion-red with acids. The sharpness of the change of color is greatly enhanced by the addition of the naphtol green.

Properties: Lacmoid occurs as a glistening brown or dark-violet powder, amorphous granules, or as blue-black scales. It consists principally of diazo-resorcin, or resazurin, also known as "Weselsky's indicator." Lacmoid is soluble in alcohol, acetone, wood-alcohol, pyroligneous acid, acetic acid, phenol, and amyl alcohol; it is less soluble in ether and in water, and insoluble in chloroform, benzene, and benzin.

Its constitution is unknown, and the empirical formula assigned it is $C_{12}H_9NO_4$.

With neutral and alkaline liquids lacmoid yields handsome blue solutions having a faint violet tinge, changed by a mere trace of acid to red. The solutions should be preserved in dark bottles, as they are very sensitive to light.

Tests: The fitness of lacmoid as an indicator is tested by treatment with water. If but little or no color is imparted to water, the sample should be rejected.

According to Traub, a few drops of decinormal ammonia suffice to clearly show the blue color in a solution containing 1:2,000,000 of the indicator.

Application: The application of lacmoid as an indicator is very similar to that of litmus. It is useful for titrating both **caustic alkalies** and **acids.** Aqueous solutions of **calcium** or **magnesium bicarbonate** affect it very sharply. Normal **alkali sulphites** are strongly alkaline, and **bisulphites** are neutral, to lacmoid. The indicator is affected by the **hydrogen sulphide** liberated in titrating sulphides, hence it is unserviceable for them, but the latter, as well as **carbonates, sulphites, phosphates, arsenates,** and **borates,** may be readily and accurately titrated by means of lacmoid paper, a drop of the liquid being dropped on the paper, which is best washed, previous to use, with pure distilled water.

To **acid phosphates** and **arsenates** the lacmoid is neutral; nevertheless, the paper is most serviceable, and shows 50% of the alkali. Towards **arsenous acid** the solution is neutral, and good results are obtainable with both solution and paper. Lacmoid paper may be used for **borax, sodium** and **ammonium carbonates, effervescent preparations** of **magnesium, lithium**, and other **carbonates**, etc., as well as for the **alkali** of the **alkali silicates** (for these latter the lacmoid solution answers equally well).

Lacmoid may be used hot for titrating the **alkali** in **carbonates** or **bicarbonates,** but the change of color does not take place until all the carbonic-acid gas has been replaced. **Barium, magnesium,** and **calcium carbonates** may be titrated by first adding an excess of acid, and then titrating back with sodium hydrate.

Lacmoid solution is useless for **sulphites** and **sulphides,** but is applicable for **borates.** Towards **thiosulphates** it is neutral. **Borax, silicic acid,** and **arsenic acid** do not affect the indicator in the cold. **Arsenic** and **phosphoric acids** behave like monobasic acids towards it.

Potassium and **sodium bichromates** are neutral to lacmoid, but the **neutral chromates** are alkaline; hence a mixture of **bichromate** with **chromate,** or of **chromic acid** and a **bichromate,** may be readily titrated by means of lacmoid.

Oxalic, acetic, lactic, tartaric, and **nitric acids,** as well as **organic acids** in general, cannot be titrated by means of the indicator.

The **sulphates** and **chlorides** of **iron, copper,** and **zinc,** which are all more or less acid to litmus, are neutral towards lacmoid; hence any **free acids** present in solutions of these salts may be easily estimated by its means. For **alumina,** lacmoid will not answer.

LITMUS

ALKALIES = Blue ACIDS = Red

Synonym: Lacmus.

Source: Litmus is a pigment obtained principally from *Rocella tinctoria* Acharius, but also from

Lecanora tartarea Ach., *R. fuciformis* Ach., *Variolaria dealbata*, etc., lichens found growing sometimes on trees, sometimes on cliffs, on the coasts of the Mediterranean Sea, Spain, France, Holland, England, and Sweden, and also on the Canary Islands, Orkney Islands, and Corsica.

Preparation : Litmus does not exist as such in the plants. By the action of ammonia and air alone on the lichens, a peculiar substance, orcein, discovered by Robiquet in 1829 is formed ; but when potassa is permitted to act in conjunction with the other substances, a new coloring-matter is the result, a compound of chiefly azolitmin and potassa. Hence, the lichens are ground, and mixed with ammonia and potassa ; they are then permitted to ferment until the mixture acquires a violet color, when lime, potassa, and generally urine also, are added, and the whole allowed to stand for 2 or 3 weeks, or until a blue color has been acquired. Chalk and gypsum in variable quantities are then added, and the mixture is strained through a hair sieve, and finally formed into little cakes or cubes.

Properties : Litmus occurs in the form of small, light, friable, finely granular cakes or cubes posessing a handsome, violet-blue color. It has a peculiar, characteristic odor recalling that of indigo, and has a pungent and somewhat saline taste. It is partly soluble in water with a blue, and in dilute alcohol with a purplish-blue, color, which is changed to red by acids. Its principal coloring-matter, and the one on which its value as an indicator depends, is azolitmin, which was discovered by Kane in 1841 (see Azolitmin).

Tests: The quality of the litmus of the market is apt to vary greatly, hence the article should invariably be tested when a new lot is purchased. For the test, equal quantities of the litmus to be tested and an article known to be good are weighed, and both treated with equal volumes of distilled water for 12 to 24 hours, shaking every now and then. When the mixtures have settled, they are filtered, and the colors then compared.

A still better plan is to heat the cold aqueous extract so obtained to boiling, and then to add hydrochloric acid by drops until a permanent onion-red color is had on boiling for 6 to 8 minutes. The solution is then rapidly cooled, and mixed with an equal volume of alcohol. The tincture so obtained is then tested as to its sensitiveness to acids and alkalies. This should be such that when sufficient of the tincture is added to 250 Cc. of recently boiled and cooled distilled water to color the latter a distinct violet (indicating neutrality), a solution is had which is sharply changed to an onion-red or pure blue by one drop of decinormal hydrochloric acid or decinormal alkali respectively. On standing for a minute or so, either solution will acquire a violet tint. In these solutions two drops of the decinormal acid will give a permanent onion-red with the blue solution; whereas two drops of the decinormal alkali suffice to give a permanent blue with the red solution.

0.2 Cc. of a 10-per-cent. solution of purified litmus added to 100 Cc. of distilled water should require about 0.05 Cc. of decinormal hydrochloric acid, or 0.1 Cc. of decinormal potassa to effect changes of color.

Application: Since the value of the litmus as an indicator depends entirely on the azolitmin present, and since the latter is accompanied by three other coloring-matters which detract from its sensitiveness because yielding violet tints, it is desirable, in preparing solutions for titrimetric observations, to effect a separation of the coloring-matters so that only azolitmin will be present in the solution. This separation is effected by exhausting the coarsely powdered litmus with successive portions of hot alcohol, in which azolitmin is insoluble, but in which the others are soluble. The residue is then digested with cold dilute acid, in order to remove the excess of free alkali present, and then with five times its weight of boiling water, which dissolves out the azolitmin. The solution is then filtered.

Of the solution made as above detailed, about 5 drops are added to 100 Cc. of liquid to be titrated.

Litmus solution is best kept in comparatively wide-mouthed, half-filled bottles, closed by a plug of cotton to keep out dust, but not air. In the absence of the latter, the solution undergoes a peculiar fermentation, evidenced by a disagreeable odor and loss of color. An apparently spoiled solution recovers its original color and valuable properties, however, on exposure to air in a shallow dish ; it does not require filtering or boiling, simple exposure, with exclusion of dust, sufficing. The solution should not be kept in an acidified condition, as it is then very prone to become mouldy. Many substances have been proposed for the purpose of preserving the solutions, among others, carbolic acid. No special advantages have, however, been found to accrue from their use, and the practice of adding preservatives is not general.

Litmus yields a deep blue color with alkalies, and an onion-skin red with acids. **Carbonates** of the **alkalies** also produce the blue color, and the indicator may therefore be used for titrating **hydroxides** of the **alkalies** only when no carbonates are present. With **carbonates** and **bicarbonates,** it can only be used when the liberated carbonic-acid gas is expelled from the solution by boiling, as the dissolved gas would otherwise cause the red color to persist even though the liquid is alkaline, and thus prove a source of error.

When a diluted **mineral acid** is added drop by drop to a solution of a carbonate of an alkali to which litmus has been added, no change of color takes place until from 60% to 64% of the carbonate has been neutralized, when the solution assumes a purplish or violet color. On now heating the solution, carbonic-acid gas is copiously evolved, and on the continued addition of acid to the boiling solution, the latter acquires an onion-red color as soon as the least excess of acid is added. The color is permanent, not being affected by the boiling; and the end of the reaction is readily recognized when the color, at the point where the dropping acid reaches the solution, cannot be distinguished from that possessed by the solution in general.

The end of the reaction is very sharp with **caustic alkalies, alkaline earths,** and their **carbonates**; and also with **sulphides,** but with these the **hydrogen sulphide** liberated must also be driven off by boiling, as with **carbonic-acid gas.**

Litmus is fairly good for titrating **ammonia,** and, under certain conditions, for **ammonium carbonate** also. With **silicates** of the **alkalies** the reaction is very sharp. With **borates** of the **alkalies** and of **magnesium,** as well as with the **sulphates** and **phosphates** of the **alkalies,** and also **arsenates,** the end of the reaction is uncertain, as the change of color is too gradual. With **arsenites,** however, the change is sharp.

With **sulphites** the colors yielded are somewhat indefinite, but the change is very sharp and certain the moment saturation is complete.

Litmus is useless for titrating **tartaric** and **citric acids,** but is serviceable for **benzoic** and **oxalic acids.** The indicator may also be employed in titrating the acids in the normal salts of **quinine, strychnine, morphine, narceine** and **papaverine,** as these are neutral to litmus. **Caffeine, narcotine,** and **theobromine** alkaloids are neutral to litmus, but their salts behave like a corresponding quantity of free acid. In titrating **quinine,** oxyacids are unsuitable for use, because they cause too much fluorescence, hence decinormal hydrochloric acid is most suitable. For **emetin,** litmus is useless.

Litmus is most serviceable for indicating the **neutrality** of **milk** when the acidity of the latter is neutralized previous to the estimation of fat. It is also useful for estimating the acidity of urine.

Aniline, toluidine, and **quinoline** are neutral to litmus, and so are also **anhydrides** and **concentrated anhydrous acids.** With these latter the change of color occurs only when water is present. Litmus is not well adapted for use by gas- or lamp-light, hence when it is desired to perform titrations at night with it, the use of a sodium-flame will be found to be necessary. The sodium-flame may be obtained by placing on a retort ring a circular piece of asbestos, in the center of which a small hole has been cut out. Through this hole the flame from a Bunsen-burner is allowed to pass, while it touches the margin of the hole. Around the margin some sodium chloride or borax is sprinkled; or, the margin may be impregnated with a concentrated solution of sodium chloride. In the monochromatic light so obtained, the onion-red color of the litmus appears perfectly colorless, while the blue is distinct and appears black.

LUTEOL

$C_6H_2.OH_2(NC).(C_6H_5)_2Cl$

ALKALIES = Yellow ACIDS = Colorless

Synonyms: Oxychlordiphenylquinoxaline; Autenrieth's Indicator.

Preparation: Luteol is prepared by heating one molecular weight of ethoxyphenylenediamine with one molecular weight of benzile in alcoholic solution, and recrystallizing the precipitated ethoxyphenylquinoxaline from alcohol. This is then heated with phosphorus pentachloride to a temperature of from 70° to 90° C. in a paraffin bath, when some of the chlorine enters into the compound, while phosphorus trichloride and hydrochloric acid distil off. The ethoxychlordiphenylquinoxaline so obtained is next heated to from 180° to 200° C. with hydrochloric acid in a sealed tube, when the alkyl, ethylene chloride, is split off. The residue, which constitutes the luteol, is then purified by repeated recrystallization from alcohol.

Properties : Luteol occurs as fine, woolly, yellowish needles that melt at 246° C., and sublime without decomposition at higher temperatures. It is insoluble in water, and sparingly soluble in cold alcohol, but is readily soluble in hot alcohol and in ether. In concentrated sulphuric acid it dissolves with a red color, but is reprecipitated by the addition of water. It is sparingly soluble in concentrated hydrochloric acid, but is perfectly insoluble in the diluted acid. It is readily soluble in alkaline solutions, yielding a yellow color. Chemically, luteol is a phenol, its formula being: $C_6H_2.OH_2(NC).(C_6H_5)_2Cl$.

Application : Luteol was recommended as an indicator by W. Autenrieth. In point of sensitiveness it far exceeds both litmus and phenolphtalein; 5 to 10 Cc. of a solution containing 1 drop of dilute soda lye in a liter are distinctly colored yellow by a few drops of an alcoholic luteol solution. To **ammonia**, luteol is even more sensitive than is Nessler's solution, as 5 to 10 Cc. of a solution containing 1 drop of ammonia water per liter are colored yellow immediately, whereas with Nessler's test a reaction was obtained only after some time.

Luteol expels **carbonic acid** from carbonates, and the acid character of the phenol is greatly increased by the introduction of the chlorine atom into the preparation.

It is superior to phenolphtalein in that it may be used in the presence of **ammonia**; and better than litmus because no intermediate colors appear during the change, hence insuring greater accuracy. The yellow color produced by **alkalies** is discharged by **acids**, the solution becoming colorless.

Solution of luteol for indicating is prepared by dissolving 1 part of the substance in 300 parts of alcohol. Of this solution from 4 to 8 drops are added to 100 Cc. of the solution to be titrated.

MALLOW

ALKALIES = Green ACIDS = Red

Source: The purple flowers of several species of Mallow yield a pigment that has been applied as an indicator. The species from which the pigment is most generally obtained are *Althæa rosea* Cavanilles (*Alcea rosea* Linn.), hollyhock; *Malva sylvestris*, common mallow; and *Malva vulgaris*. The mallows are biannual plants, and are indigenous to the Orient, but are found cultivated over all of southern and central Europe.

Preparation: The pigment of the mallow flowers is extracted by exhausting the latter with hot water, or with alcohol, and carefully evaporating the solvents.

Properties: The aqueous extract of the hollyhock is violet-red in color, the margins of the solutions presenting a dark-violet color, whereas the alcoholic extract is purplish-red, and deposits the pigment, on evaporation of the alcohol, in the form of a blackish, nitrogenous substance. Solutions of the pigment are colored a fine red by **acids**, and green by **alkalies**, in which respect it is closely allied to the pigment obtained from the common Dahlia, and with which it is, in fact, believed to be identical. Alum yields with the pigment-solution a lilac color, and baryta-water causes the gelatinization of the solution with a green color.

The flowers of Malva vulgaris yield, when extracted with water, a reddish-brown infusion which is colored a wine-red by **acids**; **alkalies**, however, deepen the color at first, but afford a reddish-yellow later. With this infusion alum and baryta-water yield yellowish-white precipitates.

Application: Mallow pigment is now but seldom used as an indicator. It is, however, largely used for intensifying the color of **red wine**. A test-paper is still sometimes used (see under Test-Papers).

MESITYLENE-QUINONE

$C_6H_4(CH_3)_2OH.O$

ALKALIES = Reddish-violet ACIDS = Yellow

Synonyms: Oxymeta-xyloquinone; Trimethylbenzene-quinone; Oxy-iso-xyloquinone; Fittig's Indicator.

Preparation: Mesitylene-quinone is obtained by subjecting a mixture of 5 Gm. of diamidomesitylene hydrochlorate, 250 Gm. of water, 12 Gm. of sulphuric acid, and 1 Gm. of potassium bichromate to distillation so long as a yellow distillate is received. When this ceases 1 Gm. more of potassium bichromate is added to the mixture, and water to make up the original volume, and the whole again subjected to distillation. The distillates are then mixed and shaken out with ether, which removes the mesitylene-quinone, and deposits it, on evaporation.

Properties: Mesitylene-quinone forms orange-red needles which are very readily soluble in alcohol and in ether, quite readily soluble in hot water, and difficultly so in cold water. It is easily volatilized by steam, melts at 103° C., and sublimes in the form of deep, golden-yellow, long needles. Its formula is believed to be $C_6H_4(CH_3)_2OH.O$.

Application: Mesitylene-quinone is exceedingly sensitive to **alkalies**, being colored by them a reddish violet. It is far more sensitive than litmus, and is colored even by **calcium carbonate** and by **spring water.** It has been employed in testing the latter.

METHYL ORANGE

$C_6H_4.N(CH_3)_2.N_2.C_6H_4.SO_3Na$

ALKALIES = Yellow ACIDS = Red

Synonyms: Dimethylaniline Orange; Mandarin Orange; Tropæolin D.; Orange III; Poirrier's Orange III; Helianthine; Gold Orange; Sodium (or Ammonium) Dimethylaniline-azobenzene-sulphonate; Parasulphobenzene-azodimethylaniline Sodium (or Ammonium); Sodium (or Ammonium) Dimethylamidoazobenzene-sulphonate; Lunge's Indicator.

Preparation: Methyl orange is obtained by the action of diazobenzenesulphonic acid on dimethylaniline, and converting the acid so obtained into its sodium or ammonium salt. It may be prepared by dissolving 10 parts of aniline, 13 parts of dimethylaniline, and 23 parts of hydrochloric acid in 360 parts of water, and adding gradually a solution of 7.4 parts of sodium nitrite and 4 parts of caustic soda in 54 parts of water. The precipitate is collected, dissolved in hydrochloric acid, and reprecipitated by caustic soda. It is again collected, washed, and crystallized from hot alcohol. The dimethyl-amidoazobenzene so obtained is then converted into a sulphonate by dissolving it in 20 times its weight of concentrated sulphuric acid, pouring the solution into cold water, and dissolving the precipitate in sufficient caustic-soda solution; the solvent is then evaporated, and yields the sodium salt.

Properties: Methyl orange occurs as an ocher-yellow powder, readily soluble in hot water, moderately soluble in cold, and only slightly soluble in alcohol, but more so in dilute alcohol.

Tests: There are on the market a number of preparations bearing the name "methyl orange" which are totally unfit for use as indicators; hence every new sample must be carefully tested. Alfred H. Allen states that when any doubt exists as to its fitness, the suspected methyl orange should be purified by precipitating the hot concentrated solution with hydrochloric acid, and, after washing the precipitate, dissolving it in ammonia. The following are the tests given whereby a good methyl orange may be identified, and differentiated from other oranges:

The aqueous solution is orange-yellow, and is not precipitated by alkalies (Orange I gives a reddish-brown; Orange II a brownish-red).

Hydrochloric acid precipitates from hot, concentrated solutions the free sulphonic acid, as microscopic needles, which soon become lustrous plates or prisms having a violet reflection (Orange I gives a yellowish-brown precipitate; Orange II gives a brownish-yellow precipitate).

With concentrated sulphuric acid a reddish or yellowish-brown solution is afforded, the color of which is yellow in thin layers, and a splendid red on copious dilution.

Barium- or calcium chloride affords no precipitate (Orange I yields a red precipitate with calcium chloride).

Basic lead acetate precipitates the methyl orange as an orange-yellow powder (Acid Yellow is not precipitated).

Magnesium sulphate precipitates the indicator from dilute solutions in the form of microscopic crystals.

With gold chloride methyl orange gives a red color (Orange IV gives a violet, then green color).

Application: Methyl orange was recommended as an indicator by Lunge in 1881. For titration, a solution is prepared by dissolving 1 Gm. of methyl orange in 1000 Cc. of water. Of this solution 4 or 5 drops are added to 100 Cc. of the solution to be titrated. The color of the solution is yellow, and remains unaffected by **alkalies** or **carbonates** of the **alkalies**, but is changed by **acids** to a handsome red.

Methyl orange is an excellent indicator, but requires a practised eye, as well as considerable care, in its use, as the readings are apt to be misleading on account of the **sulphates** or **chlorides** formed during titration; these have an influence on the sharpness of the change, an onion-red color being first formed when acids are added. The final coloration is also not quite so intense as with phenolphtaleine; and if more than 4 or 5 drops of the solution be used to 100 Cc. of fluid in order to obtain sharper results, there is a diminution in the sensitiveness, hence an excess must be avoided.

In titrating alkaline solutions, the yellow color first changes suddenly to a yellowish-red on approaching neutralization, and the fine red develops immediately on the further addition of a drop of the normal acid employed.

Methyl orange possesses comparatively strong acid properties, therefore only strong acids can be titrated by means of it, and hence, also, it is much more sensitive to alkalies than to acids.

Carbonic, boric, silicic, sulphydric and **arsenous acids**, as well as the ordinary **organic acids, oxalic, tartaric, acetic, citric, carbolic**, etc., and the **fatty acids, oleic, palmitic, stearic**, etc., yield no red color with the indicator. Hence oxalic or acetic acid cannot be used with methyl orange for titrating alkalies.

Ammoniacal salts, sulphates, nitrates, and **chlorides** seriously diminish the sensitiveness of the indicator; their absence should therefore be assured in order not to increase the liability of error which the formation of these salts during titration already induces.

Sulphites and **hyposulphites** of the alkalies have no effect on the color, as they are neutral. Sulphites may be titrated only if no carbonate is present, otherwise the readings are apt to be inaccurate. On titrating sulphites with methyl orange, the red color is yielded when a bisulphite is formed.

Nitrites of the **alkalies** (which are neutral to rosolic acid, phenacetolin, litmus, and phenolphtalein) either prevent the red color or rapidly discharge it in acid solutions, with decomposition of the indicator. **Nitrous acid** also decomposes the indicator.

Arsenic and **phosphoric acids**, when titrated with methyl orange, behave like monobasic acids; i.e., they are rendered neutral to it when one-third of the acid has combined with the base used in titrating, the end reaction being very sharply defined (with phenolphtalein these acids indicate neutrality when two-thirds of the acids have entered into combination). Hence **monophosphates** and **monoarsenates** afford alkaline reactions with methyl orange.

Arsenous acid is neutral to methyl orange; hence it and **arsenites** can be accurately titrated, the reaction being very sharp.

Methyl orange answers well for **ammonia**, but is useless for **lactic, citric, tartaric, succinic, butyric, acetic**, and in fact almost all organic acids.

The indicator is very serviceable for estimating **sulphides, carbonates**, and **bicarbonates** of the **alkalies**, as the liberated hydrogen sulphide or carbonic-acid gas does not affect its color. It is also the best indicator, probably, for estimating the **sodium, potassium, ammonium, calcium**, and **magnesium, borates**, as the liberated boric acid has no influence on the color.

Methyl orange is serviceable for titrating the **silicates** of the **alkalies**; it is also useful for estimating **mineral acids** in the presence of fatty acids, as the latter do not affect the color of alkaline solutions. It is also useful for estimating **free acids** present in solutions of metallic salts, or in **alum, cupric chloride, ferrous sulphate,** etc.

The indicator is also applicable for the estimation of **alkaloids,** such as **strychnine, quinine, cinchonidine, atropine,** and especially for **morphine.**

The use of **alcoholic solutions** must be avoided when methyl orange is used as the indicator, otherwise the readings will be erroneous.

Methyl orange is unsuitable for titrating **alkali** in the presence of **alumina,** as the aluminum sulphate formed during titrating is neutral to it. In this case only the alkali and alumina together can be determined, and the alumina determined by the difference after again titrating, using phenolphtalein (the latter is affected by aluminum sulphate). The operation is best conducted in lukewarm liquids, because in cold liquids the color-changes take place but slowly.

Aniline, toluidine, and **quinoline** are alkaline toward methyl orange, but their salts are neutral; hence the bases may be titrated by its means.

Methyl orange may be advantageously used for determining one ingredient in a substance, after a previous titration with some other indicator has been made of another substance present. For instance, in a mixture of **sodium carbonate** and **sodium acetate**, the former may be estimated by means of phenacetolin, and after the red color has disappeared, the acetate may be titrated using methyl orange. Or, **soda** in **soap** may be first titrated by means of methyl orange and sulphuric acid, and then the **salt** present in the same solution estimated by adding an excess of potassium chromate and neutralizing with silver nitrate. Or, again, in a mixture of **alumina** and **soda**, or in **caustic soda** containing alumina, the sodium may be estimated by adding phenolphtalein to the solution, heating, and titrating with sulphuric acid until the red color disappears, then adding methyl orange, and continuing the titration of the warm fluid with acid to a close.

As a rule, titrations with methyl orange are best carried on at the ordinary temperature.

METHYL-ORANGE AND PHENOLPHTALEIN SOLUTION

ALKALIES=Red NEUTRAL=Lemon-Yellow ACIDS=Pink

Preparation: The solution is prepared by dissolving 10 parts of phenolphtalein and 1 part of methyl orange in 1000 parts of dilute (50 per cent.) alcohol.

Application: The mixture of methyl orange and phenolphtalein was recommended by Gawalowski as an excellent neutrality indicator. The neutral point is indicated by a lemon-yellow color. The slightest excess of either acid or alkali causes a change of color, the acid affording a deep pink, the alkali a fine red.

Five to ten drops of the solution are added to the liquid to be titrated.

METHYL VIOLET

$2C_6H_4N(CH_3)_2.C_6H_4.N.C.CH_3.HCl$

ALKALIES = Violet ACIDS = Blue, Green, or Yellow

Synonyms: Gentian Violet 3B.; Paris Violet; Direct Violet; Methylaniline Violet; Dahlia; Pyoktanin.

Preparation: Methyl violet is prepared by mixing a saturated aqueous solution of 3 parts of cupric nitrate, 3 parts of sodium chloride, and 1 part of acetic acid, with 100 parts of clean, washed sand, then adding 10 parts of pure dimethylaniline, and heating the mixture at a temperature of 140° C. for about 24 hours. The mass obtained is then comminuted and washed with a solution of sodium sulphide, which dissolves out the salts, leaving the sand, copper sulphide, and the dye. The latter is then taken up by water acidulated with hydrochloric acid, and reprecipitated by salting out with sodium chloride.

Properties: Methyl violet is a mixture of the hydrochlorates of penta- and hexa-methyl-pararosaniline, and results from the oxidation of the dimethylaniline. It occurs as a green powder of metallic luster, and is soluble in alcohol, amyl alcohol, and in water. Its aqueous solution has a bright-violet color, which is changed by acids, according to their degree of concentration, to a blue, green, or even yellow, color. Alkalies restore the violet color. Acetic acid, and other very weak acids, have no effect on the color.

Application: Methyl violet is useful for determining the quantity of **sulphuric** or other **strong acid** present in a sophisticated acetic acid. This it does directly, because it is unaffected by acetic acid.

ORANGE-PEEL EXTRACT

ALKALIES = Lemon-Yellow ACIDS = Colorless

Synonym: Bornträger's Indicator.

Preparation: Orange-peel extract is prepared by macerating 1 part of fresh-cut orange-peel with 5 parts of absolute alcohol, expressing, shaking with an equal volume of ether to remove the volatile oil, and then separating the alcoholic layer for use.

Application: This indicator is known as Bornträger's indicator. One part of the extract yields with 100 parts of water a colorless solution which is colored a lemon-yellow by alkalies, the color being again discharged by acids.

The indicator is unserviceable in the presence of **free ammonia.** Bornträger states, however, that in his hands it has given closer results in the presence of **ammoniacal salts** than have litmus, corallin, and phenolphtaleine.

PARA-NITROPHENOL

$C_6H_4.NO_2.OH$

ALKALIES = Yellow ACIDS = Colorless

Synonym: Nitrophenylic Acid.

Preparation: Para-nitrophenol is prepared by the action of 1 part of phenol on 2 parts of nitric acid diluted with 4 parts of water, and separating the para product from the accompanying ortho compound simultaneously produced, by distilling with steam. The ortho compound is carried over; the para compound remains behind with tarry matters, and is purified by repeated crystallization from xylene.

Properties: Para-nitrophenol forms colorless needles melting at about 112° to 114° C., and readily soluble in alcohol, but only slightly so in water. Its composition is $C_6H_4(NO_2).OH$.

Application: A colorless, 1 : 10,000 aqueous solution of para-nitrophenol is distinctly colored yellow by a trace of alkali, and hence the indicator is sufficiently sensitive to serve in 1 : 5000 solution for estimating the hardness of **spring-** or **well-water.** This is done by adding 5 Cc. of the titrating soluto 100 Cc. of the water, and to 100 Cc. of distilled water, in separate beakers. The well-water acquires a more or less deep-yellow color, according to its degree of hardness, while the distilled water remains colorless. To the latter, normal potassa solution is then added drop by drop until a color equal in depth to that acquired by the well-water is developed. Each Cc. of solution added will represent 0.00028 Gm. of CaO. The results are verified by adding normal acetic-acid solution to the beaker containing the well-water. The quantity of normal acid required to neutralize the potassa solution used should, when added to the well-water tested, be sufficient to render the latter colorless, or almost so.

Para-nitrophenol is not much used as an indicator, because it is applicable only in colorless or faintly colored liquids.

Its sensitiveness is said to be such that 0.5 Cc. of centinormal alkali solution suffices to develop the yellow color in 50 Cc. of the liquid to be titrated, and to which some of the indicator had been added.

PHENACETOLIN

$C_{16}H_{12}O_2$

ALKALIES = carbonates: Red
caustic: Yellow
ACIDS = Yellow

Synonym: Degener's Indicator.

Preparation: Phenacetolin is obtained by heating equal molecular weights of concentrated sulphuric, carbolic, and glacial acetic acids in a vessel provided with a reflux condenser, the product being then treated with water until all free acids have been washed out; the residue, phenacetolin, is then dried.

Properties: Phenacetolin, also known as Degener's Indicator, is considered to be identical with phenacetein, $C_{16}H_{12}O_2$. It occurs in the form of a yellowish-brown powder, slightly soluble in water, but soluble in alcohol, yielding a green solution.

Application: Phenacetolin may be used in the form of an aqueous 1:500 solution, or in the form of an alcoholic 1:200 solution. The solutions yield with **caustic alkalies** a pale yellow, scarely perceptible color, but with **carbonates** of the **alkalies** and **alkaline earths,** as well as with **sulphides** of the **alkalies** and with **ammonia,** it yields intensely red compounds, all but those of the alkaline earths being soluble, and affording red solutions. **Acids,** even **organic**, color the solutions yellow, hence in sodium acetate containing sodium carbonate the latter may be titrated by means of phenacetolin, by using hydrochloric or sulphuric acid until the color changes from red to yellow, then adding methyl orange, and finding the content of sodium acetate by titrating until the red color reappears.

Phenacetolin is very useful for estimating **calcium hydrate** in the presence of calcium carbonate, or **sodium hydrate** in the presence of sodium carbonate, or **potassium hydrate** in the presence of potassium carbonate, when the caustic alkali is present in not too small a quantity; otherwise the color-change is apt to be very uncertain. For carrying out the titration, sulphuric or hydrochloric acid is rapidly added until a faint, permanent rose color is apparent, which will indicate the caustic alkali or lime; further addition of acid will afford a red, then yellowish-red, and finally a yellow color which is suddenly and sharply produced, and which will then show the quantity of carbonate present.

On adding a dilute acid to a mixture of **baryta** and **barium carbonate**, to which a few drops of phenacetolin solution have been added, the color becomes more and more red until the baryta has been saturated, and the acid begins to attack the carbonate. A further addition of acid then causes the momentary disappearance of the color.

The indicator cannot, however, be used in mixtures of **caustic alkalies** and their **carbonates** when ammonia is present.

Bicarbonates yield a red color with phenacetolin.

Sulphates, nitrates, and **chlorides** of the **alkalies,** or of the **alkaline earths** (Ba, Ca, Mg, and Sr), do not affect the sensibility of the indicator.

Sulphites are prone to yield mixed colors, but the change of color to red is very sharp and sudden, however, when the point of saturation is complete.

For estimating **alkalies** with **oxalic acid,** phenacetolin is useless. It is also useless for titrating the ordinary **organic acids.** With **arsenates,** the change of color is too gradual for the indicator to be of service ; with the **arsenites,** however, the color-changes are very good, and accurate results are obtainable.

PHENOL NITROSYLSULPHONATE

ALKALIES = Blue ACIDS = Red

Synonym: Lehman and Petri's Dye.

Preparation: Phenol nitrosylsulphonate is prepared by mixing 5 Cc. of phenol and 5 Cc. of concentrated sulphuric acid while keeping the mixture cold, and then adding 20 Cc. of nitrosylsulphonic acid (obtained by dissolving 5 Gm. of potassium sulphite in 100 Gm. of cold sulphuric acid) drop by drop. The colorless solution is then heated on a water-bath to 80° C. until the mass acquires a dark bluish-violet color. The mass is then mixed with 2 liters of cold water, when the dye separates as a dark-violet, amorphous substance. This is separated by filtration, then washed, and dried at 100° C. It is then dissolved in ether, and finally obtained in a condition fit for use as an indicator by evaporating the ether.

Properties: Phenol nitrosylsulphonate occurs as a dark, bluish-violet, amorphous solid or powder, soluble in acetone, ether, and amyl-, ethyl-, or methyl-alcohol, affording yellow solutions; slightly soluble in chloroform, difficultly so in benzene and toluene, and insoluble in benzin.

Application: Phenol nitrosylsulphonate was recommended as an indicator by Theodor Lehman and Julius Petri. These authors claim it to possess properties like those of litmus, while being much more sensitive than phenolphtalein, and that it is therefore well adapted for use in titrimetry. Compared with phenolphtalein, its sensitiveness is such that whereas when phenolphtalein is added to 50 Cc. of recently boiled, distilled water, 0.5 Cc. of centinormal caustic alkali are required to show a distinct red, while, when 2 drops of an alcoholic phenolnitrosylsulphonate solution are added to 50 Cc. of recently boiled, distilled water, the latter is colored distinctly blue by 2 drops of centinormal caustic alkali.

The indicator yields a blue color with **alkalies,** and a red with **acids.** Like litmus, it is affected by **carbonic-acid** gas; it is also unserviceable for **ammonia.** It gives very good results, however, with **alkalies, alkaline earths, mineral acids,** and **oxalic, acetic,** and **formic acids.**

PHENOLPHTALEIN

$C_6H_4CO.O.C(C_6H_4OH)_2$

ALKALIES = Red ACIDS = Colorless

Synonym: Dioxyphtalophenone; Luck's Indicator.

Preparation: Phenolphtalein is prepared by heating together 5 parts of phtalic anhydride ($C_8H_4O_3$), 10 parts of phenol, and 4 parts of concentrated sulphuric acid for several hours at a temperature between 120° and 130° C. The resulting red mass is then boiled with water, and the resinous residue, consisting of impure phenolphtalein, is filtered off, and dissolved in dilute soda lye. The solution is filtered and precipitated by neutralizing with acid, the precipitate being finally purified by recrystallizing from alcohol.

Properties: Phenolphtalein occurs as a nearly white or yellowish-white, crystalline powder, nearly insoluble in water, but soluble in 10 parts of alcohol, and in dilute alcohol. It melts at 150 C. Its composition is $C_{20}H_{14}O_4$.

Tests: It is very important that the purity of phenolphtalein be assured, because on this depends the sensitiveness of the indicator. Many samples are likely to contain impurities in the form of some of the resinous substance produced during their manufacture. A good article should respond to the following tests:

0.5 Gm. of phenolphtalein heated on platinum foil should leave no residue; it should yield a clear solution with 10 parts of alcohol, and a 1:100 solution in alcohol should be colorless. Its sensitiveness should be such that not more than 0.08 to 0.09 Cc. of decinormal alkali should be required to produce a violet (not red) color in 250 Cc. of recently boiled and cooled distilled water to which a few drops of phenolphtalein solution have been added. To produce a distinct redness, 0.5 Cc. of centinormal potassa solution are required when 0.5 Cc. of phenolphtalein solution are added to 100 Cc. of distilled water.

Application: Phenolphtalein was recommended as an indicator by Luck, and, after litmus and methyl orange, is the one most favored. It is exceedingly sensitive, and changes very sharply and suddenly from a fine red with fixed alkalies, to a colorless solution with acids (even carbonic), and vice versa. Its sensitiveness is such that, as Luck states, the slightest trace of alkali, even in highly dilute solution (1 : 100,000), gives a distinct color. It possesses the properties of a very weak acid.

Solution of phenolphtalein for use is made by dissolving 1 Gm. of phenolphtalein in 100 Cc. of 50% alcohol. But, in view of the slight acid properties of the indicator, the solution must be rendered neutral by cautiously adding a few drops of centinormal alkali until very faint redness, and then adding a drop of centinormal acid. About 5 drops of the solution are added to 100 Cc. of the solution to be titrated.

Salts of the **fixed alkalies** have no influence on the delicacy of the reaction, but the **ammonium salts** have, most probably from the action of the ammonia on the phenolphtalein, resulting in the formation of phenol di-imidophtalein, which yields colorless solutions with alkalies. The reaction occurring may be expressed as follows:

$$\underset{\text{phenolphtalein}}{C_{20}H_{14}O_4} + 2NH_3 = \underset{\text{phenol di-imidophtalein}}{C_{20}H_{16}N_2O_2} + 2H_2O.$$

The indicator is, hence, useless for **ammonia.** Phenolphtalein is, however, one of the best indicators for titrating **caustic alkalies** and their **carbonates,** and for the **alkali earths.** By its means also, caustic alkalies may be titrated in the presence of carbonates or bicarbonates, and carbonates may be estimated in the presence of bicarbonates, which are neutral to the indicator, and the solution becomes colorless as soon as the alkali or carbonate has been neutralized. The indicator is very sensitive to **carbonic acid,** however, hence the estimations must be conducted in boiling solutions. The residual bicarbonate may then be estimated, if desired, with methyl orange. Caustic alkali in the presence of carbonate may also be estimated by first diluting the solution so that not more than about 0.5% of total alkali is present, then precipitating the carbonate with barium chloride in excess, and rapidly titrating to avoid the formation of new carbonate from the caustic alkali in the solution. The solution containing the precipitated barium carbonate need not be filtered, as the salt does not interfere with the reaction.

Phenolphtalein may be used for titrating **alkali**

sulphides. These yield a red color with the indicator, which is discharged when half the alkali has been converted into sodium- (or potassium-) hydrogen sulphide. The total alkali may also be titrated, but in this case the operation must be effected in boiling solutions, since the liberated hydrogen sulphide destroys the color of the solution.

The **alkali radical** of **borax** cannot be estimated with phenolphtalein, because the color produced on adding acid fades away. The **boric acid** in borax may be titrated accurately, however, by employing a *n* 5 sodium-hydrate solution, but it is necessary to first add about 30% of glycerin to the liquid to be titrated.

Normal sulphites are neutral to phenolphtalein, in both hot and cold solutions. Reddened phenolphtalein solutions are decolorized by **boric** and **arsenous acids, potassium bichromate** and **gum arabic.** For **arsenites** the indicator is not very serviceable, as it only shows about 90% of the combined sodium or potassium. With the **arsenates,** however, a well-defined change occurs when one-third of the alkali is neutralized. With the **bibasic phosphates,** which are almost, but not quite, neutral to the indicator. the results are not very satisfactory.

Codeine, morphine, cinchonine, quinine, quinidine, brucine, strychnine, aniline, quinoline, and paratoluidine are neutral to phenolphtalein, and may be readily titrated by its means, their salts being dissolved or suspended in a few Cc. of alcohol and then titrated with alkali to redness. The **acid radicals** of all the alkaloids excepting **coniine, nicotine,** and **codeine,** may also be estimated.

Phenolphtalein is excellent for estimating the **organic acids,** such as **oxalic, acetic, tartaric, citric, lactic,** etc., and particularly in mixtures of alcohol and ether, in which many organic acids which are insoluble in water may be readily titrated. It is best to titrate the organic acids in cold or only moderately warm solutions when using potassium- or sodium hydrate as a titrating fluid. The indicator is also exceedingly useful for titrating **fatty acids** in alcoholic solution, and for **free alkali** in soap where litmus is inapplicable.

The indicator can be used with only those metals that yield white precipitates with sodium sulphide or with a carbonate of an alkali. It is also useful in many cases where the solutions to be titrated are colored, because in these the color-changes may be quite readily observed.

It has been pointed out by Messrs. N. and C. Draper that the color of phenolphtalein solutions colored red by potassa or soda is partially discharged on the addition of alcohol, the reason ascribed being the formation of some bicarbonate by taking up carbonic acid from the air. On heating, or on dilution with water, the color is restored.

Phenolphtalein is also used in the form of test-paper (see Test-papers).

PHENYLENE DIAMINE, META-

$C_6H_4(NH_2)_2$

Synonym : Meta-diamido Benzene.

Preparation : Meta-phenylene-diamine is obtained by the reduction of dinitrobenzene, or nitraniline, with tin and hydrochloric acid.

Properties : The meta-phenylene diamine occurs as a crystalline powder or mass, readily soluble in alcohol and in ether, and but little so in water. It is a strong di-acid base, and capable of forming well-defined salts with acids.

Tests : Meta-phenylene diamine is readily prone to change on contact with air, when it loses its originally white color and becomes reddish. A 1 : 20 aqueous solution should be colorless, or only faintly yellow ; if the color is deeper, the preparation should be rejected. On account of its readiness to decompose, the preparation must be kept in small, well-closed bottles.

Application : Meta-phenylene diamine, as well as its hydrochloride, $C_6H_4(NH_2)_2.2HCl$, which occurs as a white or faintly reddish-white crystalline powder soluble in water, is very useful for detecting **nitrites** in potable water. On adding sulphuric acid to the suspected water, the **nitrous acid** liberated from any nitrites that may be present affords a yellow color even if the slightest traces of nitrites are present. For this purpose a 1 : 200 aqueous solution of the base or its salt is used. 1 Cc. of the solution is added to 100 Cc. of the suspected water, and 1 Cc. of diluted sulphuric acid (1 : 3) added. The color so obtained is then compared with a known standard, by which means the quantity of nitrites present may be estimated.

Meta-phenylene diamine hydrochloride gives also an exceedingly sharp reaction with **aldehydes,** and is used for detecting the latter in alcohol.

PHYLLOCYANIN

ALKALIES = Green, then Yellow, and finally almost Black

Synonyms: Pellagri's Indicator; Phyllocyanic Acid.

Source: Phyllocyanin was discovered (and named) by Frémy, as being one of the two constituents (Filhol, and also Stokes, claim there are four) to which chlorophyll owes, in part, its color. Frémy separated it from the accompanying yellow phylloxanthin, also named by him, by shaking chlorophyll with a mixture of two parts of ether and one part of dilute hydrochloric acid. The latter dissolves the phyllocyanin, and the former dissolves the phylloxanthin. The immiscible solvents were then separated.

Preparation: Phyllocyanin is prepared by Frémy's process, or by boiling chlorophyll with a strong alcoholic solution of potassium hydroxide, neutralizing the solution with hydrochloric acid, and then filtering. On evaporating the filtrate the phyllocyanin is obtained.

Properties: Phyllocyanin occurs as a dark blue mass soluble in water and alcohol, the solutions having an olive color with bronze-red or violet reflection. It is acid in character, and yields brown or green salts, those of the alkalies being soluble in water. With sulphuric and hydrochloric acids it yields solutions which are green, reddish, violet, or a handsome blue, according to the strength of the solutions.

Application: For use a solution of phyllocyanin is prepared to which just sufficient acid is added to change the color of the solution to a purple.

The indicator is quite sensitive to **alkalies,** which change the color of the acid solution to green, then yellow, and finally almost black.

POIRRIER BLUE, C4B

Alkalies = carbonates: Blue
caustic: Red

Acids = Blue

Preparation: Poirrier Blue, C4B, is obtained by the action of sulphuric acid on triphenylrosaniline, and is closely allied to Gentian Blue in properties.

Properties: Poirrier Blue, C4B, occurs as a blue powder having a coppery luster. It is soluble in water and in alcohol, yielding blue solutions. That obtained with alcohol is lighter in color than the aqueous solution, but the color is deepened on the addition of water. Potassium and sodium hydrates change the color to a red, the blue being restored on adding an acid. Ammonia, however, decolorizes the solution, but the blue is also restored in this case by an acid.

Application: Poirrier Blue, C4B, was first recommended as an indicator by Engel and Ville. An aqueous 1 : 500 solution of the indicator is employed, of which one or two drops are added to 100 Cc. of the liquid to be titrated. In the presence of only **alkali carbonates** the color remains blue, but if **caustic bases** are present, the color changes to red. **Ammonia, ethylamine,** and other **amines** do not change the color. The indicator is exceedingly sensitive to **acids,** and the results obtained by its means are very good, compared with those obtained with litmus or methyl orange. **Borax** and **boric acid** sharply change the color to blue, the solutions only becoming red when the total acid has been completely neutralized. **Phosphates** and **arsenates** act similarly. This is a valuable property peculiar to the Poirrier Blue; many indicators are affected by alkalies before neutralization is complete. **Bicarbonates** of the **alkalies** afford a blue color which does not change until the bicarbonates have been converted into basic carbonates.

Morphine, phenols, resorcin, chloral, and **hydrocyanic acid,** act like acids towards the indicator, and may be titrated by its means. **Phosphoric** and **arsenic acids** are tribasic with the Blue, but as the tribasic phosphates are very unstable, and the change of color is not very marked in consequence, the indicator is unserviceable for titrating them. **Carbolic acid** is monovalent, and **resorcin** is bivalent with the Blue; **monovalent alcohols** are neutral, and **polyvalent alcohols** are acid. The **aldehydes** are all neutral.

Poirrier Blue has the character of a very weak acid, and its salts are so unstable that they are decomposed by water alone when in very great dilution, hence readings with the indicator may be misleading unless sufficient of the indicator is present. The change of color in the latter case is very sharp, and is facilitated if a little alcohol is added to the solution to be titrated.

POLYSULPHIDE SOLUTION

ALKALIES = No Precipitate ACIDS = Turbidity

Synonym: Bolton's Indicator.

Preparation: The polysulphide indicator is a very concentrated solution of sublimed sulphur in a solution of an alkaline sulphide. The solution must be concentrated in order to avoid the necessity of using too large a quantity of the indicator, which would vitiate the results because of the natural alkalinity of the solution; while at the same time sufficient dissolved sulphur must be present to afford a clearly visible precipitate on neutralization.

Application: The polysulphide solution was recommended as an indicator by Bolton. Its action depends on the fact that sulphur is precipitated in neutral or acid solutions, but is soluble in alkaline sulphide solutions. For the application of the indicator a drop or two of the solution is a sufficient addition to 250 Cc. of the liquid to be titrated. The liquid is then heated, the titration being best effected in an Erlenmeyer flask, and when it boils, the titrating acid is permitted to flow in. So long as the liquid remains alkaline, the liberated sulphur redissolves, but on the least excess of acid, the sulphur renders the liquid milky. Of course the indicator can only be used in alkaline solutions. The natural alkalinity of the polysulphide solution may be determined beforehand, and the necessary corrections in the acid-readings be made.

POTASSIUM BICHROMATE

$K_2Cr_2O_7$

ALKALIES = Reddish-Yellow ACIDS = Pale-Yellow

Synonyms: Potassium Dichromate; Acid Potassium Chromate; Red Potassium Chromate; Potassium Anhydrochromate; Richter's Indicator.

Preparation: A mixture of finely powdered chrome ironstone ($FeOCr_2O_3$), caustic lime, and potassium carbonate is heated for several hours. Oxidation ensues, carbon dioxide, potassium chromate, calcium chromate, and iron oxide resulting as follows:

$$2FeOCr_2O_3 + 3K_2CO_3 + CaO + 7O = 3K_2CrO_4 + CaCrO_4 + Fe_2O_3 + 3CO_2.$$

The greenish-yellow mass so obtained is exhausted with a little boiling water which dissolves out the soluble chromates. The calcium salt is then decomposed by potassium hydroxide, and the potassium chromate in solution converted into a bichromate by the addition of sufficient sulphuric acid.

The salt is then crystallized, and purified by recrystallization.

Properties: Potassium bichromate occurs as large, orange-red, translucent crystals having a bitter, metallic taste, and soluble in 10 parts of water at 15° C. Its formula is $K_2Cr_2O_7$.

Tests: Potassium bichromate should be tested for sulphuric acid by dissolving 3 Gm. in 100 Cc. of distilled water, and adding hydrochloric acid and barium-chloride solution. No change or precipitate should be observed within 12 hours. Too little hydrochloric acid should be guarded against, otherwise a misleading precipitate of barium chromate may be formed.

It is important that the salt be tested for any sulphuric acid that might be present, when intended for use as an oxidizer. Fresenius tests it by adding hydrochloric acid and alcohol, and after complete reduction, adding the barium chloride and permitting the mixture to stand for 12 hours.

The salt is tested for chlorides by adding some nitric acid, warming the solution, and then adding a few drops of silver-nitrate solution. No precipitate should be formed. Calcium salts may be detected by adding 1 Cc. of ammonia water to 10 Cc. of a 1 : 20 aqueous solution of the salt, and then adding a little ammonium-oxalate solution. No precipitate should be formed.

Application: Potassium bichromate was recommended as an indicator by M. Richter. The bichromate is dissolved in water, a very little phenolphtalein is added, and potassium-hydrate solution added cautiously until a very faint yellowish-red solution results. The change of color from a pale-yellow with **acids** to a reddish-yellow with **alkalies** is very sharp. The indicator is useful for titrating **caustic alkalies** and **ammonia**, the formation of monochromates being readily observed.

POTASSIUM CHROMATE

K_2CrO_4

SILVER SALTS = Red

Synonyms: Potassium Monochromate; Neutral Potassium Chromate; Yellow Potassium Chromate.

Preparation: Potassium chromate is obtained by a process exactly similar to that described in the preparation of potassium bichromate, only the final conversion into a bichromate is omitted, the yellow liquid being filtered, concentrated by evaporation, and set aside to crystallize. The crystals are then purified by recrystallization.

The chromate is also obtained by passing chlorine gas into a hot solution of caustic potassa containing chromium hydroxide in suspension.

A pure, chlorine-free preparation is secured by fusing 25 parts of potassium bichromate with 20 parts of pure potassium nitrate (or a corresponding quantity of potassium carbonate). This yields 34 parts of pure neutral potassium chromate.

Properties: Potassium chromate occurs as yellow, translucent crystals, permanent in air, and soluble in 2.7 parts of water at 15.5° C. and in 1.57 parts at 100° C. It is insoluble in alcohol.

On adding an acid to the solution of the salt, the yellow color is changed to red, due to the formation of a bichromate.

Solutions of the salt are faintly alkaline towards litmus and curcuma, but are neutral, according to De Vrij, to phenolphtalein.

Tests: Potassium chromate should be tested for free alkali by dissolving 0.1 Gm. of the salt in 25 Cc. of water, and adding a few drops of phenolphtalein solution.

Sulphates and chlorides are tested for as described under potassium bichromate.

Alumina and alkaline earths are tested for by adding ammonia and ammonium oxalate to a 1:20 solution of the chromate; there should be no precipitate.

Application: Potassium chromate is used as an indicator in the titration of **halogen salts**, using silver-nitrate solution as a titrating fluid. The moment when all the halogen radical of the salt has combined with the silver is indicated by a red precipitate or color, due to the formation of silver chromate.

It has also been employed in the estimation of **quinine.**

For use a solution of 1 Gm. in 10 Cc. of distilled water is prepared.

POTASSIUM FERRICYANIDE

K_6FeCy_{12}

FERROUS SALTS = Blue   FERRIC SALTS = Colorless

Synonyms: Red Prussiate of Potash; Potassium Ferridcyanide; Potassio-ferric Cyanide.

Preparation: Potassium ferricyanide is prepared by passing chlorine gas into a 1 : 8 solution of potassium ferrocyanide until a small sample of the solution no longer gives a blue reaction with ferric chloride.

Reichard proposes bromine as a substitute for chlorine gas, and states that 1 part of bromine suffices for 5 parts of potassium ferrocyanide.

Properties: Potassium ferricyanide occurs as red crystals soluble in 4 parts of cold water and yielding a brownish-yellow solution. The dilute solution is lemon-yellow. The salt is but slightly soluble in alcohol.

Tests: Potassium ferricyanide should be tested for sulphuric acid by adding to a 1 : 20 solution a little hydrochloric acid followed by barium-chloride solution. Any ferrocyanide present may be detected by adding a little ferric-chloride solution, which would give a blue color.

Chlorides may be detected by fusing 0.5 Gm. of the permanganate with 1 Gm. of pure potassium nitrate, exhausting the fused mass with water, filtering, acidulating the filtrate with nitric acid, and then adding silver-nitrate solution.

Sodium salts are detected by dissolving 1 Gm. of the permanganate in water, acidulating with hydrochloric acid, adding ferric chloride in excess to precipitate the excess of iron, filtering, and then testing the filtrate with potassium metantimoniate.

Application: Potassium ferricyanide is employed as an indicator in the titration of **ferrous salts** by means of potassium bichromate. The latter oxidizes the ferrous salts to ferric, the end of the reaction being known when a blue color ceases to be yielded, on adding the bichromate solution. The process does not yield very satisfactory results, because the indicator cannot be added directly to the ferrous-salt solution, but a drop or two of the latter, after every addition of bichromate, is brought into contact with the indicator solution on a porcelain tile. The method is thus very troublesome, and takes up too much time.

The ferricyanide is also used in the volumetric gas analysis of **hydrogen dioxide,** and also for **alkalies,** and **alkali earth.** It is, besides, used in estimating **phosphoric acid** by means of uranium acetate.

For use a recently prepared 1 : 10 solution is prepared.

POTASSIUM HYDRORUFIGALLATE (?)

ALKALIES = Carmine-red ACIDS = Yellow

Synonym: Oser and Kalmann's Indicator.

Preparation: On treating gallic acid with potassium permanganate, hydrorufigallic (tetrahydroellagic) acid, $C_{14}H_{10}O_8$, is obtained in the form of yellow needles readily soluble in alcohol and in ether, but difficultly soluble in water. It has been found, however, that a sensitive indicator may be obtained by fusing 1 part of the hydrorufigallic acid so obtained with 5 parts of caustic potassa, until a reddish-violet mass results, an isomeric compound being thus formed, and which, when decomposed by sulphuric acid, affords a greenish-yellow residue. This is finally purified by recrystallization from boiling water.

Properties: The preparation obtained as above occurs as greenish-yellow, microscopic crystals, which sublime at 200° to 220° C., decompose above 230° C., and dissolve in solutions of caustic alkalies and yield a green solution, the color of which changes to a carmine-red on contact with air. The red color is changed to yellow by acids, and restored again by alkalies.

Application: The indicator is useful in titrating **mineral waters,** because it is reddened by **carbonates**

of the **alkalies, magnesium, calcium,** and **iron,** but is unaffected by **carbonic-acid gas.** The **combined carbonic acid** in well-water, springs, etc., is also readily determined by its means.

POTASSIUM PERMANGANATE

$KMnO_4$

REDUCERS AND ORGANIC MATTER = Decolorization

Synonyms: Potassium Hypermanganate; Potassium Oxymanganate; Potassium Supermanganate.

Preparation: Potassium permanganate is prepared by heating 10 parts of caustic potassa, 7 parts of potassium chlorate, and 8 parts manganese dioxide in a crucible until a test taken from the mass dissolves and yields a deep-green solution. The mass is then boiled with water until the potassium manganate has become converted in a permanganate, evidenced by a change of color from green to red. The solution is then concentrated by evaporation, and set aside to crystallize.

According to an improved process proposed by Boettger, 2 parts of caustic potassa and 1 part of potassium chlorate are fused together, and then 2 parts of finely powdered manganese dioxide carefully added, the heat being continued for a short time. The fused mass is then comminuted and boiled with 40 parts of water, while a stream of carbon dioxide is forced through the liquid until a few drops of the latter placed on white paper no longer show a green, but red, color. The solution is then concentrated and allowed to crystallize. Instead of carbon dioxide, chlorine gas and bromine have also been used, and with good results.

Properties: Potassium permanganate occurs as dark-violet, anhydrous crystals presenting a metallic luster. It is soluble in 16 parts of water at 15° C., yielding neutral solutions having a deep-purple color.

Potassium permanganate is an exceedingly powerful oxidizer, and is readily reduced by all organic matter; hence, it must not be carelessly brought into contact with readily oxidizable substances. On being heated it yields 10.5% oxygen.

Its solutions are decomposed by mineral acids and by alkalies, manganous salts resulting with the former and manganates with the latter.

Carbonates of the alkalies are indifferent toward potassium permanganate, but ammonia decomposes and decolorizes it. The dry salt, treated with concentrated sulphuric acid, yields ozone.

Tests: Sulphates and chlorides when present may be detected by boiling 0.5 Gm. of the salt with 2 Cc. of alcohol and 25 Cc. of distilled water, and acidulating the colorless solution with nitric acid. On now adding barium nitrate or silver nitrate, white precipitates will form.

Nitrates are tested for by dissolving 0.5 Gm. of the permanganate in 5 Cc. of hot water, and gradually adding oxalic acid until decolorization is complete. 2 Cc. of the filtrate are then mixed with 2 Cc. of concentrated sulphuric acid, and the mixture overlaid on 1 Cc. of a concentrated ferrous-sulphate solution. If a nitrate is present, a brown zone will form at the point of contact of the two liquids.

Application: Potassium permanganate is not used as an indicator *per se*. It does, however, indicate the end of the reaction by being decolorized when used as an oxidizer. It is thus useful in estimating **ferrous salts,** which it oxidizes to ferric salts when in acid solution. The end of the reaction is known to be at hand when decolorization ceases to be complete, the end point being reached when the liquid acquires a faint, permanent pink tint.

Potassium permanganate is also used in the estimations of **sulphur, hypophosphites, thiosulphates, oxalates,** and **hydrogen peroxide.**

REFLECTING GALVANOMETER

The reflecting galvanometer has but very recently been employed by Prof. Küster as a physico-chemical substitute for the indicators commonly employed in titrations. As is well known, many mixtures offer very serious obstacles to the analyst, at times so great as to render the ordinary analytical methods useless, and permit accurate results to be obtained only by circuitous and tedious means. In these cases the author has found a reflecting galvanometer to be of great use. For instance, if potassium permanganate is gradually added to a solution containing free iodine, potassium iodide, potassium bromide, and potassium chloride, and which has been acidulated with sulphuric acid, it will be found that the iodine of the iodide will be liberated first by the oxidation, and only after this will further oxidation result in the liberation of free bromine and in the formation of iodic acid.

Since these different oxidation processes are accompanied by decidedly varying electrical potentials, a reflecting galvanometer, interposed in the circuit by means of suitable electrodes, will exhibit a very decided and sudden deviation as soon as the oxidation of the iodide is at an end and that of the bromide begins. The deviation here takes the place of the color-change afforded by the indicators ordinarily used in titration. The results obtained in titrations by means of the reflecting galvanometer are stated to be in no wise inferior to those obtained by the employment of good indicators. The application of the galvanometer is certainly a novel one, and deserves to be carefully tested.

RESAZURIN

$C_{18}H_{10}N_2O_6$? or : $C_{12}H_7NO_4$? or : $C_{12}H_9NO_4$?

ALKALIES = Blue ACIDS = Red

Synonyms: Azoresorcin ; Diazoresorcin ; Resazoin ; Weselsky's Indicator; Crismer's Indicator.

Preparation : Resazurin is obtained by dissolving 4 Gm. of resorcin in 300 Cc. of anhydrous ether, and then adding 40 or 45 drops of fuming nitric acid (sp. gr. 1.25, and prepared by the action of nitric acid on starch). After standing in a cold (– 5° to – 8° C.) place for 2 days, the blackish or brownish-red crystals are separated from the red liquid holding in solution resorufin and other nitroresorcins, by decanting. The crystals are then washed with ether, and finally with water, until the washings have a pure blue color free from any violet tint (which would indicate the presence of some resorufin). Resazurin is also formed by the action of manganese dioxide and sulphuric acid on an alcoholic solution of resorcin and nitrosoresorcin.

Properties : Resazurin occurs as reddish-brown crystals, slightly soluble in water, more so in alcohol, and quite soluble in acetic ether. It is a monobasic acid, and is easily decomposed by alkalies. Considerable confusion appears to exist regarding its composition. According to Weselsky and Benedikt it appears to have the composition $C_{18}H_{10}N_2O_6$, and to be formed as follows: $3C_6H_6O_2 + 2NO_2 = C_{18}H_{10}N_2O_6 + 4H_2O$. According to Brunner and Kramer, it is formed thus: $2C_6H_4(OH)_2 + 4N_2O = C_{12}H_9NO_4 + 2H_2O$. The formulas $C_{12}H_7NO_4$ and $C_{18}H_{12}N_2O_6$ have also been assigned it.

Application: Resazurin is a comparatively new indicator, and was proposed for use by Crismer. A solution of 0.2 Gm. of resazurin, 40 Cc. of decinormal ammonia, and sufficient water to make 1000 Cc. affords an extremely sensitive means for titrating **alkalies.** This solution has a deep-blue color by reflected light, but a red by transmitted light, and is quite stable; 2 or 3 drops suffice for 200 Cc. of liquid to be titrated. The blue color of the solution is changed to red by acids, and restored by alkalies and carbonates of alkalies.

Resazurin is especially serviceable for titrating decinormal **sodium-borate** solution, for which neither litmus nor phenolphtalein will answer. On the other hand it is unsuitable for **nitric acid** or **monobasic organic acids,** the indications being too uncertain. It is also sensitive to **carbonic acid,** but much less so than litmus or phenolphtalein.

Resazurin is so delicate a reagent for alkalies, that water boiled in a Florence flask is colored blue by it, due to the alkalinity produced by some of the glass entering into solution.

A test-paper is also prepared, and is noted under Test-papers.

RESORCINBENZEIN

$C_6H_5.C.C_6H_3(OH)_2.C_6H_3.O.OH$

ALKALIES=Yellowish-brown ACIDS=Yellowish-red

Preparation: Resorcinbenzein is obtained by warming a mixture of 2 molecular weights of resorcin with 1 molecular weight of benzotrichloride, and then raising the temperature to 180°–190° C., when vapors of hydrochloric acid are evolved. The reaction that takes place may be expressed as follows:

$$\underset{\text{resorcin}}{2C_6H_4(OH)_2} + \underset{\text{benzotrichloride}}{C_6H_5.CCl_3} = \underset{\text{resorcinbenzein}}{C_6H_5.C.C_6H_3(OH)_2.C_6H_3.O.OH} + 3HCl.$$

A deep, reddish-brown, fused mass, having a metallic reflection, is thus obtained. The mass dissolved in dilute soda lye, and precipitated by adding acetic acid, in the form of yellow crystals, which are finally recrystallized from a mixture of alcohol and glacial acetic acid.

Properties: Resorcinbenzein crystallizes from a mixture of glacial acetic acid and alcohol in the form of prisms which are violet-red when viewed by reflected light, but yellow by transmitted light.

The precipitated product is soluble in alcohol, but the crystals are difficultly so, and more readily soluble on adding hydrochloric or acetic acid.

Resorcinbenzein yields yellowish-red solutions having, when dilute, a green fluorescence. Alkalies change the color to a yellowish-brown.

Application: The indicator is rarely if ever used. It appears to possess no advantages over other indicators, but may be used like the other benzotrichloride derivatives of phenols.

ROSE COLORING-MATTER

ALKALIES = Deep-red with Green Fluorescence ACIDS = Light-red

Preparation: The coloring-matter of rose leaves, *Rosa Gallica,* was obtained by Harold Senier by digesting the leaves with ether, whereby the fat and quercetin were removed, and after filtering, extracting the coloring-matter with alcohol. By this means a colorless solution is obtained, which acquires a color with age. Water may also be used to extract the coloring-matter, and in this case the solution is colored. From the alcohol, the coloring-matter was precipitated by lead acetate as a green lead compound, which was then washed, dried, and finally decomposed, either by a current of hydrogen sulphide while suspended in water, or by the addition of sulphuric acid. By this means a bright-red solution of the coloring-matter was obtained, which yielded the matter on evaporation.

Properties: A solution of the coloring-matter of rose leaves is brightened by acids; alkalies change the color to a deep red with green fluorescence. Carbonates of the alkalies act like the alkalies, but the change is accompanied by effervescence, carbon dioxide being evolved. Hydrogen sulphide destroys the color, changing it brown; stannic chloride changes it a magenta. Mercuric nitrate and chloride yield with the coloring-matter a white and pink precipitate respectively. With barium and calcium hydrates, yellowish-green precipitates are afforded, which, on drying, become brown. The coloring-matter has the properties of a weak acid, and its solution exhibits an acid reaction.

Application: The coloring-matter of rose leaves is rarely used, as it possesses no advantages over the more commonly used indicators.

ROSOLIC ACID, COMMERCIAL

$(C_6H_4OH)_2.C_6H_4CO$

ALKALIES = Rose-red ACIDS = Yellow

Synonyms: Para-rosolic Acid; Aurin; Corallin; Aurin Red.

Preparation: Commercial rosolic acid is a mixture of aurin, $C_{19}H_{14}O_3$, oxidized aurin, $C_{19}H_{16}O_6$, methylaurin, $C_{20}H_{16}O_3$, and pseudorosolic acid, $C_{20}H_{16}O_4$, but chiefly the last. It is obtained by heating a mixture of 6 parts of phenol, 3 parts of sulphuric acid, and 4 parts of anhydrous oxalic acid (the last being gradually added) to a temperature of from 130° to 150° C., for 5 to 6 hours, or until the liberation of gas ceases. The reaction occurs between the phenol and oxalic acid, and is shown to take place as follows:

$$\underset{\text{phenol}}{3C_6H_6O} + \underset{\text{oxalic acid}}{C_2H_2O_4} = \underset{\text{aurin}}{C_{19}H_{14}O_3} + \underset{\text{formic acid}}{CH_2O_2} + 2H_2O$$

The product of the reaction is boiled with water in order to purify it, and is then dried.

Rosolic acid is also obtained by heating phenol with formic acid and tin chloride; on boiling diazopararosaniline with water; by heating together dioxybenzophenon chloride and phenol; and also by the action of salicylaldehyde on phenol in the presence of sulphuric acid.

Properties: Commercial para-rosolic acid occurs as yellowish-brown resinous lumps having a greenish fracture, and affording a yellow powder. It is insoluble in water, but is soluble in alcohol to the extent of 50 per cent., the solution having a yellow color. It is also soluble in glacial acetic acid, and may be obtained by crystallization from alcohol in the form of dark-red, rhombic crystals, or red needles with greenish luster, which decompose when heated above 220° C., but do not melt.

With sulphuric acid para-rosolic acid yields a yellow solution; with alkalies, a handsome cherry red. With the bisulphites of the alkalies it yields colorless, readily soluble compounds, which are decomposed by acids. With hydrochloric acid it gives very unstable compounds. By reducing-agents para-rosolic acid is converted into leukoaurin ($C_{19}H_{16}O_3$, trioxytriphenylmethane). At a temperature of 120° C. it is converted into pararosaniline.

Tests: 0.5 Cc. of a 1% solution in 60% alcohol, added to 100 Cc. of the solution to be titrated, requires 0.7 Cc. of centinormal hydrochloric acid, 0.8 Cc. of centinormal ammonia, and 4.1 Cc. of centinormal potassium hydrate to effect changes of color.

Application: Solution of para-rosolic acid for titrimetric use is made by dissolving 1 Gm. of the substance in 100 parts of 60% alcohol; of this solution about 0.5 Cc. are used for 100 Cc. of the solution to be titrated.

With **caustic alkalies** and their **carbonates**, and also with **baryta solution**, the indicator affords a fine, rose-red color, changed by acids, even carbonic acid, to a yellow. Para-rosolic acid yields very sharp end-reactions in the presence of notable quantities of the **sulphates, nitrates**, and **chlorides of the alkalies** and of **barium, calcium**, and **magnesium** (at least the soluble salts). When **ammonium salts** are present, however, the indicator is useless. It is serviceable for use by **artificial light.** The **total alkalinity** of a solution may be titrated with the indicator, but the solution to be titrated must be boiled during the operation to expel **carbonic-acid gas,** which affects the indicator.

For **ammonia,** para-rosolic acid is not as good as litmus. **Sulphides** of the **alkalies** yield a red color with the indicator, but on adding an acid, the liberated **hydrogen sulphide** destroys the color; if the solution be boiled to expel the gas, the color is restored, hence titrations of **sulphides** must be effected in hot liquids.

With **sulphides,** para-rosolic acid yields a sharp change. In cold solutions, normal **calcium sulphide** is practically neutral, but is distinctly alkaline in boiling solutions. With **arsenates** the result is poor; with **arsenites,** good.

The indicator is useless for **acetic acid,** because the **acetates** of **potassium** or **sodium** formed act toward the para-rosolic acid like alkalies.

Care must be taken not to mistake for the commercial rosolic acid the *true* rosolic acid, trioxy-diphenyl-carbinol anhydride, also known as rosaurin, and which is obtained by the action of nitrous acid on rosaniline.

SALICYLIC ACID

$C_6H_4(OH)CO_2H$

ALKALIES = Yellow   ACIDS = Violet, then Colorless

Synonym : Weiske's Indicator.

Preparation : The salicylic acid most commonly found on the market is that obtained synthetically, by the action of carbon dioxide on phenol, according to various processes. The oldest, and probably simplest, of these is that of Kolbe. This process consists in saturating phenol with caustic soda, so that sodium phenate, C_6H_5ONa, is formed, the solution being then dried on a water-bath and powdered. This is now introduced into an iron retort, and heated to 100° C. on an oil-bath, dry carbon dioxide being then conducted into it, while the temperature is gradually raised. When the temperature has reached 170° to 180° C. the phenol begins to distill over, half the quantity present being obtainable in this manner. The temperature is however raised still more, carbon dioxide being continuously conducted into the retort, and when 220° C. has been reached, and no more phenol is distilled over, the operation is at an end. The residue in the retort, which consists of disodium salicylate, is dissolved in water, and hydrochloric acid added to precipitate the salicylic acid. This is then purified either by neutralizing with calcium carbonate, and decomposing the calcium salicylate with hydrochloric acid; or by distilling the salicylic acid with superheated steam; or by dialysing the hydro-alcoholic solution of the salicylic acid.

Two reactions occur in the above process. The first is the formation of sodium phenylcarbonate, thus:

$$\underset{\text{sodium phenate}}{C_6H_5ONa} + CO_2 = \underset{\text{sodium phenylcarbonate}}{CO_2.C_6H_5.Na}$$

This latter, on heating, then becomes converted into sodium salicylate, as follows:

$$CO_2.C_6H_5.Na = \underset{\text{sodium salicylate}}{C_6H_4.OH.CO_2Na}$$

Properties: Salicylic acid occurs as colorless, odorless, acicular crystals forming a bulky mass having a rather sweetish-sour, astringent taste. It is soluble in about 500 parts of water at 15° C., and in about 15 parts of boiling water; in 2.5 parts of alcohol, in 2 of ether, in 80 of cold chloroform, in 3.5 amylic alcohol, in 60 of glycerin, in 80 benzene, and in about 65 parts of oils. Various salts, such as sodium phosphate, borax, ammonium acetate, ammonium citrate, etc., greatly increase its solubility in water. Its specific gravity is 1.443 to 1.457, and its melting-point lies between 156° and 157° C. Salicylic acid may be sublimed when carefully heated. If rapidly heated, however, it decomposes into phenol and carbon dioxide.

Salicylic acid and its salts yield with ferric salts a violet color, which is destroyed by strong acids. With silver nitrate it yields a white precipitate. On heating with methyl alcohol and concentrated sulphuric acid, the characteristic odor of wintergreen oil (methyl salicylate) is observed. Bromine water affords even in dilute solutions a crystalline precipitate of bromated salicylic acid.

Application: Salicylic acid was recommended as an indicator by Weiske. The solution for use is prepared by adding a drop of ferric-chloride solution to a hydro-alcoholic solution of salicylic acid, and then cautiously adding caustic alkali until exact neutrality, evidenced when a brownish-red color is formed. A small quantity of the solution so obtained is added to the acid to be titrated, when a violet color first develops, which is decolorized by strong acids, but not by acetic acid. On adding an alkali, however, the color passes again through violet, and suddenly into yellow, ferric hydrate being precipitated.

SANTALIN

$C_{15}H_{14}O_5$ (?) or: $C_{17}H_{16}O_6$ (?)

ALKALIES = Violet ACIDS = Red

Synonym: Santalic Acid.

Source: Santalin is a coloring-matter obtained from red sandal-wood, *Pterocarpus santalinus* L., one of the

Leguminosæ indigenous in India, and also found in the mountains of Coromandel and Ceylon. It was first isolated and named by Pelletier, who observed it to possess the properties of an acid. This observation was later on confirmed by Leo Meier, in 1849, who also named the preparation "santalic acid."

Preparation: Meier's process for obtaining santalin is to first exhaust with water the residue obtained by evaporating the alcoholic or ethereal extract of the wood, then to dissolve it in alcohol, and precipitate it with an alcoholic lead-acetate solution. The precipitate of lead santalate, after treatment with boiling alcohol, is heated with a little alcohol and diluted sulphuric acid, and the blood-red solution obtained after filtering evaporated.

The santalin so prepared may be obtained perfectly pure, according to Weyermann and Häffley, by precipitating with water its alcoholic solution acidulated with a little hydrochloric acid, washing the precipitate with water, dissolving in alcohol, and then evaporating to dryness.

Dussance recommends precipitating the alcoholic extract of the wood with an excess of lead oxyhydrate, washing the precipitate with alcohol, and dissolving it in acetic acid. The solution is then precipitated by adding a large volume of water. The santalin so obtained is said to be impure, however.

Properties: Santalin occurs as a crystalline, inodorous, tasteless powder of a handsome red color; or in the form of red prisms. It is insoluble in water, but is soluble in alcohol, ether, acetic acid, and turpentine oil. It is also soluble in concentrated sulphuric acid with a deep-red color, and in volatile oils of cinnamon, lavender, rosemary, cloves, bergamot, and bitter oil of almonds, but is insoluble in most fixed oils.

It is present to the extent of about 16% in sandalwood, and its composition is, according to Weyermann and Häffley, $C_{15}H_{14}O_5$; it is $C_{17}H_{16}O_6$ according to Franchimont, who, however, obtained the santalin in an amorphous form only.

Santalin possesses the properties of a weak acid, and its alcoholic solution has an acid reaction. With lime, baryta, and salts of the heavy metals it yields insoluble lakes. Muspratt appears to have shown that sandal wood contains two dyes, one of which is formed from the other by oxidation. Old, deeply colored woods are believed to contain the oxidation product, whereas fresh and unchanged woods contain the unoxidized dye. In aqueous solutions of the alkalies, santalin dissolves with a violet color, which is changed to red by acids.

Application: Santalin is rarely, if ever, used now as an indicator, as it possesses no marked advantages.

SODIUM SALICYLATE

FERRIC SALTS = Violet FERROUS SALTS = Colorless

Preparation: Sodium salicylate may be made extemporaneously by mixing 60 parts of pure sodium bicarbonate (or 37.8 parts of anhydrous carbonate) and 100 parts of salicylic acid, with 100 parts of diluted alcohol, gradually, and then drying, after the reaction is completed, on a water-bath at a moderate heat.

Commercially the salt is obtained as in the process described in the preparation of salicylic acid.

Properties: Pure sodium salicylate forms small, white crystalline plates, or a crystalline powder, permanent in the air, odorless, having a sweetish taste, and a feebly acid reaction. It is soluble in 1.5 parts of water, and in 6 parts of alcohol; it is very soluble in boiling water and in boiling alcohol. The salicylate should be kept in dark or amber bottles.

Application: Sodium salicylate has been used as an indicator in titrating **ferric salts** with sodium thiosulphate. The violet color of ferric salts is discharged at the end of the reaction.

STARCH

$C_6H_{10}O_5$

IODINE = Blue

Source: Under the name of "Starch" is recognized the fecula obtained from various graminaceous plants, solanaceous tubers, etc., the principal varieties being obtained from wheat, potatoes, arrowroot, rye, rice, maize, sweet potatoes, oats, etc. It is also found in large quantities in peas, beans, chestnuts, etc.

Preparation: Starch is obtained by reducing the seeds, tubers, etc., containing it, to a state of minute division, agitating with cold water, and collecting and drying the fecula after it has subsided.

Properties: Starch is too well known to require any lengthy description. It will suffice to say that it occurs generally as a fine white powder, or in the form of irregular, sometimes columnar, masses readily reducible to powder. The starch granules are insoluble in cold water, but with boiling water the enveloping coat bursts, and the contents swell up and dissolve, yielding a thick paste, which, on drying, forms a horny, translucent mass. Its formula is believed to be $C_6H_{10}O_5$, or a multiple of this.

Application: Starch solution is exceedingly useful as an indicator in the titration of **iodine,** by means of sodium thiosulphate. With the minutest traces of iodine it affords a characteristic, intensely blue color, visible even in solutions containing the iodine yielded by one part of potassium iodide in 600,000 parts of water at 0° C.

It is also used in the titration of **arsenous acid,**

sulphites and **sulphurous acid, thiosulphates, chlorine, ferric salts,** and **hydrogen dioxide.**

The solution for use is made by triturating 1 part of starch with a little cold water, and then adding 200 parts of boiling water, under constant stirring. The solution is then set aside to cool, when it is filtered or allowed to settle. It is then ready for use.

Starch solution is prone to spoil, hence preservatives are frequently added, the substances most generally employed being sodium chloride, zinc chloride, calcium chloride, or salicylic acid. Zinc chloride has the best preservative power, but starch solution preserved by means of it cannot be used with sulphides or when hydrogen sulphide is liberated, and with a carbonate is prone to yield a disturbing precipitate; sodium chloride is least valuable, but interferes least in the application of the indicator, hence it is preferred; calcium chloride, proposed by Flückiger, is good, but also yields a precipitate with a carbonate; salicylic acid is also good, but cannot be used in the presence of sodium carbonate, because it then itself decolorizes iodine solutions.

A spoiled starch-solution must not be employed, because it no longer gives a blue, but a brown, color with iodine.

TETRABROMOPHENOLPHTALEIN

$C_2O_2.C_6H_4(C_6H_2Br_2OH)_2$

ALKALIES = Violet ACIDS = Colorless

Preparation: Tetrabromophenolphtalein is prepared by adding a mixture of 10 parts of bromine and 10 parts of glacial acetic acid to a boiling solution of 5 parts of phenolphtalein and 20 parts of alcohol.

Properties: Tetrabromophenolphtalein crystallizes from ether in the form of colorless needles that melt between 220° and 230° C. with decomposition. They are difficultly soluble in alcohol and in glacial acetic acid, but readily soluble in ether. They are dissolved by alkalies with a violet color, which, however, immediately disappears on adding an excess of alkali, from the formation of an acid having the composition $C_{20}H_{12}Br_4O_5$. On heating with warm sulphuric acid, dibromoxyanthraquinone is formed. Solutions made violet by alkalies are rendered colorless on addition of acids.

Application: Tetrabromophenolphtalein has been proposed for use in cases similar to those in which phenolphtalein is used. It appears to be in no wise superior to the latter, however.

THYMOLPHTALEIN

$C_2O_2.C_6H_4.(C_6H_3.CH_3.C_3H_7.OH)_2$

ALKALIES = Blue ACIDS = Colorless

Preparation: Thymolphtalein is prepared, according to M. C. Traut, as follows: Equal parts of thymol, phtalic acid, and zinc chloride are treated in a flask at a temperature not exceeding 150° C. until the melted mass, which, under proper conditions, has a handsome red color, flows quietly. The mass is washed first with very dilute hydrochloric acid, then with water, and finally with benzin to remove unchanged thymol. The residual thymolphtalein is purified by repeated treatment with ether, and recrystallization from a mixture of ether and alcohol.

Properties: Thymolphtalein forms colorless, prismatic needles, easily soluble in alcohol, less readily so in benzene, ether, or chloroform, and only very slightly so in water. It melts between 252° and 254° C. Its alcoholic or aqueous solution is colorless, but develops an intense, blue color on the addition of traces of alkali, the solutions appearing reddish by transmitted daylight, but decidedly red by transmitted artificial light. The blue color is discharged on the addition of an acid.

Application: Thymolphtalein, it is claimed, is equally as serviceable as phenolphtalein, and may be used like the latter.

TOLUYLENE RED

$(CH_3)_2.N.C_6H_4.NH.(NH_2)C_7H_6$

ALKALIES = Yellow ACIDS = Red

Synonym: Neutral Red.

Preparation: Toluylene red was discovered in 1879 by O. N. Witt. It is prepared by simply boiling an aqueous solution of toluylene blue. It is also obtained by the oxidation of a mixture of equal molecular weights of dimethylparaphenylenediamine and metatoluylenediamine at the boiling point.

Properties: Toluylene red forms orange-red needles containing 4 molecules of water of crystallization, and having the composition

$$(CH_3)_2NC_6H_4.NH.(NH_2)C_7H_6.$$

At a temperature of 150° C. it is converted into the blood-red anhydrous modification. It also occurs as a greenish-black powder, easily soluble in water with a crimson color, and in alcohol with a magenta-red, having a faint brownish-red fluorescence. With alkalies it yields an intense, yellow color, restored to red by acids.

Application: Toluylene red is rarely used; it possesses no advantages whatever over other indicators.

TROPÆOLIN OO

$C_6H_4.SO_3Na.N_2.C_6H_4NH.C_6H_5$

ALKALIES = Yellow ACIDS = Yellowish-red to Red

Synonyms: Orange GS.; Orange N.; Orange iv; New Yellow; Fast Yellow; Acid Yellow D.; Diphenylamine Orange; Orange M.; Diphenylamine Yellow; Von Müller's Indicator.

Preparation: Tropæolin OO is prepared by heating 5 parts of fuming sulphuric acid (20% anhydride) and 1 part of phenylamido-azobenzene for four hours at a temperature of 60° to 70° C., cooling, and pouring the mass into 50 parts of water. The precipitate is then collected, washed, and converted into a sodium salt, which is the commercial form of the article.

Properties: The base, phenylamido-azobenzene-sulphonic acid, forms graphite-like needles, difficultly soluble in water and yielding a reddish-violet solution.

The sodium salt occurs in the form of orange-yellow scales or powder, soluble in water and yielding an orange-yellow solution. Its composition is $NaSO_3.C_6H_4.N_2.C_6H_4. = NH.C_6H_5$. When hydrochloric acid is added to the aqueous solution, a violet precipitate is formed. With concentrated sulphuric acid it affords a violet-colored solution.

Application: Tropæolin OO was recommended by von Müller as an indicator. For use a solution of 0.5 Gm. of tropæolin OO in a liter of water, or a cold saturated alcoholic solution, is prepared; 2 Cc. of the aqueous, or a few drops of the alcoholic, solution are added to 50 Cc. of the liquid to be tested. The light-yellow solution is colored yellowish-red by **acids**, even by **oxalic** and other **organic acids**; on adding an **excess** of **acid** a red color is obtained. **Alkalies** restore the yellow color.

The indicator is not affected by free **carbonic-acid gas**, **bicarbonates**, or by **acid salts**, in which respect it is superior to litmus, because normal sodium-carbonate solution may be used instead of caustic-soda solution for titrating.

The color of tropæolin OO is changed to red only by **free acids**, and not by solutions of **metallic salts**. Hence small quantities of added acids may be readily determined. **Hydrogen sulphide** also does not affect the indicator.

Tropæolin OO must be employed only in cold solutions.

Tropæolin OO is a good indicator, but its quality cannot be depended on; hence, readings given by it may be unreliable. It behaves very much like methyl orange, but is less sensitive to acids. It may be distinguished from methyl orange, according to Engel, by means of gold chloride, as this affords a violet, then green color with tropæolin

OO, whereas with methyl orange it yields a red color.

The indicator is also used in the form of a test-paper (see under Test-Papers).

TROPÆOLIN OOO No. 1

$C_6H_4.N_2.C_{10}H_6OH.SO_3Na$

ALKALIES = Brown   ACIDS = Brownish-yellow

Synonyms: Orange II; Betanaphtol Orange; Mandarin G. Extra; Chrysaurein; Gold Orange; Orange Extra; Atlas Orange; Orange A; Sulpho-azobenzene-beta-naphtol.

Preparation: Tropæolin OOO No. 2 is obtained by the action of para-diazobenzene-sulphonic acid on beta-naphtol in alkaline solution, the process being quite similar to that whereby tropæolin OOO No. 2 is prepared. The product is converted into the sodium salt, which is the commercial form of the article.

Properties: The base, $C_6H_4.HSO_3.N_2.C_{10}H_6.HO$, occurs as orange-yellow scales insoluble in water; on drying they lose water and are converted into a red powder.

The sodium salt occurs as a bright orange powder, soluble in water and yielding an orange-colored solution. On adding hydrochloric acid to the solution it occasions a brownish-yellow flocculent precipitate. Caustic alkalies change the color to a dark brown. With concentrated sulphuric acid it yields a dark-red solution which, on dilution with water, becomes a reddish-brown.

Application: Like Tropæolin OOO No. 2.

TROPÆOLIN OOO No. 2

$C_6H_4.SO_3Na.N_2.C_{10}H_6(OH)$

ALKALIES = Red ACIDS = Yellow

Synonyms: Orange I; Sodium α-Naphtolazobenzene Sulphonate; Alpha-Naphtol Orange; Orange B.; Naphtol Orange; Alpha-Naphtol Yellow; Sulphoazobenzene-alpha-naphtol; Von Müller's Indicator.

Preparation: Tropæolin OOO No. 2 is prepared as follows: 25 parts of caustic soda are dissolved in 450 parts of boiling water, 100 parts of sulphanilic acid added, and the solution cooled, when 64 parts of sulphuric acid, and finally, 41 parts of sodium nitrite dissolved in 200 parts of water added. To the solution so obtained, a solution prepared by boiling 80 parts of alpha-naphtol and 30 parts of caustic soda in 400 parts of water, is slowly added with constant agitation. The precipitate is then collected, dried, and converted into the sodium salt, which is the commercial form of the article.

Properties: The acid base forms almost black scales having a greenish shimmer, and the composition $C_6H_4(SO_3H).N_2. = C_{10}H_6(HO)$. The sodium salt occurs as reddish-brown powder, readily soluble in water and yielding an orange-red solution, the color of which is changed to red or brownish-red by alkalies. In concentrated sulphuric acid it dissolves with a magenta color. Its solutions yield with hydrochloric acid a brownish-yellow coloration or flocculent precipitate.

Application: Tropæolin OOO was recommended as an indicator by W. von Müller. For use a cold, saturated, aqueous solution is most suitable. A few drops of the solution are added to the liquid to be titrated. This colors it a scarcely perceptible yellow, which is sharply and suddenly changed to red by alkalies. **Ammoniacal salts** do not affect it, nor does **carbonic-acid gas**; it is, hence, applicable in the presence of the latter.

ZINC-IODIDE AND STARCH

Preparation: Zinc-iodide and starch solution is prepared by heating 4 parts of starch, 20 parts of zinc chloride, and 100 parts of water over a free flame for an hour or more, until a clear solution is obtained, the evaporated water being replaced from time to time. Sufficient water is then added to make the whole measure 1000 Cc., and the mixture is then set aside for a week or two, when the solution is filtered, and 2 parts of zinc-iodide then added.

Application: The solution is used in iodometric determinations as an indicator. It is colored blue by the slightest traces of **free iodine.**

PART III

TEST-PAPERS

FOR the preparation of test-papers only the finest quality of filtering-paper should be used, and even then, before impregnation with the indicator-substance, it should be treated with very dilute hydrochloric acid, then with very dilute ammonia, then again with the hydrochloric acid, and finally thoroughly washed, to remove all traces of impurities, with plenty of recently distilled, freshly boiled water, and finally dried in an ammonia-free atmosphere.

The paper so treated is immersed in the indicator-solution, the surplus of the latter is removed by passing the paper over glass rods held horizontally, and the paper then hung over stretched cords, or suspended by two corners by means of clips. When the dripping has ceased, the paper should be reversed, i.e., hung by the two corners that had been lowermost. If this is not done, the paper, when dry, will have received a surcharge of the indicator-substance at its lower end, because of a greater quantity of the solution having accumulated there during the hanging. It is well, therefore, to reverse the position of the paper several times during the period it is drying, in order to insure uniformity of color and sensitiveness.

During the drying care must also be taken that the paper be not exposed to ammoniacal, acid, or sulphurous fumes, because many test-papers are exceedingly sensitive to them, and may in consequence suffer an impairment of delicacy after exposure to them.

Where the substance to be applied is in the form of a paste, as in making ultramarine-, starch-, etc., papers, the paste is best applied by means of a broad, flat, camel's-hair brush, care being taken to touch every part of the paper but once.

Test-papers are used either by dipping directly into the liquid to be tested, and observing the color-changes, if any, that occur; or better, by applying a drop or two of the solution taken up on a glass rod to the paper. For titrimetry proper, test-papers are not very serviceable, as a rule, because very many trials must be made before the end reaction can be determined with precision. This occasions a great loss of time, besides rendering the final result slightly inaccurate on account of the withdrawal of repeated appreciable quantities of the liquid being titrated.

For the qualitative detection of metals, etc., however, the test-papers are excellent, and are very serviceable.

All test-papers should be preserved in dark, or amber-colored, carefully stoppered bottles, and be as little exposed to light and air as possible, as these have a disturbing effect on a very large number of the dyes of which the indicators for the most part consist.

ALKANIN PAPER

ALKALIES = Green or Blue ACIDS = Red

Synonym: Anchusin Paper; Boettger's Test-Paper.

Preparation: Paper is impregnated with a 3-per-cent. alcoholic solution of alkanin, or with an ethereal extract of alkanet-root bark. The paper so obtained possesses a rose-red color when dry, and should be very carefully preserved in an ammonia-free atmosphere.

Application: Alkanin paper is extremely sensitive to free **alkalies** and **alkaline salts**, and particularly to **ammonia**, even the slightest traces of which color the paper green. It is sensitive to a 1 : 25 000 solution of potassium hydrate, and to a 1 : 80 000 solution of ammonia.

Blue Alkanin Paper may be obtained by immersing the red paper, prepared as above, in a 1-per-cent. solution of sodium carbonate, and drying. This paper is sensitive to a 1 : 60 000 solution of sulphuric acid, and to a 1 : 80 000 solution of hydrochloric acid.

AZOLITMIN PAPER

ALKALIES = Blue ACIDS = Red

Preparation: Azolitmin paper is prepared by impregnating filter-paper with a solution obtained by dissolving 1 part of azolitmin and 0.5 part of crystallized sodium carbonate in 1000 parts of water, and adding to the solution just sufficient phosphoric acid to cause a faint redness. The paper when dry has a reddish-violet color which is changed to a red by acids and to a blue by alkalies.

Application: Azolitmin paper is very sensitive, and it is used like litmus. Before use, its sensitiveness should be invariably tested. It is sensitive to sulphuric acid 1 : 40 000; and to hydrochloric acid 1 : 50 000, according to Dieterich.

BENZOPURPURIN PAPER

ALKALIES = Brownish-red ACIDS = Bluish-violet

Preparation: A solution of Benzopurpurin B. is made violet with a small quantity of acid, and white filtering-paper impregnated with the solution and dried.

Application: Benzopurpurin paper affords a very sensitive means of detecting **ammonia**, the slightest traces of which change the bluish-violet color of the paper to a red on drying.

BRAZILIN PAPER

ALKALIES = Blue ACIDS = Yellow

Synonyms: Pernambuco Paper; Fernambuco Paper.

Preparation: Unsized, white paper is impregnated with a solution of brazilin, and dried; or, the paper may be immersed in a 12.5-per-cent. infusion of Brazil wood, to which ammonia has been added until a bluish-red color is had, and dried.

Application: Brazilin paper is very sensitive to **acids**, and may be used in their estimation. The paper should be very carefully preserved in the dark, and from air as much as possible.

Concentrated or gaseous **hydrofluoric acid**, and also **phosphoric** and **oxalic acids**, have no action on the paper until water has been added to the concentrated acids.

The paper is sensitive to 1 : 80 000 of ammonia, and to a 1 : 30 000 solution of potassium hydrate.

BRUCINE PAPER

NITRIC ACID = Red CHLORINE = Red

Preparation: Filter-paper is impregnated with an aqueous, concentrated solution of brucine sulphate, and dried in a warm place.

Application: Brucine paper is applied for the detection of **chlorine** and **nitric acid.**

BUCKTHORN PAPER

ALKALIES = Greenish-yellow ACIDS = Red

Preparation: Paper is immersed in a decoction of buckthorn berries (*Rhamnus cathartica*), and dried.

Application: Buckthorn paper is used similarly as georgina paper. **Acids** change its color to red; **alkalies** to a greenish-yellow.

The paper is sensitive to a 1 : 15 000 solution of potassium hydrate, and to a 1 : 35 000 solution of ammonia.

CARMINE PAPER

ALKALIES = Purplish-red ACIDS = Yellowish-red

Preparation: A red carmine paper is prepared by immersing pure filter-paper in an ammoniacal solution of carmine.

Application: The carmine paper is at times used in analytical work, although infrequently. It is used like the carmine tincture.

CITRO-MERCURIC-CHLORIDE PAPERS

ALBUMIN = Precipitate

Synonym: Geissler's Test-Papers.

Preparation: Geissler's test-papers are prepared by saturating strips of paper with a concentrated citric-acid solution and drying; other strips of paper are impregnated with a solution containing 3 per cent. of mercuric chloride and from 12 to 15 per cent. of potassium iodide.

Application: The papers are employed for the detection of **albumin** in urine, and as follows: A strip of the acid paper is first dipped into the urine to be tested, and stirred; then a mercury-potassium-iodide paper is immersed. If albumin is present a precipitate forms.

CITRO-MOLYBDIC-ACID PAPER

MOISTURE = Decolorization

Synonym: Mann's Paper.

Preparation: One part of molybdic acid and two parts of citric acid are fused together, and then dissolved in water. With the solution filtering-paper is impregnated, and dried at a temperature of 100° C.

Application: The paper is blue when dry, and is applied for the detection of **water** in alcohol, etc., as exposure to moisture discharges the blue color.

CITRO-POTASSIUM-FERROCYANIDE PAPERS

ALBUMIN = Precipitate

Synonym : Oliver's Albumin Papers.

Preparation : Some strips of filtering-paper are impregnated with a concentrated solution of citric acid, while other strips are impregnated with a concentrated solution of potassium ferrocyanide. The strips are then dried.

Application: The papers are used for detecting the presence of **albumin** in urine. For this purpose, a strip of the citric-acid paper is first stirred in the suspected urine, and then a strip of the ferrocyanide paper. Albumin, if present, occasions a precipitate.

CITRO-SODIUM-TUNGSTATE PAPER

ALBUMIN = Precipitate

Synonym: Oliver's Tungstate Paper.

Preparation: Paper is immersed in a strong solution of sodium tungstate and citric acid, and then dried.

Application : The paper is used for detecting the presence of **albumin** in urine. A small piece immersed in the suspected fluid occasions a precipitate if albumin is present.

COBALT- AND METHYLENE-BLUE PAPER

SULPHIDE EXCESS = Black

Preparation: Paper is immersed in a solution of cobaltous chloride colored with some methylene blue.

Application: Cobalt- and mythelene-blue paper is employed as an indicator in estimating **zinc, copper,** and **nickel**, by means of sodium sulphide. The paper may also be made so that only one half of the strip is impregnated with the solution, the other half being left white. In using this paper, a drop of the mixture to be tested for zinc, copper, etc., is placed, after the addition of the sodium sulphide, on the white end so that the solution may diffuse to the colored end, which will be colored black if any excess of sulphide is present.

COBALT PAPER

SULPHIDE EXCESS = Black

DRY = Blue
MOIST = Red

Synonym: Stahl's Paper.

Preparation: Paper is impregnated with an almost neutral solution of cobaltous chloride, representing 0.3 Gm. of CoO in 100 Gm. of solution, and then dried.

Application: The paper is used in the estimation of **zinc** by means of sodium sulphide; and also for hygroscopic determinations.

COCHINEAL PAPER

ALKALIES = Violet ACIDS = Red

Preparation: Cochineal paper is prepared by immersing strips of good white filtering-paper in an aqueous cochineal solution, and drying.

Application: The paper is used like the tincture. Its sensitiveness has been determined by Dieterich to be such as to indicate the presence of 1 part of sulphuric acid and of hydrochloric acid in 8000 and 10,000 parts of water, respectively.

COLEÏN PAPER

ALKALIES = Yellow ACIDS = Red

Synonym: Boettger's Test-Paper.

Preparation: Coleïn paper is prepared by immersing sheets of filtering-paper in an alcoholic solution of coleïn, and then drying. Care must be taken in making it, however, that the color be not too dark or too light, as on the one hand it will not be sufficiently sensitive, and on the other hand it will not yield a decided and sharp change of color. Paper made too weak may be remedied by immersing it in water containing a mere trace of ammonia.

Application: Coleïn paper is said to constitute a very sensitive indicator for titrimetric determinations. It is colored yellow by alkalies, and red by acids.

The paper is sensitive to a 1 : 8000 solution of sulphuric acid; to 1 : 10 000 hydrochloric acid; to 1 : 8000 potassium hydrate, and to 1 : 20 000 ammonia solution.

CONGO-RED PAPER

ALKALIES = Red ACIDS = Blue

Synonyms: Herzberg's Paper; Riegel's Paper.

Preparation: Both a red paper and a blue are prepared for use. The **red paper** is prepared by impregnating suitable paper with a solution obtained by dissolving 1 part of Congo red in 1000 parts of 30-per-cent. alcohol. The **blue paper** is obtained by passing red paper, prepared as above, through a faintly acidulated bath.

The blue paper must be carefully preserved, because of its tendency to become red. It is also reddened by aniline and alkaloids generally.

Application: The red paper is useful for testing paper for **free acids**, because of its extreme sensitiveness to these. The paper may also be used for estimating **organic bases**, such as **aniline, quinine, brucine, morphine**, etc. It is also serviceable in many cases in which litmus and phenolphtalein are useless. It is not as sensitive as litmus paper, however, and is of no special value, except that the dye adheres very tenaceously to the paper, and is not washed out readily on prolonged immersion in water, as is the case with litmus paper.

The papers are sensitive to acids and alkalies to the extent of about 1 : 3000.

CORROSIVE-SUBLIMATE PAPER

ARSENIURETTED HYDROGEN = Yellow, then Brown

Synonym: Flückiger's Sublimate Paper.

Preparation: Paper is immersed in a concentrated solution of corrosive sublimate, and dried.

Application: Corrosive-sublimate paper is chiefly employed for the detection of arsenic. With **arseniuretted hydrogen** it affords a, at first yellow, then brown, color, which is blackened by silver nitrate. The paper is sufficiently sensitive to detect 0.00005 Gm. of arsenous acid.

CURCUMA PAPER

ALKALIES = Brown ACIDS = Yellow

Preparation: Curcuma paper is prepared by impregnating white, unsized paper in an alcoholic solution of curcumin. It may be prepared from the root directly, also, but in this case the powdered root must first be exhausted with water to remove a water-soluble coloring-matter which interferes with the sensitiveness of the color-change; then drying the root in the dark, and finally exhausting it with alcohol, the paper being then imbued with this solution.

Tests : Curcuma paper should always be tested before use as to its sensitiveness towards potassium hydrate and ammonia. A good paper will respond to a 1 : 18 000 potassium-hydrate solution, and to a 1 : 35 000 ammonia solution.

Application : Curcuma paper has a yellow color, which is changed to brown by alkalies. The paper is useful for estimating **alkali hydrates** and **earths,** but is unsuitable generally for alkalimetry proper, because the change of color is scarcely sharp enough. It may be successfully used, however, for titrating **citric, acetic, tartaric, oxalic, lactic,** and **succinic acids** by means of fixed alkalies, and especially in dark colored solutions.

With **ammonia** the end-reaction is indefinite, and only 97% of NH_3 is shown ; with **ammoniacal salts,** a similarly indefinite reaction is obtained ; hence curcuma paper is inapplicable for ammonia or its salts. The paper is also unserviceable for **sodium** and **potassium carbonates** and **sulphides,** and for a similar reason.

With **boric, molybdic,** or **phosphoric acid,** the paper, after drying, is brown. **Borax,** after the addition of an acid, yields a similar result, and paper browned by boric and hydrochloric acids is colored a handsome blue by alkalies.

In **silicates** and **borates** of **sodium** and **potassium,** 90% of the combined alkali is shown in the former, and 50% in the latter, the reactions being good.

Thiosulphates are neutral to curcuma paper; **normal sulphites** and **monophosphates** are slightly alkaline.

For **fatty acids**, when ascertaining the saponification numbers of fats, oils, etc., the paper is of no value, because the change of color is not sharp enough, and the soaps formed are distinctly alkaline to the paper. The paper is very useful, however, for ascertaining the close of the alkaline reaction in the Pettenkofer process of air analysis.

Thompson recommends also a reddish-brown paper obtained by impregnating suitable paper with an alcoholic solution of curcumin or curcuma extract rendered alkaline by the addition of caustic soda. Paper so prepared becomes darker in color on moistening with pure water, neutral, or alkaline solutions, but when immersed in an acid solution, the immersed part becomes a bright yellow, while the part outside of the liquid draws up some of the water only from the solution by capillary action, and appears much darker by comparison. This paper is very useful for ascertaining acidity in alcohol.

DIMETHYL-PARAPHENYLENEDIAMINE PAPER

OZONE = Bluish-violet

Synonym: Wurster's Red Ozone Paper.

Preparation: White, unsized paper is charged with a solution of dimethyl-paraphenylenediamine, and then dried.

Application: The paper is employed for the detection of **ozone, sulphuretted hydrogen, hydrogen dioxide, turpentine, colophony,** etc., and also for **wood-pulp** in paper.

ELDERBERRY PAPER

ALKALIES = Blue to Green ACIDS = Red

Preparation : Elderberry paper is prepared by impregnating filtering-paper with the juice of the elderberry, *Sambucus nigra* L. and *S. canadensis* L.

Application: The elderberry paper is used like georgina paper, though it is somewhat less sensitive. It will react with 1 part of potassium hydrate in 5000 parts of water, and 1 part of ammonia in 10 000 parts of water.

FERMENT PAPER

UREA = Brown

Synonym: Musculus' Paper.

Preparation: Ferment paper is prepared by filtering decomposing urine through white filtering-paper, then washing the latter, and coloring it with turmeric.

Application: Ferment paper is applied for the detection of **urea,** with which it yields a brown color, due to the decomposition of the urea induced by the ferment in the paper, ammonium carbonate being one of the products of the decomposition and affording the reaction with the turmeric.

FERROUS-SULPHATE PAPER

HYDROCYANIC ACID AND CYANIDES = Blue

Preparation: Ferrous-sulphate paper is prepared by impregnating paper with a solution of pure, crystallized ferrous sulphate and drying.

Application: Ferrous-sulphate paper is applied for the detection of **hydrocyanic acid,** and for **soluble cyanides.**

FUCHSINE PAPER

AMMONIA = Red

Synonyms : Rosanilin Paper; Kroupa's Paper.

Preparation: Paper is impregnated with an aqueous solution of fuchsine, to which sufficient sulphuric acid has been added to give the solution a yellowish-brown color. When dry, the paper has a yellow color. It must be kept in well-closed, glass vessels.

Application: Fuchsine paper is exceedingly sensitive to gaseous **ammonia**, by which it is colored a carmine red, the acid fuchsine in the paper becoming converted into the neutral fuchsine. Kroupa reports having been enabled to detect 0.0005 Gm. of ammonium chloride and 0.0005 Gm. of ammonium carbonate by means of the paper.

Fuchsine paper is also used for the detection of **sulphurous acid.**

GEORGINA PAPER

ALKALIES = Green ACIDS = Red

Synonyms: Dahlia Paper; Anthocyanin Paper.

Preparation: Georgina paper is prepared by impregnating unsized paper with an aqueous decoction or spirituous extract of the corollas of *Georgina (Dahlia) purpurea* Willdenow. The coloring-matter is believed to be closely allied to Hoffmann's Violet, and also to anthocyanin.

Tests: Dieterich estimates the paper to be sensitive to sulphuric acid 1 : 8000; to hydrochloric acid 1 : 10 000; to potassa 1 : 8000; and to ammonia 1 : 20 000.

Properties: The dry paper has a handsome, bluish-violet color. Should the color be too reddish, as may perhaps occur, it may be readily remedied by immersing the paper in water to which a mere trace of ammonia has been added. **Acids** color the paper red, and **alkalies** change the color to a handsome green, while with concentrated **caustic alkalies** the color becomes yellow.

Cherry paper, prepared from the juice of red cherries, is also used like Georgina paper.

GOLD-CHLORIDE PAPER

OZONE = Violet

Synonym: Boettger's Paper; Ozone Paper.

Preparation: Paper is simply impregnated with a neutral solution of gold trichloride, and dried.

Application: The paper is applied for the detection of **ozone**, by which it is colored violet.

GUAIAC PAPER

HALOGENS AND OZONE = Green or Blue NITRIC AND CHROMIC ACIDS = Blue

Preparation: White, unsized paper is impregnated with a 1 : 100 tincture of guaiac resin, and dried.

Application: Guaiac paper is applied for the detection of **ozone, chlorine, bromine, iodine, nitric acid,** and **chromic acid.** It is very sensitive to these, and is colored by them green or blue.

GUAIAC- AND COPPER-SULPHATE PAPER

HYDROCYANIC ACID = Blue

Synonyms: Schönbein and Pagenstecher's Test-Paper; Schönbein's Hydrocyanic-acid Paper.

Preparation: For the preparation of guaiac- and copper-sulphate paper, a good quality of white filtering-paper is first impregnated with a solution of 1 part of guaiac resin in 100 parts of alcohol. After the paper has dried, it is passed through a solution of 1 part of cupric sulphate in 2000 parts of distilled water, and then dried again.

Application: The paper is used for the detection of **hydrocyanic acid**, with the slightest traces of which it gives a blue color.

HÆMATOXYLIN PAPER

ALKALIES = Blue ACIDS = RED

Synonym: Chevreuil's Test-Paper.

Preparation: Since hæmatoxylin is exceedingly sensitive to even traces of calcium carbonate, paper intended to be impregnated with it must be previously freed from these traces by treatment with dilute hydrochloric acid, and washing with distilled water. Paper so treated is impregnated with a solution of hæmatoxylin, or with an extract prepared, according to Hager; by digesting 10 parts of finely ground log-wood which had been freshly cut, with 40 parts of alcohol and 120 parts of distilled water, in a stoppered glass vessel for several hours. The strained liquid is heated with 0.7 part of potassa alum free from iron, and 7 parts calcium chloride dissolved in a little water acidulated with a few drops of hydrochloric acid, sufficient to give the paper a faintly red color.

The paper may also be prepared from an extract made by digesting 1 part of finely ground, recently cut log-wood in 20 parts of distilled water, in a well-closed glass vessel for two days. It is important that the log-wood be carefully selected, and that only freshly exposed sections of the wood be used, because both air and light affect it.

Tests: The paper is sensitive to a 1 : 80 000–90 000 ammonia, and to 1 : 35 000 potassium hydrate.

Application : The dried paper is faintly yellow or reddish, on drying, and is extremely sensitive to **ammonia,** for which it is used as a very delicate indicator. It is also serviceable for the **fixed alkalies** and for **alkaline earths** and **mineral acids,** but for these it is not as sensitive as litmus.

The paper is exceedingly difficult to keep in good condition on account of its sensitiveness to ammonia, traces even of which suffice to change its color to blue. It must be rigorously preserved, hence, in an ammonia-free atmosphere, in well-closed, glass containers, and in the dark.

HOUZEAU'S OZONE PAPER

OZONE = Blue

Preparation: Houzeau's ozone paper is prepared by dipping strips of red litmus paper half way into a solution of potassium iodide, and then drying.

Application: **Ozone** acts on the potassium iodide in the half of the paper, and liberates the potassium, which at once reacts with the litmus and affords a blue color; the other half of the paper remains red, of course. Sulphurous acid does not afford the reaction, but would color the entire paper red, hence any possible error from this source is eliminated.

HUCKLEBERRY PAPER

ALKALIES = Grayish-blue ACIDS = Red

Synonym : Uffelman's Test Paper.

Preparation : Paper is immersed in a hydro-alcoholic extract of huckleberries, and then dried. According to Uffelmann an amyl-alcoholic extract may also be used for the preparation of the paper.

Tests : The paper is said to be sensitive to a 1 : 6000 potassium-hydrate, and to a 1 : 15 000 ammonia solution.

Application : The paper is employed as an indicator for **ammonia** and **fixed alkalies**. The paper is also applied for the detection of free **hydrochloric acid**, which changes the grayish-blue color of the paper to a red.

HYACINTH PAPER

AMMONIA = Green

Synonym : Selle's Paper.

Preparation : Hyacinth paper is prepared by impregnating white filtering-paper with a strong tincture of blue hyacinth flowers.

Application: Hyacinth paper is applied for the detection of **ammonia vapors**, which color it green.

INDIGO PAPER

CHLORINE = Green

Preparation : Filtering-paper is impregnated with a solution of indigo.

Application: The paper is chiefly applied for the estimation of **chlorine.**

INDIGO-CARMINE PAPER

OXYGEN = Yellow SUGAR = Violet to Yellow

Synonym : Blue Carmine Paper.

Preparation: Paper is imbued with an aqueous solution of indigo-carmine.

Application: Used in the estimation of **oxygen**; and also as a test for **sugar** in urine.

INDIGO-CARMINE AND SODIUM-CARBONATE PAPERS

GLUCOSE = Colorless or Yellowish

Synonym: Oliver's Glucose Papers.

Preparation: Separate strips of filtering-paper are impregnated respectively with solutions of indigo-carmine and of sodium carbonate, and dried.

Application: The papers are employed for the detection of **glucose** in urine. By immersing a strip of each paper in the suspected fluid, the bluish color imparted to the latter by the indigo-carmine fades away if glucose is present, due to the reducing action of the latter on the indigo-carmine.

IODATE PAPER

SULPHUROUS ACID = Blue

Preparation: Iodate paper is prepared by impregnating paper with a solution prepared by heating 2 Gm. of starch with 100 Cc. of water, and after solution, adding 0.2 Gm. of potassium iodate dissolved in 5 Cc. of water.

Application: Iodate paper may be employed for the detection of the slightest traces of **sulphurous acid,** which reduces the iodate present in the paper, the liberated iodine then reacting with the starch and affording the well-known blue color.

IRIS PAPER

ALKALIES=Green NEUTRAL=Blue ACIDS=Red

Synonym: Greenwalt's Paper.

Preparation: Iris paper is prepared by immersing strips of filtering-paper in a hot, aqueous extract of *Iris versicolor*, Blue Flag, and then drying them. The paper was recommended by Greenwalt for titrimetric use. The neutral paper has a blue color, changed to red by acids, and to green by alkalies.

LACMOID PAPER

ALKALIES = Blue ACIDS = Red

Preparation: Both a red and a blue paper are made and used. The latter is prepared from a solution made by adding sulphuric acid to an alcoholic solution of lacmoid until white paper shows a red color on impregnation. If not too much acid is used, the red paper, on drying, becomes blue.

Red paper is made by first treating the paper to be employed with dilute sulphuric acid and drying, because paper not so treated is very prone to lose its red color and become blue. Just sufficient acid should be used for the paper to retain a rose-red, but not darker, color, after several hours; if too much acid has been added, the sensitiveness is materially impaired. The paper must be very carefully preserved in well-stoppered bottles, as it is very prone to take on the blue color. Nor must it be handled much, as the moisture of the hand suffices to color it blue.

Application: Blue lacmoid paper is very useful for application by lamp- or gas-light, as a pure blue color is observed, whereas with litmus paper the color appears more or less violet. This paper is about equal in value to litmus paper, but the red lacmoid is more sensitive than the corresponding litmus paper, the change of color being much sharper, and the blue brighter.

A great advantage possessed by the lacmoid papers is the tenacity with which the color is retained on prolonged contact with water.

The papers are very useful for titrations in cold and in colored liquids. The red paper indicates at the end of the reaction the slightest trace of alkali, and even if the liquid is impregnated with carbonic-acid gas; the blue paper, on the other hand, shows only a faint red in the presence of traces of alkali, if free carbonic-acid gas is present, and the redness disappears on exposure to the air for a few moments.

Sulphides of the **alkalies** may be sharply titrated with lacmoid paper, whereas the lacmoid solution is decolorized by the liberated **hydrogen sulphide.** The paper is also useful for testing for the presence of **neutral chromates,** or **chromic acid** in the presence of **bichromates.** It can also be used for the **alkali carbonates** and **sulphites,** with which lacmoid solution cannot be used. It is also applicable for estimating the bases in the **borates** of the **alkalies** and **alkaline earths,** and also in **silicates** of the alkalies. The total alkali of **arsenites** may also be sharply titrated, since **arsenous acid** is neutral to the paper.

LEAD PAPER

SULPHIDES = Black

Preparation: White, unsized paper is dipped in a 10-per-cent. solution of lead acetate in distilled water, and dried in an atmosphere free from hydrogen sulphide. The paper must be very carefully preserved in an atmosphere free from this gas, and preferably in glass-stoppered bottles.

Application: The paper is applied to the detection of **hydrogen sulphide** and **alkali sulphides.**

LITMUS PAPER

ALKALIES=Blue NEUTRAL=Violet ACIDS=Red

Of litmus papers, three kinds are to be met with—a red, blue, and violet, the last being a neutral paper. The best paper only should be employed in making them, and should be, preferably, not too thin, and of firm texture, because much better results are obtained with a paper not too porous, the reason being that, on moistening, if the paper is too bibulous, the liquid diffuses over too great a surface, and thus materially weakens the reaction, whereas if the solution applied remains on the spot where placed, its full acidity or alkalinity is exerted on the one spot. This fact also holds good for all papers.

Preparation : **Blue Litmus Paper** is prepared by impregnating a good quality of white, unsized paper with blue litmus solution (see page 102), and drying. It is best preserved in a jar, in the bottom of which is placed a small lump of ammonium carbonate.

Red Litmus Paper is prepared by immersing the blue paper in water faintly acidulated with hydrochloric acid, and then drying in an ammonia-free atmosphere. The paper should be preserved in a jar in which is placed a small quantity of cotton moistened with a few drops of acetic acid.

Neutral Litmus Paper is prepared by impregnating a pure paper with a perfectly neutral litmus solution. The paper has a light reddish-violet tint, and is very sensitive to either acids or alkalies. Care must be taken that the paper be rather red than violet when moist, because on drying the paper is apt to acquire a blue color if the moist paper be violet. The dry paper must be very carefully preserved in small, well-stoppered bottles, and must be carefully protected from acid or ammoniacal vapors, otherwise it rapidly loses its extreme sensitiveness.

Tests: Carefully made blue litmus paper is sensitive to 1 : 60 000 sulphuric acid solution, and to a 1 : 80 000 hydrochloric-acid solution. The red paper is sensitive to a 1 : 50 000 potassa solution, and to a 1 : 80 000 solution of ammonia.

Application: Litmus paper is very serviceable for detecting the acidity or alkalinity of solutions. It is also applicable for titrations in hot or cold liquids, and also when the titrated solutions are cloudy. Even when carbonic-acid gas is present, the paper is applicable, because the gas is rapidly dissipated from the paper, and the end reaction may hence be easily observed.

MALLOW PAPER

ALKALIES = Bluish-green ACIDS = Red

Synonyms: Hollyhock Paper; Althæa Paper; Stevenin's Paper.

Preparation: Mallow paper is prepared by impregnating white filtering-paper with an extract prepared by macerating 20 parts of flowers of *Althæa rosea* in a mixture of 900 parts of alcohol, 100 parts of water, and 1 part of ammonia, expressing after a week, and filtering.

Application: The prepared paper has a purplish-blue color, and is applied as a test for **acids** and **alkalies**; the former change its color to red, and the latter to bluish-green. It is more sensitive than georgina paper to acids.

The paper may be applied for the detection of **nitrites** in potable waters. It is colored purple by traces. Its sensitiveness, according to Dieterich, is as follows: Sulphuric acid, 1 : 10 000; hydrochloric acid, 1 : 13 000; potassium hydrate, 1 : 8000; and ammonia, 1 : 20 000.

MANGANOUS-CHLORIDE PAPER

Preparation: Filter-paper is impregnated with a solution of manganous chloride, $MnCl_2 + 4H_2O$, and dried.

Application: This paper shows the presence of **nascent oxygen** on moistening with soda lye.

MANGANOUS-ACETATE PAPER

Preparation: Paper is immersed in a solution of manganous acetate, and dried.

Application: The paper is applied for the detection of traces of **ozone**.

METAPHENYLENEDIAMINE PAPER

NITRITES = Yellowish-brown

Synonym: Griess's Yellow Test-Paper.

Preparation: The paper is prepared by impregnating white, unsized paper with an alcoholic solution of metaphenylenediamine, and then drying. At times, sulphanilic acid is also added to the solution before the immersion of the paper.

Application: Metaphenylenediamine paper is an exceedingly delicate test for **nitrous acid** and **nitrites,** by which it is colored yellowish-brown.

METHYL-ORANGE PAPER

ALKALIES = Yellow ACIDS = Deep Brownish-yellow

Synonyms: Helianthin Paper; Tropæolin D. Paper.

Preparation: Paper is impregnated with an aqueous solution of methyl orange and then dried.

Application: Methyl-orange paper is applied as an indicator in the estimation of both **acids** and **alkalies.** By the latter it is colored yellow; by the former a deep, brownish-yellow. The paper will show 1 part of sulphuric acid in 10,000 parts of water, and 1 part of hydrochloric acid in 15,000 parts of solution.

OENOKRINE PAPER

Preparation : Oenokrine paper, introduced in Paris for determining the nature of foreign coloring-matters in red wine, is prepared, according to Julius Müller, by impregnating paper with a solution of lead acetate, and drying.

Application: On immersing the prepared paper in genuine red wine, allowing to drip, and then spreading on a sheet of white paper, the test-paper on drying shows a grayish-blue color. With huckleberry extract, it yields a similar color. If fuchsin has been added to the wine, a fine red color is obtained. With the coloring-matters of mallow and log-wood, a blue color results. Ammoniacal carmine or cochineal solution present in the wine will yield a pale violet. Extract of Pernambuco wood affords a dirty yellow. With indigo, the paper shows a deep blue.

Oenokrine paper is not, however, reliable.

PALLADIOUS-CHLORIDE PAPER

REDUCING GASES = Black

Synonym: Merget's Paper.

Preparation: Paper is impregnated with a solution of palladious chloride, $PdCl_2$, of such strength that every 100 Cc. of solution represents 5 Gm. of metallic Pd. A solution of 1 part of sodium and palladium chloride, $PdCl_2 + 2NaCl$, in 12 parts of distilled water may also be used for the purpose, instead.

Application: The paper is employed for detecting **carbon monoxide, hydrogen-sulphide, ozone, methane, ethane** and **illuminating gas,** which precipitate metallic palladium.

Paper impregnated with palladious chloride and mercuric chloride is also used for similar purposes. It is known as Merget's paper.

PHENOLPHTALEIN PAPER

ALKALIES = Red ACIDS = Colorless

Preparation: In making phenolphtalein paper, only the finest quality of paper should be used. The paper is simply dipped into an alcoholic phenolphtalein solution, and then dried.

Application: The paper may be applied in great measure like the solution. It is unaffected by **ammoniacal vapors** or **solutions,** or by solutions of the **carbonates** of the **alkalies.** It has been recommended as being useful for determining the comparative quantities of **carbon dioxide** in the atmosphere of schoolrooms, factories, hospitals, etc., because of its property of losing the redness caused by moistening with a drop of lime-water, when carbon dioxide is present in the air; the greater the quantity present, the more rapidly does the color fade. The paper is sensitive to a 1:20000 potassium-hydrate solution.

PHLOROGLUCIN-VANILLIN PAPER

HYDROCHLORIC ACID = Red LIGNIN = Red

Synonym: Guenzburg's Test-Paper.

Preparation: Paper is immersed in a solution of 1 part of phloroglucin and 2 parts of vanillin in 30 parts of alcohol, and then dried.

Application: The paper is at times employed instead of Guenzburg's solution for the detection of **free hydrochloric acid** in gastric juice. It is also used for the detection of **lignin** in paper.

PICRO-CITRIC-ACID PAPER

ALBUMIN = Precipitate

Synonym : Oliver's Albumin Paper.

Preparation: Paper is impregnated with a concentrated aqueous solution of picric and citric acids, and then dried.

Application: The paper is employed for detecting **albumin** in urine, by immersing a piece of the paper and stirring. If albumin is present, a precipitate is formed.

POLE-REAGENT PAPER

NEGATIVE CURRENT = Red

Preparation: Paper is impregnated with a dilute alcoholic solution of phenolphtalein and sodium sulphate, and dried.

Application: This paper is employed for the recognition of the **negative poles** of **batteries**, the paper being reddened by a negative electrical current.

POTASSIO-MERCURIC-IODIDE PAPER

ALBUMIN = Precipitate

Synonym: Hoffmann's Albumin Paper.

Preparation: A solution is prepared by dissolving 1 part of potassium iodide in 2 parts of water, and adding this to a solution of 1 part of mercuric chloride in 20 parts of water. Filtering-paper is dipped into the mixture and then dried.

Application: Hoffmann's test-paper is applied for the detection of **albumin** in urine, by dipping a piece of the paper into the suspected urine, which has been previously acidified with a few drops of acetic acid. A precipitate denotes the presence of albumin.

POTASSIUM-CHROMATE PAPER

LEAD SALTS = Yellow SILVER SALTS = Red

Preparation: Filter-paper is impregnated with a 1 : 250 solution of potassium chromate, and dried.

Application: Potassium-chromate paper is applied for the detection of **lead** and **silver salts.** It will show the presence of 1 part of lead acetate in 2000 parts of water, the paper becoming a bright yellow from the formation of lead chromate. With silver nitrate it will give a fine red color, due to silver chromate being formed, and it will show the presence of 1 part of the nitrate in 3000 parts of solution.

POTASSIUM-FERRICYANIDE PAPER

FERROUS SALTS = Blue

Preparation: Filtering-paper is immersed in a 1 : 250 solution of potassium ferricyanide, and then dried.

Application: The paper is applied for the detection of **ferrous salts,** with which it yields a blue color. It will detect 1 part of ferrous sulphate in 40 000 parts of solution.

POTASSIUM-FERROCYANIDE PAPER

FERRIC SALTS = Blue CUPRIC SALTS = Red

Preparation: Filtering-paper is impregnated with a 1 : 250 solution of potassium ferrocyanide, and dried.

Application: Potassium-ferrocyanide paper is applied for the detection of **ferric** and **cupric salts,** with which it yields a blue and red color respectively. It will detect 1 part of ferric chloride in 2500 of solution, and 1 part of cupric sulphate in 2000 of solution.

POTASSIUM-IODIDE PAPER

LEAD=Yellow BISMUTH=Black SILVER=Red

Preparation: Pure white filtering-paper is impregnated with a 1:250 solution of potassium iodide.

Application: Potassium-iodide paper is used for the detection of various metals, such as **lead, bismuth, silver,** etc. It will show the presence of 1 part of lead acetate in 500 of solution; 1 part of bismuth nitrate in 7000 parts of solution; and 1 part of silver nitrate in 1000 parts of solution

POTASSIUM-IODIDE AND STARCH PAPER

OXIDIZERS = Blue

Synonym: Schönbein's Ozone Paper.

Preparation: White filtering-paper is impregnated with a solution prepared from 10 parts of starch, 200 parts of water, and 1 part of potassium iodide. The dried paper must be preserved as carefully as possible from prolonged contact with air.

Application: The paper is applied for the detection of oxidizers, such as **chlorine, iodine, bromine, nitrous acid,** and **ozone,** etc., by which it is colored blue.

The paper will detect 1 part of chlorine in 30,000 parts of water.

POTASSIUM-SULPHOCYANATE PAPER

Free Hydrochloric Acid = Colorless   Ferric Chloride = Blood-red

Preparation: Potassium-sulphocyanate paper is prepared by immersing paper in a 10-per-cent. solution of potassium-sulphocyanate to which a little ferric-acetate solution has been added.

Application: The paper is applied according to Mohr for the detection of **free hydrochloric acid** in gastric juice.

A paper prepared without the addition of the ferric salt is applied for the detection of **ferric chloride,** with which it yields a blood-red color. Its sensitiveness to the iron salt is such as to detect 1 part of the salt in 5000 parts of solution.

RESAZURIN PAPER

Alkalies = Blue   Acids = Red

Synonyms: Diazoresorcin Paper; Azoresorcin Paper; Weselsky's Paper.

Preparation: Resazurin paper is prepared by impregnating unsized paper with a solution of resazurin made as directed under "Resazurin," and then drying.

Application: Resazurin paper can only be used when very recently prepared, because the reazurin undergoes reduction, becoming converted into resorufin. With alkalies the color of the paper is blue; acids change the color to red.

RHUBARB PAPER

ALKALIES = Red ACIDS = Yellow

Preparation: A red and a yellow rhubarb paper may be made.

Yellow Rhubarb Paper is obtained by impregnating white filtering paper in an alcoholic extract of the rhubarb root, then passing through water faintly acidulated with phosphoric acid, and finally drying.

Red Rhubarb Paper is obtained by passing the paper, after impregnation with the rhubarb extract, through water rendered alkaline with ammonia.

Application : The yellow paper yields a fine red color with **alkalies,** whereas the red paper is changed to yellow by **acids.** The yellow paper is stated by Dieterich to be sensitive enough to detect 1 part of potassium hydrate in 8000 of water; and 1 part of ammonia in 20,000 parts of water. The paper is unaffected by **boric acid.**

ROSE PAPER

ALKALIES = Bright-green ACIDS = Pink

Preparation: Rose paper is prepared by dipping paper into an infusion of the petals of the red rose (*Rosa gallica*), and drying.

Application: Rose paper is but little used, and possesses no advantage over other test-papers. The paper is colored a bright-green by alkalies, and by acids a pink.

ROSOLIC-ACID PAPER

ALKALIES = Red ACIDS = Yellow

Preparation: Rosolic-acid paper is prepared by impregnating filtering-paper with a 1-per-cent. solution in 60-per-cent. alcohol.

Application: The paper has a yellow color, and is applicable to all purposes as the rosolic-acid test solution. It is sensitive to a 1:20 000 potassium hydrate solution.

SCHIFF'S PAPER

GLUCOSE AND CARBOHYDRATES = Red

Preparation: Schiff's paper is prepared by immersing strips of filtering-paper in a mixture of equal volumes of glacial acetic acid and xylene, and a very little alcohol.

Application: Schiff's paper is applied for the detection of **glucose** and other **carbohydrates.** The substance to be tested is heated with sulphuric acid, and if carbohydrates are present, furfurol is evolved and colors the test-paper held in the vapors a fine red.

SERUM PAPER

Synonym: Richardson's Paper.

Preparation: Serum paper is prepared by impregnating filtering-paper with serum obtained from a typhoid-fever subject, and then drying carefully in an unwarmed place.

Application: Serum paper is used instead of fresh typhoid serum for carrying out Widal's typhoid reaction.

SILVER-NITRATE PAPER

PHOSPHORUS = Black
ARSENIC = Yellow
CHROMATES = Red
URIC ACID = Brown

Synonym: Schiff's Paper.

Preparation: Filter-paper is impregnated with a solution of silver nitrate, and dried in air free from hydrogen sulphide.

Application: Silver-nitrate paper is employed for the detection of **chromic** and **arsenous acids**, and for detecting **phosphorus**, by the vapors of which it is blackened. It is an exceedingly sensitive means of detecting **arsenic.**

Silver-nitrate paper is also used for detectiug **uric** acid in urine. The paper is stained brown by uric acid.

STARCH PAPER

IODINE = Blue

Preparation: Starch paper is prepared by applying with a broad, camel's-hair brush a solution obtained by triturating 10 parts of starch with 10 parts of cold water, and then adding 890 parts of boiling water. Care should be taken that no spot on the paper be touched twice, otherwise fibers of the paper are carried off mechanically. The paper should be dried in an unwarmed place.

Application: Starch paper is exceedingly sensitive to traces of **free iodine**, with which it strikes a blue color owing to the formation of starch iodide. One part of iodine in 25000 may be detected by means of this paper.

STARCH- AND AMMONIUM-PERSULPHATE PAPER

IODIDES = Intensely Blue

Preparation: According to Bourget, filtering-paper is impregnated with a 5-per-cent. starch solution, dried, and then cut up into squares of 5 Cm. each. Two or three drops of a 5-per-cent. ammonium-persulphate solution are dropped in the center of each square, and the pieces dried in the dark.

Application: Paper so prepared, and immersed in a fluid containing even traces of **iodine,** develops an intensely blue color, a distinct reaction being visible in solutions containing 0.00005 per cent. of **potassium iodide.** Paper prepared with sodium- or potassium-persulphate may also be used, but is decidedly less sensitive. Bourget recommends the paper especially for the investigation of **saliva** and **urine** at the bedside.

SULPHANILIC-ACID AND ALPHA-NAPHTYLAMINE-SULPHATE PAPER

NITRITES = Red

Synonym: Griess's Red Test-Paper.

Preparation: White, unsized paper is impregnated with an alcoholic solution of sulphanilic acid and alpha-naphtylamine sulphate (or hydrochlorate), and dried.

Application: The paper is employed in the detection of **nitrous acid** and **nitrites,** which change the color of the paper to a deep red. It is also used to detect bilirubin and aldehydes, in urine.

TANNIN PAPER

ALKALIES = Brown

FERRIC SALTS = Black

Preparation: Tannin paper is prepared by immersing filter-paper in a concentrated solution of tannin, and drying in a warm place.

Application: Tannin paper is employed for **caustic alkalies, alkaline earths, ammoniacal salts,** and **iron salts.**

TETRAMETHYL-PARAPHENYLENEDIAMINE PAPER

OZONE = Violet

Synonyms: Wurster's Blue Ozone Paper; Tetra Paper.

Preparation: White, unsized paper is impregnated with a solution of tetramethyl-paraphenylenediamine, and dried.

Application: The paper is employed for detecting **ozone** and **ozonizers,** as **turpentine, pine wood,** and also **hydrogen dioxide.** Traces of ozone or nascent oxygen in neutral or acetic-acid solutions color the paper intensely violet or bluish-violet.

THALLOUS-HYDRATE PAPER

OZONE = Brown

Synonyms: Boettger's Ozone Paper; Thallium-Hydroxide Paper.

Preparation: Paper is impregnated with a 10-per-cent. solution of thallous hydrate recently prepared by precipitating a solution of thallous sulphate by the proper stoichiometrical quantity of baryta water. The paper should be rapidly dried, and is colorless.

Application: The paper is applied for the detection of **ozone,** which colors it brown from the formation of thallium oxide. The absence of **nitrous acid** must be, however, assured, as this may partly, or even entirely, prevent the reaction.

TROPÆOLIN PAPER

ALKALIES = Yellow ACIDS = Red

Synonyms: Boas' Paper; Lutke's Paper.

Preparation: Tropæolin paper is prepared by dipping white filtering-paper in a 1 : 1000 solution of tropæolin OO and then drying.

Application: The paper may be applied like tropæolin-OO solution. It is reddened by **free acids,** and the yellow color is restored by **alkalies.** It is excellent for **oxalic** and **organic acids,** and is not affected by **carboni-acid gas, bicarbonates,** or **acid salts.**

ULTRAMARINE PAPER

ACIDS = Colorless

Preparation: A convenient quantity of ultramarine is carefully washed with water, and then mixed with a decoction of Irish moss in water (1 : 30 or 40). The mixture so obtained is then painted on unsized paper as evenly and thinly as possible, by means of a flat brush.

Application: Ultramarine paper is applied for the detection of **free acids** in alum, aluminium sulphate, etc. The acids decolorize the paper.

WHITE-LEAD PAPER

METALLIC SALTS = Color of Sulphides

Synonyms: Schott's Paper; Polka Paper.

Preparation: The paper is prepared by coating sized paper with a mixture of white lead and starch paste.

Application: White-lead paper is used as an indicator in titrating solutions of **metallic salts** with sodium sulphide.

ZINC-IODIDE AND STARCH PAPER

IODINE = Blue

Preparation: Paper is impregnated with the solution prepared as detailed under Zinc-Iodide and Starch, and dried.

Application: The paper is sometimes employed in iodometric determinations. It is rendered blue by traces of **free iodine.**

PART IV

TABLES AND TABULAR SUMMARY

H. TROMMSDORFF'S TABLE, SHOWING THE SENSITIVENESS OF INDICATORS TO ACIDS AND ALKALIES

Indicators	Strength of Indicator Solution	Cc. of Indicator Solution added to 100 Cc. of titrated Fluid	Cc. of titrating Fluid required
Azolitmin....	1:100 water	0.5	$1.2\,\frac{n}{100}$HCl; $3\,\frac{n}{100}$KOH
Carminic acid	1:100 water	0.5	$0.7\,\frac{n}{100}$HCl; $0.8\,\frac{n}{100}NH_3$; $1.2\,\frac{n}{100}$NaOH
Cochineal....	1:80 water	0.5	$3\,\frac{n}{100}$HCl; $2.8\,\frac{n}{100}$NaOH
Congo red....	1:100, 30%-alcohol	0.1	$0.7\,\frac{n}{100}$HCl; $0.6\,\frac{n}{100}NH_3$; $2.5\,\frac{n}{100}$KOH
Corallin......	1:100 water	0.5	$0.6\,\frac{n}{100}$HCl; $0.8\,\frac{n}{100}NH_3$; $2.8\,\frac{n}{100}$NaOH

H. TROMMSDORFF'S TABLE—*Continued*

Indicators	Strength of Indicator Solution	Cc. of Indicator Solution added to 100 Cc. of titrated Fluid	Cc. of titrating Fluid required
Ethyl orange.	1:400, 30%-alcohol	0.2	3 $\frac{n}{10}$HCl
Fluorescein ..	1:100 alcohol	0.1	Fluorescence neutralized by 0.5 $\frac{n}{10}$HCl
Gallein (commercial)....	1:2 alcohol	0.1	1.2 $\frac{n}{100}$HCl brownish; 1.6 $\frac{n}{100}$$NH_3$ violet. 1.2 $\frac{n}{100}$HCl to last restores color, which is changed again by 0.7 $\frac{n}{100}$KOH
Litmus (purified)........	1:10 water	0.2	0.05 $\frac{n}{10}$HCl; 0.1 $\frac{n}{10}$KOH
Methyl orange	1:200 water	0.05 0.1 0.2	1 $\frac{n}{100}$HCl; restored by 0.9 $\frac{n}{100}$$NH_3$; again acid by 1 $\frac{n}{100}$HCl, and restored by 1 $\frac{n}{100}$KOH; quantity of indicator immaterial
Orange-peel tincture....	1:5 water	1	0.1 $\frac{n}{10}$KOH
Phenacetolin.	1:200 alcohol	0.1 0.2	0.1 $\frac{n}{10}$KOH; with 0.2 Cc. the change is more distinct

H. TROMMSDORFF'S TABLE—*Continued*

Indicators	Strength of Indicator Solution	Cc. of Indicator Solution added to 100 Cc. of titrated Fluid	Cc. of titrating Fluid required
Phenolphtalein........	1:100 alcohol	0.5	0.5 $\frac{n}{100}$KOH necessary for distinct redness
Poirrier blue, C4B........	1:200 water	0.1	0.7 $\frac{n}{100}$KOH colorless when titrated hot; restored by 1.2 $\frac{n}{100}$HCl to violet
Rosolic acid..	1:100, 60%-alcohol	0.5	0.7 $\frac{n}{100}$HCl; 0.8 $\frac{n}{100}$$NH_3$ 4.1 $\frac{n}{100}$KOH
Tropæolin....	1:400, 30%-alcohol	0.2	2.5 $\frac{n}{10}$HCl

R. T. THOMSON'S TABLE, SHOWING THE HYDROGEN ATOMS REPLACED BY NAOH OR KOH WHEN A COMPOUND NEUTRAL TO THE INDICATOR IS FORMED. THE BLANK SPACES INDICATE THAT THE END-REACTION IS OBSCURE

Acid	**Formula**	**Methyl Orange**	**Phenolphtalein**		**Litmus**	
		Cold	Cold	Boiling	Cold	Boiling
Sulphuric	H_2SO_4	2	2	2	2	2
Hydrochloric	HCl	1	1	1	1	1
Nitric	HNO_3	1	1	1	1	1
Thiosulphuric	$H_2S_2O_3$	2	2	2	2	2
Carbonic	H_2CO_3	0	1 dilute	0	—	0
Sulphurous	H_2SO_3	1	2	—	—	—
Hydrosulphuric	H_2S	0	1 dilute	0	—	0
Phosphoric	H_3PO_4	1	2	—	—	—
Arsenic	H_3AsO_4	1	2	—	—	—
Arsenous	H_3AsO_3	4	—	—	0	0
Nitrous	HNO_2	indicator destroyed	1	—	1	—
Silicic	H_4SiO_4	0	—	—	0	0
Boric	H_3BO_3	0	—	—	—	—
Chromic	H_2CrO_4	1	2	2	—	—
Oxalic	$H_2C_2O_4$	—	2	2	2	2
Acetic	$HC_2H_3O_2$	—	1	—	1 nearly	—
Butyric	$HC_4H_7O_2$	—	1	—	1 nearly	—
Succinic	$H_2C_4H_4O_4$	—	2	—	2 nearly	—
Lactic	$HC_3H_5O_3$	—	1	—	1	—
Tartaric	$H_2C_4H_4O_6$	—	2	—	2	—
Citric	$H_3C_6H_5O_7$	—	3	—	—	—

DIETERICH'S TABLE SHOWING SENSITIVENESS OF VARIOUS TEST-PAPERS

Test-papers	SO_3	HCl	KOH	NH_3
Alkanin, Blue	60 000	80 000	——	——
" Red	——	——	25 000	80 000
Brazil Wood	——	——	30 000	80 000
Buckthorn	——	——	15 000	35 000
Cochineal	8 000	10 000	——	——
Congo Red	2 500	3 000	——	——
Curcuma	——	——	18 000	35 000
Elderberry	——	——	5 000	10 000
Georgina	8 000	10 000	8 000	20 000
Hæmatoxylin	——	——	35 000	90 000
Huckleberry	——	——	6 000	15 000
Litmus, Blue	40 000	50 000	——	——
" Red	——	——	20 000	60 000
Phenolphtalein	——	——	20 000	——
Rhubarb	——	——	8 000	20 000
Rosolic Acid	——	——	20 000	90 000
Tropæolin	10 000	15 000	——	——

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$5 00
75
1 50
1 50
2 00
1 50
4 00
2 50
1 00
1 50
3 00

50

00
50
25
00