Pure & Appl. Chem., Vol. 50, pp. 463–498.
Pergamon Press Ltd. 1978. Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ANALYTICAL REACTIONS AND REAGENTS

REDOX INDICATORS. CHARACTERISTICS AND APPLICATIONS

Prepared for publication by

A. HULANICKI and S. GŁAB
Institute of Fundamental Problems in Chemistry,
Warsaw, Poland

PERGAMON PRESS
OXFORD · NEW YORK · PARIS · FRANKFURT

Analytical Chemistry Division

Commission on Analytical Reactions and Reagents[+]

REDOX INDICATORS. CHARACTERISTICS AND APPLICATIONS

Adam Hulanicki and Stanisław Głąb

Institute of Fundamental Problems in Chemistry, University,

02-093 Warsaw, Poland

Abstract - The basic definitions concerning redox indicators and parameters influencing the titration error as well as corresponding equations are presented. According to the proposed scheme the characteristic of 14 mostly used redox indicators is given together with their common applications.

CONTENTS

INTRODUCTION

Visual indicators for titration procedures have been widely used for more than a century. So far, their broad application has not been seriously restricted by the introduction of modern physico-chemical methods of end-point detection; accordingly, they still maintain importance in analytical processes. However, they have been mostly applied on at least a semi-empi-

---

[+] Titular Members: R.Belcher, Chairman (UK), A.Hulanicki, Secretary(Poland) J.Bartos (France), J.Inczedy (Hungary), M.Kapel (UK), F.J.Reidinger (USA), S.Siggia (USA), H.Weisz (FRG); Associate Members: G.Ackermann (GDR), Yu.A. Bankovski (USSR), G.den Boef (Netherlands), N.Jordanov (Bulgaria), E.Lucena-Conde (Spain), F.Pellerin (France), M.Pesez (France), W.I.Stephen (UK); National Representatives: G.Duyckaerts (Belgium), S.B.Savvin (USSR), E. Bishop (UK).

rical basis, partly because of lack of corresponding data and partly because it was often not sufficiently clear which data should be determined for analytical purposes. Even the most comprehensive monographs on indicators, which contain all the available data for a very large number of compounds, do not provide the necessary information completely. It is not an easy matter to select material from this wealth of information especially when little attempt has been made to recommend particular indicators. Strictly speaking it is not the purpose of such monographs to provide such information; their main purpose is to collect together all the available information. Recommendations can only be purely objective when they are the result of the considered opinion of several experiences investigators. Commission V-1 has examined this problem and has attempt to make suitable recommendations for practical analytical work.

The general requirements have been carefully discussed and some aspects have been studied in detail e.g. the titration error . Numerical data have been collected from the original papers and only in the case of very doubtful results has the work been checked experimentally. For practical reasons it was not possible to verify the data for all compounds. It is hoped, however, that this collection of data may stimulate other workers to fill the various gaps.

Some controversy exists concerning the best and representative choice of indicators. The present list is a compromise and certainly some other species might be included, according to personal experiences and even prejudices.

As an example of the present situation the case of diphenylamine can be quoted. It is no longer the best redox indicator, but probably for traditional reasons it is still used and even recommended.

I GENERAL

1. Remarks on the analytical characteristics of redox indicators

The indicator may be classified as reversible when the cycle of reactions in titration operations (reduction followed by oxidation, or oxidation followed by reduction) gives a product identical with the initial one. The potentiometric titration curve should be within the limits of experimental error the same in both directions. A truly reversible indicator should have both forms stable. However in some instances the reversibility depends on the reagents used for oxidation. Examples of such indicators are represented by ferroin and related indicators.

The indicator may be classified as pseudoreversible, when the product from the cycle of reactions (as explained above) is different from the initial one or when one of the forms is unstable and decomposes during titration, but the colour of the product is the same, or nearly the same as that of the initial product, for concentrations used in titration. A example of such indicator is N-phenylanthranilic acid.

The indicator may be classified as irreversible when in the cycle of reactions (as explained above) no reversal to the initial colour is observed. An example of such an indicator is Naphtyl Blue Black.

Several other properties are also useful for characterization of an indicator for analytical purposes.

Formal redox potential, corresponds to the redox potential in solution at which the analytical concentrations of the reduced and oxidized forms of the indicator are equal. This should not depend on the concentration of the indicator, unless the stoichiometric coefficients are not equal. In such instance the formal redox potential should be replaced by half-oxidation potential. The formal redox potential is a function of ionic strength, acidity and its value should be given under the specified conditions, in which it is used in determinations. The formal redox potential should be given at least for the acidity range in which the indicator is applicable. The formal redox potential has a precise meaning only for strictly reversible indicators. In the case of other indicators it should be understood as the potential for half-oxidized indicator. Because of difficulties of determination corresponding activity coefficient the rigorous definition for formal redox potential based on activities is never used in practice.

Because of difficulties concerning the rigorous definition for formal redox potential a more practical term used in this report in parallel is **half-oxidation potential**.

Transition potential is often given instead of the formal redox potential. It corresponds to the colour change (its appearance or disappearance) at which the end-point is said to occur. It is a function of the formal redox potential, the total concentration of the indicator, (especially for one colour indicator), the depth of the colour layer, the minimal observable absorbance (which depends on wavelength and eye sensitivity) and the absorptivity. In an ideal two-colour indicator the "apparent absorptivities" of both forms should be equal and then the transition potential approaches the formal one. This is never the case in one-colour indicator. As for formal redox potential it should be given at least for the acidity range of indicator application. The transition potential may be given for pseudoreversible indicators. Because the transition point is usually different for oxidimetric and reductiometric titrations it is sometimes useful to distinguish those two values. In general in oxidimetric titrations the transition potential is more positive, than that for reductimetric titrations. This is due to addition of an excess of the titrant, which is necessary to change distinctly the colour of the indicator. For pseudoreversible indicators the irreversibility of the chemical reaction is another reason for differentiation of both potential values.

For the sake of uniformity with other types of reactions several authors, instead of potential, use in redox reactions the value of $pe=E(2.3RT/F)^{-1}$. Thus in standard conditions (25°C) pe=16.9 E (when E expressed in volts).

Protolytic reactions characteristics (acid dissociation constants) of the indicator for both reduced and oxidized form are useful guides in considering the dependence of the potentials on pH value. The protonation of the oxidized form is sometimes difficult (or impossible) to evaluate because of its instability. This may not be the case for some several reversible indicators.

Spectral characteristics of an indicator are important e.g. the position of the absorbance maximum, the stability of the spectrum (constancy of absorbance with time) expressed as the half-life time of the absorbance decay at the maximum, the effect of acidity and the presence of differently coloured intermediate or back-reaction products. The half-life time depends on the nature of the oxidant, its amount and probably the presence of contaminants. The colour of the indicator solution obtained through reduction of the initially oxidized sample should be also mentioned (indicated as RERED).

Reaction mechanism, (in so far as it gives analytically useful information). Useful analytical information includes the intermediate steps in the oxidation or reduction, decomposition of the reaction product with time, the number of electrons consumed (or formed) per one mole of indicator. Such data are useful in predicting applications of the indicator, factors influencing its blank value etc.

In addition of the properties which are useful in characterizing the indicator for analytical purposes the following informations are of practical importance.

Purity of indicator sample, especially when it influences directly the practical utility of the indicator. The way of testing purity.

Preparation of indicator solutions, i.e. the solvent, desirable and practically useful concentration, the stability of such solutions (effect of oxygen, light etc.) .

The manner of use, of the indicator: amount of solution for best colour change, the special conditions in which it works properly (e.g. temperature, pH range).

The systems in which the indicator has been used successfully.

2. Indicator error in redox titrations

The indicator error in redox titrations is due to the following factors which influence the accuracy of determination:

The end-point error - the systematic error occuring because under given conditions of titration the equivalence point potential differs from the end-point potential. The equivalence point potential depends on the formal potentials of the analyte and titrant and the number of electrons participating in half-reactions. The end-point potential is the function of the indicator, the absorptivities of both indicator forms, its concentrations (especially but not exclusively for one-colour indicators), solution layer depth and the ability of the analyst's eye to observe the colour appearance or change. When the transition potential, corresponding to the end-point, is close to the equivalence point potential the effect of above mentioned factors may be diminished.

The indicator consumption error - the systematic error occuring because of the finite consumption of the oxidant during oxidation of the indicator. This amount is easily determined for two-colour reversible indicators - being in those instances strictly proportional to the amount of indicator. This is not the case with irreversible or even pseudoreversible indicators which form intermediate products, or the oxidized form is unstable and undergoes slow decomposition. In such cases the electrons lost by the indicator at local oxidant excesses will be not fully back-consumed under the action of untitrated reductant. With those indicators the correction is always greater than for reversible indicators and depends on factors which are not readily evaluated. These are:

- the mechanism and rate of indicator oxidation
- the rate of oxidant consumption by the analyte
- the manner of oxidant addition (increments, rate)
- the efficiency of stirring during titration.

The effect of mechanism has been mentioned, and it is obvious that when the rate of indicator oxidation is small compared to that of the analyte, the error due to irreversible electron loss is smaller. The addition of the titrant in infinitely small increments at a sufficiently low rate with good stirring could probably eliminate or lower this undesirable effect. The detailed mathematical treatment of the end-point error and indicator consumption error are given in the Appendix. The final conclusions from these considerations are those that it is not possible to give the value of indicator correction without precise description of titration conditions: the formal potentials of titrant and analyte the transition potential of the indicator and the concentration of the indicator used. Because of the nonlinearity of this correction with indicator concentration it is in general not possible to include in the indicator characteristics even the approximate value of the correction. The experimental determination of this correction should not be performed by a blank titration in the absence of analyte. The only correct way is to compare titration with a standard sample or with titration with a potentiometric end-point detection, performed in identical conditions.

APPENDIX

Expressions for the end-point error

The half-reaction of the analyte

$$\mathrm{Ox_X} + n_X e = \mathrm{Red_X}$$

and the half-reaction of the titrant

$$\mathrm{Ox_T} + n_T e = \mathrm{Red_T}$$

give the reaction equations for oxidimetric titration:

$$n_T\mathrm{Red_X} + n_X\mathrm{Ox_T} = n_T\mathrm{Ox_X} + n_X\mathrm{Red_T}$$

and for reductimetric titration:

$$n_T\mathrm{Ox_X} + n_X\mathrm{Red_T} = n_T\mathrm{Red_X} + n_X\mathrm{Ox_T}$$

which enable the derivation of a general equation (Ref. 1,2) for the end-point error ΔV_T, expressed in the volume units of the titrant:

$$\Delta V_T = \frac{C_X V_X n_X}{C_T n_T}\left[10^{\frac{n_T(E-E_T^o)}{0.06}} - 10^{\frac{n_X(E-E_X^o)}{0.06}}\right]\left[1 + 10^{\frac{n_X(E-E_X^o)}{0.06}}\right]^{-1} \quad (1)$$

This equation is valid for both indicated reactions, when the number of electrons of half-reactions indicated above, is taken with the sign preceding when written in the direction of the reaction actually occuring.

The remaining symbols in this equation are:

C_X, C_T - molar concentrations of the analyte and titrant, respectively
V_X, V_T - volumes of the analyte and titrant up to the end-point, respectively
E - the end-point potential
E_X^o, E_T^o - the formal potentials of the analyte and titrant, respectively

The equation (1) may be transformed giving the relative end-point error:

$$\frac{\Delta V_T}{V_T} = \left[10^{\frac{n_T(E-E_T^o)}{0.06}} - 10^{\frac{n_X(E-E_X^o)}{0.06}}\right]\left[1 + 10^{\frac{n_X(E-E_X^o)}{0.06}}\right]^{-1} \quad (2)$$

The expression for the absolute and relative end-point error are valid only when for the titrant as well as for the analyte no association occurs. This means that in half-reactions the stoichiometric coefficients should be equal one. Among the rather rare exceptions are dichromate and hydrogen peroxide.

The characteristics of the redox indicator is in those equations included in the value of the end-point potential E, which is usually assumed to be equal to the transition potential of the indicator.

The end-point potential corresponding to the transition potential of the indicator is connected with the physicochemical characteristics of the system:

E_I^o - formal potential of the indicator
n_I - number of electrons in the equation of redox reaction of the indicator
a, b - stoichiometric coefficients at the oxidized and reduced form in the oxidation reaction of the indicator, respectively
ε_R, ε_O - molar absorptivities of the reduced and oxidized form of the indicator
C_I - total concentration of the indicator at the end-point
A - minimal visible absorbance of the one-colour indicator solution at the solution layer
A' - maximal already invisible absorbance of the one-colour indicator solution, which may be attributed to disappearance of the colour
M - for two-colour indicator is the ratio of absorbances of the oxidized to the reduced form, which corresponds to the transition point in oxidimetric titrations. Often it is assumed as equal to 10.
N - for the two-colour indicator is the ratio of absorbances of the reduced to oxidized form, which corresponds to the transition point in reductometric titrations. Often it is assumed as equal to 10.
l - solution layer thickness

Using those characteristics the equations can be derived which define the transition potential (Ref. 3). They are summarized in Table 1 and 2 for different examples of indicators. However it must be pointed out that this is to some extent approximate and subject to personal differences.

TABLE 1. The transition potentials for oxidimetric titrations

Indicator	General equation	Simplified equation for a=b=1
One-colour Ox-coloured added as Red.	$E=E_I^o+\frac{0.06}{n_I}\log\frac{a^bA^a(l\varepsilon_0)^{b-a}}{(alC_I\varepsilon_0-bA)^b}$	$E=E_I^o+\frac{0.06}{n_I}\log\frac{A}{lC_I\varepsilon_0-A}$
One-colour Ox-coloured added as Ox.	$E=E_I^o+\frac{0.06}{n_I}\log\frac{a^bA^a(l\varepsilon_0)^{b-a}}{b^b(lC_I\varepsilon_0-A)^b}$	
one-colour Red-coloured added as Red	$E=E_I^o+\frac{0.06}{n_I}\log\frac{a^a(lC_I\varepsilon_R-A')^a}{b^a(A')^b(l\varepsilon_R)^{a-b}}$	$E=E_I^o+\frac{0.06}{n_I}\log\frac{lC_I\varepsilon_R-A'}{A'}$
One-colour Red-coloured added as Ox	$E=E_I^o+\frac{0.06}{n_I}\log\frac{(blC_I\varepsilon_R-aA')^a}{b^a(A')^b(l\varepsilon_R)^{a-b}}$	
Two-colour added as Red	$E=E_I^o+\frac{0.06}{n_I}\log\frac{\varepsilon_R^a(aC_I)^{a-b}M^a}{\varepsilon_0^b(a\varepsilon_0+bM\varepsilon_R)^{a-b}}$	$E=E_I^o+\frac{0.06}{n_I}\log\frac{\varepsilon_R M}{\varepsilon_0}$
Two-colour added as Ox	$E=E_I^o+\frac{0.06}{n_I}\log\frac{\varepsilon_R^a(bC_I)^{a-b}M^a}{\varepsilon_0^b(a\varepsilon_0+bM\varepsilon_R)^{a-b}}$	

The practical application of the equation (2) for the relative end-point error is significantly improved when a diagram is used, shown in Fig. 1. On the coordinate axis are plotted expressions: $n_T(E-E_T^o)/0.06$ and $n_X(E-E_X^o)/0.06$

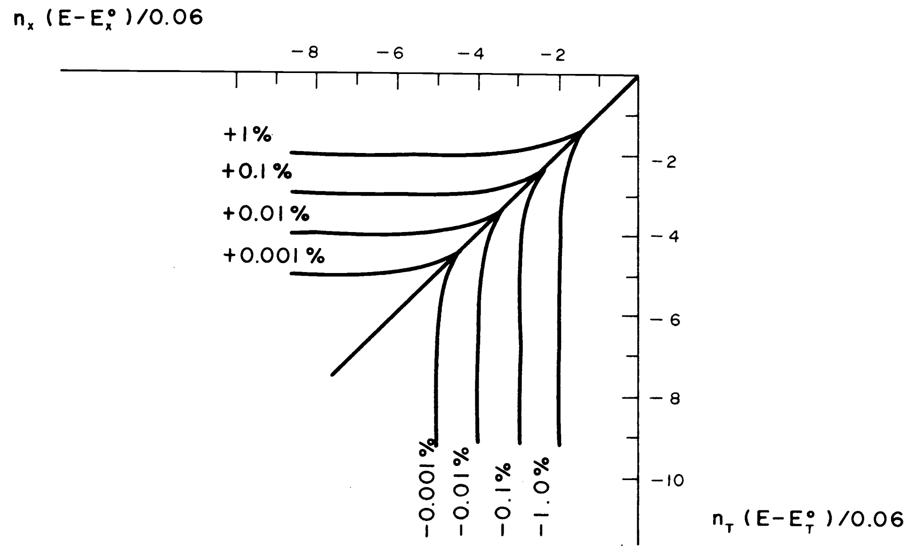


Fig. 1. The diagram indicating the dependence of systematic error of end-point in redox titrations on the potential values of the systems

TABLE 2. The transition potentials for reductimetric titrations

Indicator	General equation	Simplified equation for a=b=1
One-colour Ox-coloured added as Red.	$E=E_I^o + \frac{0.06}{n_I} \log \frac{a^b(A')^a(1\varepsilon_0)^{b-a}}{(a1C_I\varepsilon_0-bA')^b}$	$E=E_I^o + \frac{0.06}{n_I} \log \frac{A'}{1C_I\varepsilon_0-A'}$,
One-colour Ox-coloured added as Ox.	$E=E_I^o + \frac{0.06}{n_I} \log \frac{a^b(A')^a(1\varepsilon_0)^{b-a}}{(b1C_I\varepsilon_0-bA')^b}$	
One-colour Red-coloured added as Red.	$E=E_I^o + \frac{0.06}{n_I} \log \frac{(a1C_I\varepsilon_R-aA)^a(1\varepsilon_R)^{b-a}}{b^aA^b}$	$E=E_I^o + \frac{0.06}{n_I} \log \frac{1C_I\varepsilon_R-A}{A}$
One-colour Red-coloured added as Ox.	$E=E_I^o + \frac{0.06}{n_I} \log \frac{(b1C_I\varepsilon_R-aA)^a}{b^aA^b(1\varepsilon_R)^{a-b}}$	
Two-colour added as Red.	$E=E_I^o + \frac{0.06}{n_I} \log \frac{\varepsilon_R^a(aC_I)^{a-b}}{\varepsilon_0^b(b\varepsilon_R+aN\varepsilon_0)^{a-b}N^b}$	$E=E_I^o + \frac{0.06}{n_I} \log \frac{\varepsilon_R}{\varepsilon_0 N}$
Two-colour added as Ox	$E=E_I^o + \frac{0.06}{n_I} \log \frac{\varepsilon_R^a(bC_I)^{a-b}}{\varepsilon_0^b(b\varepsilon_R+aN\varepsilon_0)^{a-b}N^b}$	

which depend on the titrant and analyte, respectively. A definite combination of those expressions describes the value of the systematic error of a given titration. When both expressions are smaller than -3 the relative error is always smaller than 0.1%. When at least on one of axis the value is greater than -3, then the largest value defines the error.

The following examples may clarify the principle:
Example 1: Which value should have the formal redox potential of the analyte system for vanadium V as a titrant, N-phenylanthranilic acid or diphenylamine sulphonic acid being used as indicators?

For N-phenylanthranilic acid in 2M H_2SO_4 E=0.88 V and for the titrant E_T^o= =1.143 V, thus $n_T(E-E_T^o)/0.06=-4.7$ being not a decisive factor for the error magnitude. Therefore because $n_X(E-E_X^o)/0.06$ should not be greater than -3, i.e. $E_X^o \leq +0.70$ V.

This corresponds for example to iron(II) in slightly complexing solution, e.g. in sulphuric acid.

For diphenylamine sulphonic acid in 0.5M H_2SO_4 E=0.82 V and for the titrant E_T^o=1.00 V, thus $n_T(E-E_T^o)/0.06=-3.0$ and to keep the error at the level 0.1% the value of $n_X(E-E_X^o)/0.06 \leq -3.0$ i.e. $E_X^o \leq 0.64$ V.

This value needs some additional complexation of iron as analyte, therefore usually phosphoric acid is added to the sample.

Example 2: When $n_T=n_X=1$, and E_T^o=0.9 V, E_X^o=0.12 V in which range should lie the end-point? Let us assume, with some extra safety, that error should be included in the range ±0.01%.

From the titrant condition $n_T(E-E^o_T)/0.06 \leqslant -4$, thus $E \leqslant 0.66$ V.

From the analyte condition $n_X(E-E^o_X)/0.06 \leqslant -4$, thus $E \geqslant 0.36$ V so finally $0.36\ \mathrm{V} < E < 0.66\ \mathrm{V}$.

Expressions for the reagent consumption error (Ref. 4)

The value of the reagent consumption error depends for reversible indicators on the spectrophotometric characteristics of the indicator and on the form in which it is added to the solution: it can be added in the same form as the titrant or in the form of analyte. Therefore for oxidimetric and reductimetric titration exist six different cases: four - for one-colour indicators, two - for two-colour indicators. The expressions are given in Table 3 and Table 4. It should be noted that in some instances the error is always positive, in others - always negative, whereas in remaining - the sign depends on the relative values of indicator concentration and a term which depends on the absorption parameters. In those tables the meaning of parameters is the same as in Tables 1 and 2, except of

$$B= \frac{(V_T+V_X)\,n_I}{C_T n_T} \qquad (3)$$

For pseudoreversible, and so more for irreversible, this correction cannot be estimated precisely. It depends in a great extend on the kinetics of reaction of the indicator and technical parameters of titration (rate of titrant addition, mixing, addition of the indicator at the beginning of titration or close before the end-point etc.).

TABLE 3. The reagent consumption error for oxidimetric titrations

Indicator	General equation	Simplified equation for a=b=1
One-colour Ox-coloured added as Red.	$\Delta V_I= \frac{BA}{al\,\varepsilon_O}$	$\Delta V_I= \frac{BA}{l\,\varepsilon_O}$
One-colour Ox-coloured added as Ox.	$\Delta V_I= \frac{B}{a}\left(\frac{A}{l\,\varepsilon_O} - C_I\right)$	$\Delta V_I= B\left(\frac{A}{l\,\varepsilon_O} - C_I\right)$
One-colour Red-coloured added as Red.	$\Delta V_I= \frac{B}{b}\left(C_I - \frac{A'}{l\,\varepsilon_R}\right)$	$\Delta V_I= B\left(C_I - \frac{A'}{l\,\varepsilon_R}\right)$
One-colour Red-coloured added as Ox.	$\Delta V_I= - \frac{BA'}{bl\,\varepsilon_R}$	$\Delta V_I= - \frac{BA'}{l\,\varepsilon_R}$
Two-colour added as Red.	$\Delta V_I= \frac{BM\,\varepsilon_R C_I}{a\,\varepsilon_O+bM}$	$\Delta V_I= \frac{BM\,\varepsilon_R C_I}{\varepsilon_O+M\varepsilon_R}$
Two-colour added as Ox.	$\Delta V_I= \frac{B}{a}\left(\frac{bM\,\varepsilon_R C_I}{a\,\varepsilon_O+b\,M\varepsilon_R} - C_I\right)$	$\Delta V_I= B\left(\frac{M\,\varepsilon_R C_I}{\varepsilon_O+M\varepsilon_R} - C_I\right)$

TABLE 4. The reagent consumption error for reductimetric titrations

Indicator	General equation	Simplified equation for a=b=1
One-colour Ox-coloured added as Red.	$\Delta V_I = -\frac{BA'}{al\varepsilon_0}$	$\Delta V_I = -\frac{BA'}{l\varepsilon_0}$
One-colour Ox-coloured added as Ox.	$\Delta V_I = \frac{B}{a}\left(C_I - \frac{A'}{l\varepsilon_0}\right)$	$\Delta V_I = B\left(C_I - \frac{A'}{l\varepsilon_0}\right)$
One-colour Red-coloured added as Red.	$\Delta V_I = \frac{B}{b}\left(\frac{A}{l\varepsilon_R} - C_I\right)$	$\Delta V_I = B\left(\frac{A}{l\varepsilon_R} - C_I\right)$
One-colour Red-coloured added as Ox.	$\Delta V_I = B\left(\frac{B}{b}\,\frac{A}{l\varepsilon_R}\right)$	$\Delta V_I = \frac{BA}{l\varepsilon_R}$
Two-colour added as Red.	$\Delta V_I = \frac{B}{b}\left(\frac{aN\varepsilon_0 C_I}{b\varepsilon_R + aN\varepsilon_0} - C_I\right.$	$\Delta V_I = B\left(\frac{N\varepsilon_0 C_I}{\varepsilon_R + N\varepsilon_0} - C_I\right)$
Two-colour added as Ox.	$\Delta V_I = \frac{BN\varepsilon_0 C_I}{b\varepsilon_R + aN\varepsilon_0}$	$\Delta V_I = \frac{BN\varepsilon_0 C_I}{\varepsilon_R + N\varepsilon_0}$

REFERENCES

1. U. A. Th. Brinkman, Anal. Chim. Acta, 45, 411 (1969).
2. E. Bishop, Indicators, Pergamon Press, Oxford, (1972).
3. E. Bishop, Analyst, 96, 537 (1971).
4. A.Hulanicki and S. Głąb, Talanta 22, 363 (1975).

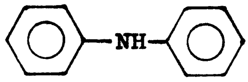
INDICATOR CHARACTERISTICS

This part contains the detailed analytical characteristics of redox indicators used in redox titrations, or titrations in which a redox indicator system is exploited. The informations are given according to the directions formulated in the general part.

Indicators No 1 - 9 are the diphenylamine and benzidine derivatives, No 10 - belongs to thiazines, No 11 - 14 are diimine chelates.

Note: Several authors claim that some of the indicators presented in this list may be considered as carcinogenic. This is most probable in the case of secondary amines, e.g. diphenylamine or diphenylbenzidine derivatives.

1. DIPHENYLAMINE



Free base

Pseudoreversible indicator RED: colourless
OX : violet
RERED: pale greenish

Transition potential (Ref. 1) for indicator conc. ~$5x10^{-5}$M:

For oxidimetric titrations: in 0.5M H_2SO_4 0.76 V

The value was obtained in titration of Fe^{2+} with $Cr_2O_7^{2-}$.

Formal half-oxidation potential for indicator conc. $5x10^{-4}$M:

in 1.5 - 9.0M H_2SO_4 0.766 V (Ref. 2) 0.76 V (Refs. 3,4)

Protolytic reactions

For reduced form: for $=NH_2^+$ pK_a = 0.78 spectrophot. (Ref. 2)
0.76 spectrophot. (Ref. 4)
0.79 spectrophot. (Ref. 5)

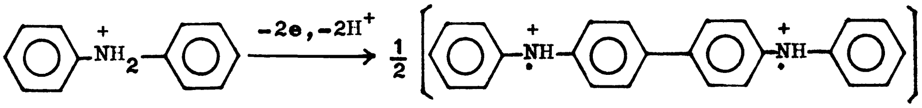
Spectrophotometric characteristics:

Initial reduced form - no absorption in VIS
Oxidized form: λ_{max} = 565 nm (violet), λ_{max} = $2.25x10^4$ in 2M H_2SO_4(Ref. 6)
calculated for molarity of the reduced form.

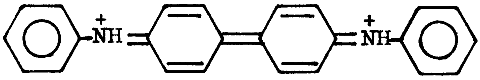
Half-life time (without excess of oxidant) 188 min in 2M H_2SO_4 (Ref. 6).
The colour is more stable in more strongly acid solutions.

Reaction mechanism:

The following mechanism, in aqueous solutions of H_2SO_4 has been suggested (Ref. 6)



The number of electrons involved has been confirmed by spectrophotometry (Refs. 2,6) and potentiometry (Ref. 2). The decomposition of the oxidized form proceeds through



Purity of indicator. Long storage may result contamination with oxidation products. The indicator should be crystallized e.g. from toluene. Also purification is achieved when the solution in conc. H_2SO_4 is diluted and crystallized in the CO_2 atmosphere (Ref. 6).

Indicator addition may be achieved using 1% solution in conc. H_2SO_4, not containing NO_3^-, in amount about 3 drops.

Condition of titrations. Usually titration can be done in 1-4M H_2SO_4 or HCl, at room temperature.

Table of applications

Titrant	Analyte	Remarks	Ref.
Chromium(VI)	Fe(II)	1-2M H_2SO_4 in presence of H_3PO_4	1
Vanadium(V)	Fe(II)	0.5-1M H_2SO_4 in presence of H_3PO_4	7
	Mo(V)	2-3M HCl	8
Tin(II)	Cr(VI), V(V)	3-3.5M HCl in carbon dioxide atmosphere	9

Table of applications Cont.

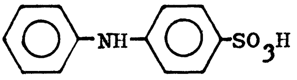
Titrant	Analyte	Remarks	Ref.
Arsenic (III)	Cr (VI)	1-2M H_2SO_4	10
Iodine (VII)	Sb (III), As (III)	0.05M H_2SO_4	11, 12
	Fe (II)	0.5M H_2SO_4	

This indicator has been included for historical reasons. Now is largely replaced by e.g. diphenylamine sulphonic acid.

REFERENCES

1. D. Stockdale, Analyst 75, 150 (1950).
2. A. Hulanicki and S. Głąb - unpublished data.
3. I. M. Kolthoff and A. Sarver, J. Amer. Chem. Soc. 52, 4179 (1930).
4. N. S. Frumina and E. G. Tregub, Zh. anal. Khim. 26, 669 (1971).
5. M. A. Paul and F. A. Long, J. Amer. Chem. Soc. 76, 3236 (1954).
6. E. Bishop and L. G. Hartshorn, Analyst 96, 26 (1971).
7. G. G. Rao, G. Aravamudan and N. C. Venkatamma, Z. analyt. Chem. 146, 161 (1955).
8. R. Lang and S. Gottlieb, Z. analyt. Chem. 104, 1 (1936).
9. Z. G. Szabó and E. Sugár, Anal. Chim. Acta 6, 293 (1952).
10. Z. G. Szabó and L. Csányi, Anal. Chem. 21, 1144 (1949).
11. V. S. Syrokomskii and S. I. Melamed, Zavods. Lab. 16, 131 (1950).
12. V. S. Syrokomskii and S. I. Melamed, Zavods. Lab. 16, 273 (1950).

2. DIPHENYLAMINE-4-SULPHONIC ACID



as a sodium or barium salt

Pseudoreversible indicator

RED: **colourless**
OX : **red-violet**
RERED: **pale greenish**

Transition potential in H_2SO_4 for indicator conc. $\sim 10^{-5}$M

For oxidimetric titrations:

0.1M	0.81 V (Ref. 1)	0.853 V (Ref. 2)
0.5M	0.85 V (Ref. 1)	0.82 V (Ref. 2)
1.0M	0.83 V (Refs. 1,2,3)	
2.0M	0.80 V (Refs. 1,2)	
4.0M	0.77 V (Ref. 1)	0.75 V (Ref. 2)
8.0M	0.71 V (Ref. 1)	

The values were obtained in titration of Fe^{2+} with $Cr_2O_7^{2-}$.

Formal (half-oxidation) potential for indicator conc. $\sim 10^{-5}$M.

in 1M H_2SO_4	0.85 V (Ref. 4)
in 0.4-2.5M H_2SO_4	0.81 V (Ref. 5)

Protolytic reactions

For reduced form: for	$=NH_2^+$	$pK_a = -1.23$	spectrophot.	(Ref. 6)
		-1.08	spectrophot.	(Ref. 5)
for	$-SO_3H$	$pK_a = 2.48$	potentiometric	(Ref. 5)

Spectrophotometric characteristics:

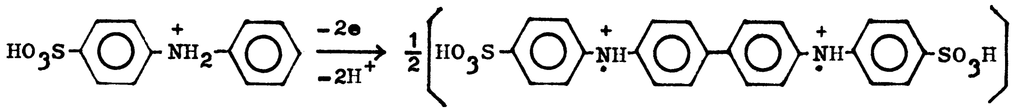
Initial reduced form - no absorption in VIS
Oxidized form (Ref. 5) - $\lambda_{max} = 585$ nm, $\varepsilon_{max} = 7.9 \times 10^3$ in 1M H_2SO_4
$\varepsilon_{max} = 8.7 \times 10^3$ in 2M H_2SO_4
$\varepsilon_{max} = 12.7 \times 10^3$ in 4M H_2SO_4

calculated for molar concentration of the reduced form.

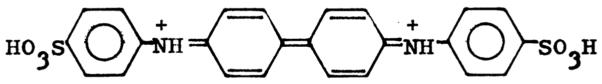
Half-life time (indicator solution and stoichiometric amount of oxidant) in 1M H_2SO_4 - 13 min ; in 2M H_2SO_4 - 30 min ; in 4M H_2SO_4 - 220 min.

Reaction mechanism.

The following one two-electron step reaction has been suggested (Ref. 7):



The decomposition of the oxidized form proceeds through the quinoid from:



Purity of indicator. The salt after prolonged storage in the presence of oxygen may be partially oxidized. Purification is carried out by crystallization from dilute H_2SO_4 in CO_2 atmosphere (Ref. 5).

Indicator solution is used as 0.2% aqueous solution of the salt (Ref. 8). For titration 7-10 drops are sufficient.

Conditions of titrations. Usually in not very concentrated (0.25 - 2.0M) sulphuric acid solutions.

Table of applications

Titrant	Analyte	Remarks	Ref.
Dichromate	Fe(II)	0.5-1.75M H_2SO_4 in presence of H_3PO_4	9, 10
		indirect determination of Cu^+, after addition of excess of Fe(III)	11
		indirect determination of ClO_3^- after addition of excess of Fe(II)	12
Vanadium(V)	Fe(II)	0.25-0.5M H_2SO_4 in presence of H_3PO_4	13

Recommended for titration of iron(II) in presence of iron(III) complexing agent, with dichromate or vanadate as titrants.

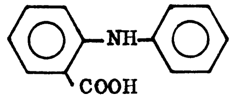
REFERENCES

1. R. Belcher, A. J. Nutten and W. I. Stephen, J. Chem. Soc. 3857 (1952).
2. D. I. Rees and W. I. Stephen, Talanta 2, 361 (1959).
3. D. Stockdale, Analyst 75, 150 (1950).
4. L. A. Sarver and I. M. Kolthoff, J. Am. Chem. Soc. 53, 2902 (1931).
5. A. Hulanicki and S. Głąb - unpublished data
6. N. S. Frumina and E. G. Tregub, Zh. analyt. Khim. 26, 669 (1971).
7. E. Bishop, Indicators, Pergamon Press, Oxford, 1972
8. I. M. Kolthoff and R. Belcher, Volumetric Analysis, Interscience, New York, 1957.
9. L. A. Sarver and I. M. Kolthoff, J. Am. Chem. Soc. 53, 2906 (1931).
10. I. Tsubaki, Bunseki Kagaku, 3, 253 (1954).

11. L. F. Hatch and R. R. Estes, Ind. Eng. Chem. Anal. Ed. 18, 136 (1946).
12. A. J. Boyle, V. V. Hughey and C. C. Casto, Ind. Eng. Chem. Anal. Ed. 16, 370 (1944).
13. G. G. Rao, G. Aravamudan and N. C. Venkatamma, Z. analyt. Chem. 146, 161 (1955).

3. N-PHENYLANTHRANILIC ACID

2-carboxy-diphenylamine



Free acid

Pseudoreversible indicator

RED: colourless
OX : purple
RERED: pale greenish

Transition potential in H_2SO_4 for indicator conc. $\sim 10^{-5}$M

For oxidimetric titrations:

1M	0.89 V (Ref. 1)
1.5M	0.89 V (Ref. 1); 0.88 V (Refs. 2,3)
	0.90 V (Ref. 4)
	1.01 V (Ref. 5); 1.08 V (Ref. 6)-unrealiable values
2M	0.885 V (Ref. 1)
3M	0.87 V (Ref. 1)

The values were obtained in titration of Fe^{2+} with $Cr_2O_7^{2-}$.

Formal (half-oxidation) potential in H_2SO_4 for indicator conc. 5×10^{-5}M (Ref. 3)

3.0M - 0.91 V
4.0M - 0.89 V
4.9M - 0.87 V
5.4M - 0.865 V
6.0M - 0.865 V
7.5-12M - 0.85 V

Protolytic reactions:

For reduced form: for $=NH_2^+$	pK_a =	-1.41	spectrophot.	(Ref. 4)
		-1.31	spectrophot.	(Ref. 3)
		-1.28	solubil.	(Ref. 7)
		-1.35	spectrophot.	(Ref. 7)
for -COOH	pK_a =	3.94	spectrophot.	(Ref. 3)
		3.86	solubil.	(Ref. 7)
		3.99	spectrophot.	(Ref. 7)

Spectrophotometric characteristics:

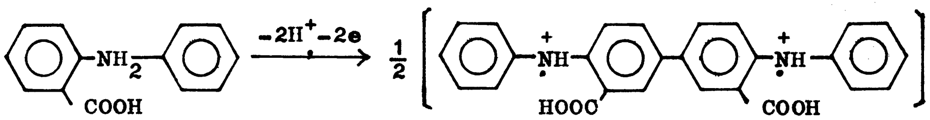
Initial reduced form - no absorption in VIS
Oxidized form (Refs. 3,8) λ_{max}= 525 nm, $\varepsilon_{max}= 8.7\times10^3$ in 0.5M H_2SO_4
$\varepsilon_{max}= 1.45\times10^4$ in 1M H_2SO_4
$\varepsilon_{max}= 2.1\times10^4$ in 4M H_2SO_4

Re-reduced form (Refs. 1,3,8) λ_{max}= 434 nm, $\varepsilon_{max}=1.2\times10^4$ in 2-12M H_2SO_4 calculated for molarity of the reduced form.

Half-life time (Refs. 3,8) (indicator solution and stoichiometric amount of oxidant) in 0.5M H_2SO_4 - 5 min ; in 1M H_2SO_4 - 7 min ; in 2M H_2SO_4 - 10 min; in 4M H_2SO_4 - 15 min. The solution is more stable for higher concentrations of H_2SO_4.

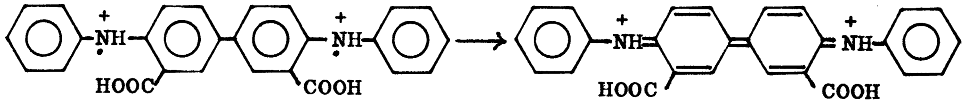
Reaction mechanism:

The following mechanism which includes one two-electron step has been confirmed by potentiometry, spectrophotometry and ESR (Refs. 3,8).



The intermediate has not been confirmed in aqueous solutions.

The decomposition of OX goes through the reaction



Parallel to this mechanism isometric compounds may be formed due to various points of attack in the first oxidation step.

Purity of indicator - The commercial samples when stored for a long time may be contaminated by oxidation products. Purification (Ref. 8) is based on crystallization of the acid from diluted H_2SO_4 in the atmosphere of CO_2.

Indicator solution may be prepared as 0.1% solution in 0.005M NaOH (Ref. 2). The 0.1% solution in equimolar solution of Na_2CO_3 (Ref. 6) is said to be less stable (Ref. 9). For titration 3-5 drops of solution are sufficient.

Conditions of titration. Usually in 1.5-6M H_2SO_4 at room temperature.

Table of applications

Titrant	Analyte	Remarks	Ref.
Cerium(IV)	Fe(II)	in 4M H_2SO_4	2
		also used for indirect determination of Tl(I), Pd(II) and Ag(I) through dissolution of reduced metal in excess Fe(III)	10,11 12
	$Fe(CN)_6^{4-}$	in 1-2M H_2SO_4	2
		also used for indirect determination of Au(III), Pt(IV), Ir(III), Co(III), Zn(II)	10,11 14,15 16
Chromium(VI)	Fe(II)	in 2-4M H_2SO_4	2
	U(IV)	in 2-2.5M H_2SO_4	13
Vanadium(V)	Fe(II)	in 2-6M H_2SO_4	17
	U(IV)	in 2M H_2SO_4	18
	Mo(V)	in 1-1.5M H_2SO_4	19
Iron(II)[x]	Cr(VI)	in 2-4M H_2SO_4	2
Vanadium(III)[x]	Cr(VI)	in 2-4M H_2SO_4	20
	V(V)	indirect determination of sulphite, hypophosphite and phosphite	21

[x] Reductimetric titrations with this indicator owing to its instability are in general not recommended.

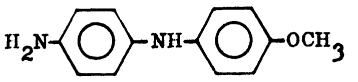
Recommended for titrations of iron(II) and $Fe(CN)_6^{4-}$, with cerium(IV) as titrant.

REFERENCES

1. K. Sriramam, Talanta 20, 383 (1973).
2. R. Belcher, D. I. Rees and W. I. Stephen, Chim. analyt. 41, 397(1959).
3. A. Hulanicki and S. Głąb - unpublished data.
4. N. S. Frumina and E. G. Tregub, Zh. analyt. Khim. 26, 669 (1971).
5. M. Lederer and F. L. Ward, Anal. Chim. Acta 6, 1 (1952).
6. V. S. Syrokomskii and V. V. Stiepin, J. Amer. Chem. Soc. 58, 928 (1936).
7. N. S. Frumina, K. G. Petrikova, E. G. Tregub and S. V. Pletnev, Zh. analyt. Khim. 25, 434 (1970).
8. E. Bishop and L. G. Hartshorn, Analyst 96, 26 (1971).
9. E. Bishop and A. B. Crafford, Analyst 74, 365 (1949).
10. O. C. Saxena, Mikrochim. Acta 719 (1968).
11. O. C. Saxena, Talanta 13, 862 (1966).
12. V. C. Gupta and S. C. Tivari, Chim. Analyt. 49, 372 (1967).
13. V. P. Rao, B. V. S. R. Murty and G. G. Rao, Z. analyt. Chem. 147, 99 (1955).
14. O. C. Saxena, Indian J. Appl. Chem. 30, 33 (1967).
15. O. C. Saxena, Microchem. J. 13, 120 (1968).
16. V. S. Negibin, A. J. Synch and A. P. Irosheva, Trudy Inst. Metalurg. AN SSSR 14, 259 (1963).
17. V. S. Syrokomskii and L. J. Antropov, Zavods. Lab. 9, 161 (1940).
18. V. P. Rao, B. V. S. R. Murty and G. G. Rao, Z. analyt. Chem. 147, 161 (1955).
19. I. M. Kolthoff and R. Belcher, "Volumetric Analysis" Vol. 3, Interscience 1957.
20. K. B. Rao and G. G. Rao, Anal. Chim. Acta 13, 313 (1955).
21. G. G. Rao and M. S. Gowda, Z. analyt. Chem. 146, 167 (1955).

4. VARIAMINE BLUE

4-amino-4'-methoxy-diphenylamine



Free base or as chloride, sulphate, acetate

Reversible indicators: RED: colourless
OX : violet blue

Transition potential for oxidimetric titrations

	pH 2	0.575 V (Ref. 1)
For indicator conc. 10^{-4}M	pH 2.1	0.55 V (Ref. 2)
For indicator conc. 3.5×10^{-4}M	pH 2.1	0.54 V (Ref. 2)

The values were obtained in titration of Fe^{2+} with vanadate.

Formal (half-oxidation) potential (Ref. 1)

pH 2	0.60 V
pH 4	0.48 V
pH 6	0.37 V

Protolytic reactions:

For initial reduced form:	for $=NH_2^+$	$pK_a = 0.13$	spectrophot. (Ref. 3)
	for $-NH_3^+$	$pK_a = 5.9$	spectrophot. (Ref. 4)
For oxidized form:	for $=NH_2^+$	$pK_a = 6.6$	spectrophot. (Ref. 4)

Spectrophotometric characteristics:

Initial reduced form - no absorption in VIS
Oxidized form: for the oxidant : indicator ratio 1:1

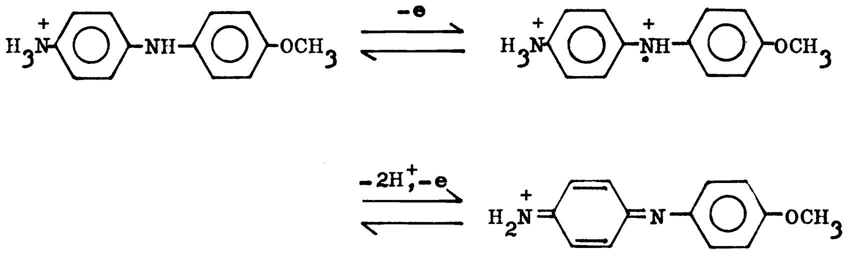
λ_{max} = 570-575 nm (violet blue), $\varepsilon_{max} = 6.7\times10^3$; pH 2-6(Refs.1,5)

for the oxidant:indicator ratio 2:1 (and more)

λ_{max} = 530 nm (violet red), $\varepsilon_{max} = 7\times10^3$; pH 2-6
(yellow) pH > 6 (Ref. 6)

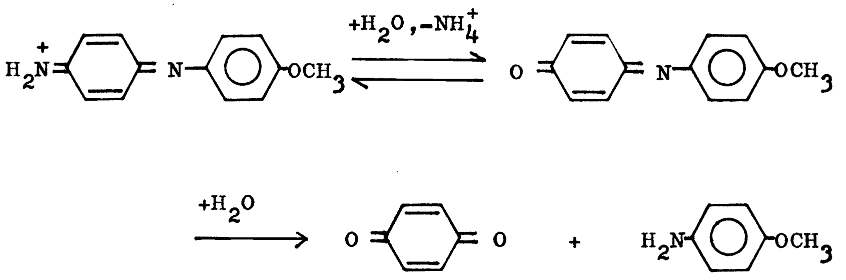
Half-life time (Ref. 2)(indicator solution and stoichiometric amount of oxidant) at pH = 1.9 - 12 min; at pH = 2.5 - 21 min; at pH = 3.0 - 36 min; at pH = 4.0 - 145 min.

Reaction mechanism: Two one-electron steps (Refs. 7,8).



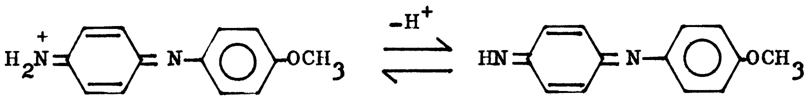
Maximal concentration of the radical bication is at pH 3-4 (Ref. 7).

Instability of OX is due to the reaction (Ref. 9).



The rate of this decomposition increases parallel to the concentration of hydrogen ions, thus the indicator should not be used in strongly acid solutions.

When pH > 6 deprotonation of OX causes change to yellow (Ref. 6).



Purity of indicator. Variamine Blue is most stable in the form of salts, but even in this form undergoes partial oxidation when stored in humid air. Purification (Ref. 10) is achieved by addition of charcoal in the presence of $Na_2S_2O_4$ and precipitation of an indicator salt by a corresponding anion in the form of Na salt. The product should be kept in a dark bottle. The solution of the indicator should be colourless or not more than faint bluish (Ref. 10).

Amount of indicator. The amount of indicator and preparation of the solution depend on the particular use. The table presents various possibilities:

Indicator form	Addition of the form	Amount needed	Stability
Variamine Blue	1% ethanolic soln.	2-3 drops	
Variamine Blue HCl	0.5% aqueous soln.	3-6 drops	1 week
	solid mixture with NaCl (1:300)	20-30 mg	stable
Variamine Blue $1/2H_2SO_4$	0.2% aqueous soln.	3-6 drops	1 week
	solid mixture with Na_2SO_4 (1:100)	20-30 mg	stable
Variamine Blue CH_3COOH	1% soln.in 20%CH_3COOH	3-6 drops	3 weeks

Conditions of titration. pH range 1.5-6.3 (Refs. 7,10) at room temperature, except for ascorbic acid as titrant at 60°C.

Table of applications

Titrant	Analyte	Remarks	Ref.
Ascorbic acid	Ag(I)	at pH 4-5	11
	Hg(II)		12
	Fe(III), J_2		13
	$Fe(CN)_6^{3-}$	at pH > 4.5	14
Iron(II)	Ag(I)	in presence of fluoride	15
	V(V)	in presence of phosphate	16
Vanadium(V) Chromium(VI)	Fe(II)	in presence of fluoride or phosphate in acid soln.	17
EDTA	Pb(II), Cd(II) Zn(II)	in presence of $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$	18
	Fe(III)	in presence of Fe(II) (monochloroacetate buffer)	19 20 21 22
	Cu(II)	in presence of NH_4SCN (acetate buffer)	23 24
	V(V)	in presence of excess of Fe(II), pH 1.7-2	25
Ferrocyanide	Bi(III)	in presence of $Fe(CN)_6^{3-}$	26
	Hg(I)	" " "	27

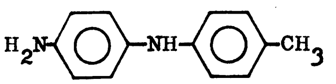
Recommended for ascorbimetric titrations and in complexometric titrations of metals in the presence of ferri-/ferrocyanide indicator system.

REFERENCES

1. L. Erdey, and A. Bodor, Z. analyt. Chem. 137, 410 (1953).
2. A. Hulanicki and S. Głąb, unpublished data.
3. N. S. Frumina and E. G. Tregub, Zh. analit. Khim. 26, 669 (1971).
4. E. Banyai and L. Erdey, Koloriszt. Ert 343 (1964).
5. L. Erdey and F. Szabadvary, Z. analyt. Chem. 155, 94 (1957).
6. L. Erdey, Cronache di Chimica N 26, 23 (1969).
7. L. Erdey, T. Meisel, B. Mohos and F. Tüdős, Talanta 14, 1477 (1967).
8. G. Farsang, M. Kovacs, T. M. H. Sabor and L. Ladanyi, J. Electroanal. Chem. 38, 127 (1972).
9. G. Farsang, L. Adorjan and L. Ladanyi, Proc. 2nd Conf. Appl. Phys. Vol. 1, 461 (1971).
10. L. Erdey, Chemist Analyst 48, 106 (1959).
11. L. Erdey and J. Buzás, Acta Chim. Acad. Sci. Hung., 4, 195 (1954).
12. L. Erdey and J. Buzás, Acta Chim. Acad. Sci. Hung., 8, 263 (1955).
13. L. Erdey, E. Bodor and M. Papay, Acta Chim. Acad. Sci. Hung. 5, 235 (1955).
14. L. Erdey and G. Svehla, Anal. Chim. Acta 40, 473 (1968).
15. L. Erdey and K. Vigh, Z. anal. Chem. 157, 184 (1957).
16. L. Erdey, K. Vigh and E. Bodor, Acta Chim. Acad. Sci. Hung. 7, 293 (1955).
17. L. Erdey, E. Bodor and J. Buzás, Acta Chim. Acad. Sci. Hung. 7, 277 (1955).
18. L. Erdey and L. Pólos, Anal. Chim. Acta 17, 458 (1957).
19. H. Flaschka, Mikrochim. Acta 361 (1954).
20. L. Erdey, and G. Rady, Z. anal. Chem. 149, 250 (1956).
21. P. Wehber, Z. anal. Chem. 158, 321 (1957).
22. N. Nakasaka and M. Tanaka, Anal. Chim. Acta 36, 422 (1966).
23. P. Wehber, Mikrochim. Acta 927 (1955).

24. P. Wehber, Z. anal. Chem. 149, 244 (1956).
25. M. Tanaka and A. Ishida, Anal. Chim. Acta 36, 515 (1966).
26. Z. Gregorowicz and B. Piwowarska, Mikrochim. Acta 755 (1963).
27. Z. Gregorowicz, F. Buhl and Z. Czekańska, Mikrochim. Acta 1000 (1962).

5. 4-AMINO-4'-METHYLDIPHENYLAMINE



May be used as a free base or hydrochloride

Reversible indicator: RED: colourless
OX : blue-violet
Irreversible in bromine titration.

Transition potential: for oxidimetric titrations (Ref. 1)

For indicator conc.	$10^{-4}M$	pH 2.5-2.7	0.54 V
For indicator conc.	$2.5\times10^{-4}M$	pH 2.5-2.7	0.525 V

Formal (half-oxidation) potential:

In the pH range 1.82-4.22 given by the equation $E=0.735-0.059$ pH (Refs.1,2)

Protolytic reactions:

For reduced form (Ref. 1): for	$=NH_2^+$	$pK_{a_1} = -0.08$	(spectrophot.)
for	$-NH_3^+$	$pK_{a_2} = 5.15$	(spectrophot.)
		$pK_{a_2} = 5.09$	(potentiom.)

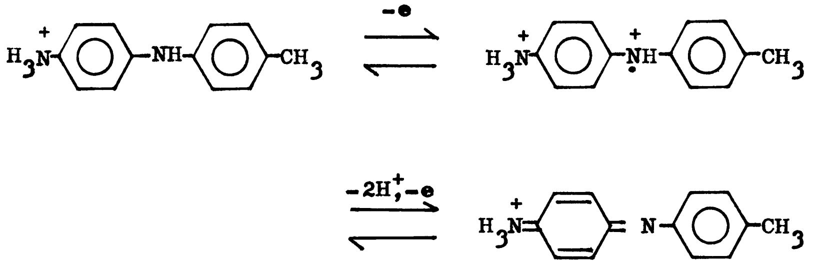
Spectrophotometric characteristics (Ref. 1)

Initial reduced form - no absorption in VIS

Oxidized form pH 1.95-5.20: amount of oxidant corresponding to one electron oxidation, $\lambda_{max} = 520$ nm (blue-violet); amount of oxidant corresponding to two electron oxidation, $\lambda_{max} = 510$ nm (purple), $\varepsilon_{max} = 6060$.

Half-life time (indicator solution and stoichiometric amount of oxidant) at pH = 1.95 - 15 min ; at pH = 2.38 - 21 min ; at pH = 3.12 - 40 min ; at pH = 3.50 - 90 min.

Reaction mechanism: Two one-electron steps (Ref. 1):



The oxidized form is unstable, and hydrolyses into p-quinone and p-toluidene.

Purity of indicator: The indicator dissolved in hot water is purified with the active carbon and crystallized. It should be stored in a dark bottle with limited oxygen excess.

Indicator solution may be used as $5\times10^{-3}M$ aqueous solution of hydrochloride (Ref. 1).

Conditions of titration. In the pH range 1.5-5.5 at room temperature.

Table of applications

Titrant	Analyte	Remarks	Ref.
Iron(II)	V(V)	in presence of H_3PO_4 at pH 2-2.6	1
EDTA	Zn(II)	in presence of $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$	1

Recommended for titration of iron(II) in presence of iron(III) complexing agent, with vanadate.

REFERENCES

1. A. Hulanicki and S. Głąb, Talanta 23, 236 (1976).
2. L. Erdey, I. Kasa, P. Klatsmanyi and T. Meisel, Acta Chim. Acad. Sci. Hung 26, 53 (1961).

6. DIPHENYLBENZIDINEDISULPHONIC ACID

Not identified substitution of sulphonate group.

Pseudoreversible indicator: RED: colourless
OX : violet

Transition potential in 1M H_2SO_4 in presence of 1.5M H_3PO_4

For oxidimetric titrations(Ref. 1) for indicator conc.

$2.5x10^{-6}$M	0.88 V
$1.25x10^{-5}$M	0.83 V
$2.5x10^{-5}$M	0.82 V

The values were obtained in titration of Fe^{2+} with $Cr_2O_7^{2-}$.

Formal (half-oxidation) potential for indicator conc. ~$6x10^{-4}$M in presence of Fe(III) in H_2SO_4 (Ref. 1)

0.5M	0.91 V
1.5M	0.91 V
3M	0.86 V
3.3M	0.82 V

Protolytic reactions (Ref. 1)

For reduced form: for $=NH_2^+$ (I) $pK_{a_1} = -2.1$
$=NH_2^+$ (II) $pK_{a_2} = -0.75$

Spectrophotometric characteristics(Ref. 1)

Initial reduced form - no absorption in VIS.

Oxidized form: $\lambda_{max} = 560$ nm

$\varepsilon_{max} = 2.82x10^4$ in 0.5M H_2SO_4
$\varepsilon_{max} = 3.32x10^4$ in 2M H_2SO_4
$\varepsilon_{max} = 3.50x10^4$ in 4M H_2SO_4
$\varepsilon_{max} = 4.10x10^4$ in 6M H_2SO_4

Half-life time (without excess of oxidant) in 0.5M H_2SO_4 - 30 min ; in 1.5M H_2SO_4 - 40 min ; in 2.5M H_2SO_4 - 70 min.

The solution is more stable for higher concentration of H_2SO_4.

Reaction mechanism - unknown.

Purity of indicator. The solid indicator is stable.

Indicator addition for titration as 0.005M aqueous solution in the amount 0.5 cm^3 per 100 cm^3 of titrated solution (Ref. 2).

Conditions of titration. Solutions should be acidic - approx. 2M H_2SO_4. Titrations at room temperature.

Table of applications

Titrant	Analyte	Remarks	Ref.
Dichromate	Fe(II)	in 1-2M H_2SO_4, H_3PO_4 as complexing agent	1, 2

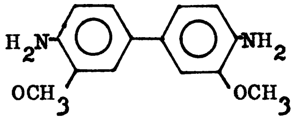
Recommended for iron(II) - in presence of complexing agent for iron(III) - using dichromate as a titrant.

REFERENCES

1. A. Hulanicki and S. Głąb - unpublished data
2. R. Belcher, G. L. Chakrabarti and W. I. Stephen, Analyst 94, 20 (1969).

7. o-DIANISIDINE

3,3'-dimethoxybenzidine



Free base

Reversible indicator: RED: colourless
OX : red

Transition potential in H_2SO_4 (Ref. 1) for indicator conc. ~10^{-5}M.

For oxidimetric titrations:				
	0.1M	0.75 V	2.0M	0.80 V
	0.5M	0.79 V	4.0M	0.81 V
			10.0M	0.78 V

The given values were obtained in titration with dichromate. For ceric ions as titrant values differ no more than 0.02 V.

Formal (half-oxidation) potential in H_2SO_4 (Ref. 2)

At pH 0 - 0.849 V
pH 0.30 - 0.829 V
pH 0.74 - 0.797 V
pH 0.81 - 0.795 V
pH 1.39 - 0.755 V

Protolytic reactions (Ref. 3)

For reduced form: $pK_{a_1} = 2.83$
$pK_{a_2} = 4.05$

Spectrophotometric characteristics (Ref. 4)

Initial reduced form - no absorption in VIS

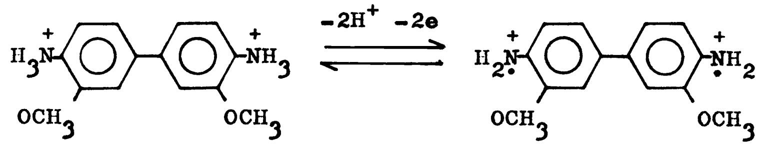
Oxidized form in 2M H_2SO_4 has two absorption maxima

$\lambda_{max} = 454$ nm $\quad \varepsilon_{max} = 3.1\times10^4$

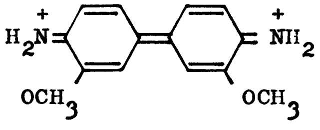
$\lambda_{max} = 510$ nm $\quad \varepsilon_{max} = 2.3\times10^4$

Half-life time 190 min in 2M H_2SO_4.

Reaction mechanism. The following reactions in aqueous solutions of H_2SO_4 have been suggested (Ref. 4).



The slow decomposition may proceed through the form:



Indicator addition is realized as 0.1-0.5% solution in anhydrous acetic acid or aqueous acetic acid, 10 drops are taken for titration.

Conditions of titration. Titrations with this indicator can be done in neutral, weakly as well as strongly acid solutions at room temperature.

Table of applications

Titrant	Analyte	Remarks	Ref.
Hydroquinone	Au(III)	neutral or weakly acid	5
Ferricyanide	Sn(II)	9M HCl	6
Ferrocyanide	Bi(III)	in acetic acid media in presence of small amount of ferricyanide	7
Zinc(II)	Ferrocyanide	in presence of small amount of ferricyanide	8
Silver(I)	I^-	in presence of small amount of iodine	2

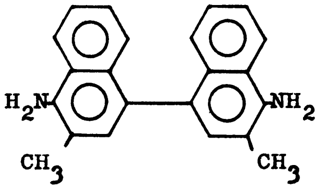
Recommended for titration of Zn^{2+} with $Fe(CN)_6^{4-}$.

REFERENCES

1. D. I. Rees and W. I. Stephen, Talanta 2, 361 (1959).
2. A. B. Crawford and E. Bishop, J. Roy. Tech. Coll. 5, 52 (1950).
3. A. Hulanicki and S. Głąb, Talanta 21, 679 (1974).
4. E. Bishop and L. G. Hartshorn, Analyst 96, 26 (1971).
5. W. B. Pollard, Analyst 62, 597 (1937).
6. H. Basińska and W. Rychlík, Talanta 10, 1299 (1963).
7. H. Basińska and K. Orylska, Chem.Anal. 4, 523 (1959).
8. H. F. Frost, Analyst 68, 51 (1943).

8. 3,3'-DIMETHYLNAPHTHIDINE

3,3'-Dimethyl-4,4'-diamino-1,1'-dinaphthyl



Free base

Reversible indicator: RED: colourless
OX : purple red

Transition potential in H_2SO_4 solution (Ref. 1) for indicator conc.~10^{-5}M.
For oxidimetric titrations: in 0.1-4.0M 0.70-0.71 V
The value were determined using dichromate as a titrant. For cerium(IV) titrations in 4.0M H_2SO_4 - 0.67 V.

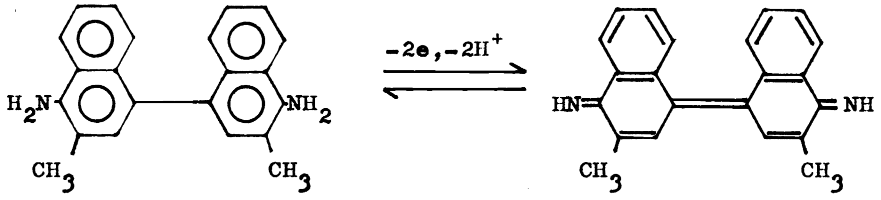
Formal (half-oxidation) potential in H_2SO_4 (Ref. 2)
At pH = 0 - 0.776 V ; at pH = 0.28 - 0.755 V ; at pH = 0.50 - 0.726 V
at pH = 0.79 - 0.714 V ; at pH = 1.00 - 0.711 V.

Protolytic reactions
For reduced form: $pK_{a_1} = 2.62$ spectrophot. (Ref. 3)
$pK_{a_2} = 3.33$ spectrophot. (Ref. 3)

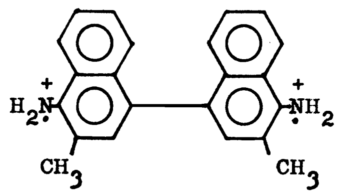
Spectrophotometric characteristics:
Initial reduced form - no absorption in VIS.
Oxidized form: λ_{max}=550 nm (purple red), $\varepsilon_{max}=3\times10^4$ 1M H_2SO_4 (Ref. 1)
λ_{max}=560 nm $\varepsilon_{max}=3\times10^4$ 4M H_2SO_4 (Ref. 1)
λ_{max}=543 nm $\varepsilon_{max}=3.5\times10^4$ 2M H_2SO_4 (Ref. 4)

Half-life time in 2M H_2SO_4 - 80 min. (Ref. 4).

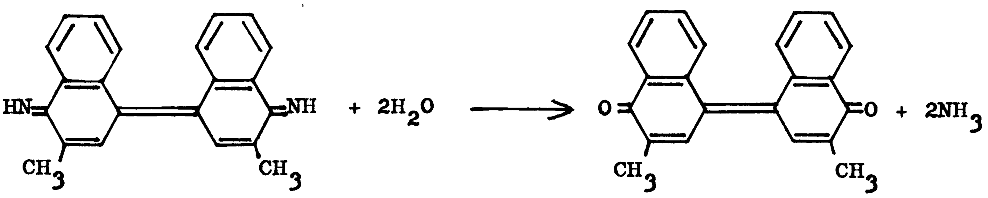
Reaction mechanism. One two-electron step (Refs. 1,4,5)



The oxidized form is equivalent to the biradical (Ref. 4)



The oxidized form undergoes decomposition (Ref. 5) according to:



Purity of indicator. 3,3'-dimethylnaphthidine is stable as a solid. When necessary may be purified by crystallization from o-dichlorobenzene(Ref. 6).

Indicator addition for titration as 1% solution in anhydrous acetic acid. Usually 2-3 drops are sufficient for good end point. The indicator solu-

tion should be colourless.

<u>Condition of titrations</u>. Solutions should be acidic or weakly acidic. Titrations at room temperature.

<u>Table of applications</u>

Titrant	Analyte	Remarks	Ref.
Ferrocyanide	Cd(II), Ca(II)	in presence of $Fe(CN)_6^{3-}$	7
	Ga(III)	" " "	8
Zinc(II)	In(III)	in presence of $Fe(CN)_6^{3-}$	7
		after addition of excess of $K_4Fe(CN)_6$	9
Ferricyanide	Sn(II)	in 9M HCl	10
EDTA	Zn(II)	in presence of $Fe(CN)_6^{3-}$ $Fe(CN)_6^{4-}$ at pH 5	11
Zinc(II)	Zn(II), Cd(II) Pb(II), Fe(III)	in presence of $Fe(CN)_6^{3-}$ $Fe(CN)_6^{4-}$ after addition of excess EDTA, at pH 5	12
	Mn(II)		13
	Ga(III)		14
	Al(III)		15
	R.E.		16

Recommended for direct complexometric titrations of Zn^{2+} or back-titrations with Zn^{2+}.

REFERENCES

1. R. Belcher, A. J. Nutten and W. I. Stephen, <u>J. Chem. Soc.</u> 4454 (1958).
2. R. Belcher, A. J. Nutten and W. I. Stephen, <u>J. Chem. Soc.</u> 3857 (1952).
3. A. Hulanicki and S. Głąb, <u>Talanta 21</u>, 679 (1974).
4. E. Bishop and L. Hartshorn, <u>Analyst 96</u>, 26 (1971).
5. L. Landayi, M. Vajda, M. Bendly and G. Farsang, <u>Acta. Chim. Hung.</u> <u>73</u>, 285 (1972).
6. M. E. Fierz-David, L. Blangley and H. Dubendorfer, <u>Helv. Chim. Acta</u> <u>29</u>, 1661 (1946).
7. R. Belcher, A. J. Nutten and W. I. Stephen, <u>J. Chem. Soc.</u> 3444 (1951).
8. R. Belcher, A. J. Nutten and W. I. Stephen, <u>J. Chem. Soc.</u> 2438 (1952).
9. R. Belcher, A. J. Nutten and W. I. Stephen, <u>J. Chem. Soc.</u> 1520 (1951).
10. H. Basińska and W. Rychlik, <u>Talanta 10</u>, 1293 (1963).
11. E. G. Brown and T. J. Hayes, <u>Anal. Chim. Acta</u> <u>9</u>, 6 (1953).
12. H. Flaschka and W. Franschitz, <u>Z. anal. Chem.</u> <u>144</u>, 421 (1955).
13. I. Sajó, <u>Magyar Kom. Foly.</u> <u>61</u>, 195 (1955).
14. H. Flaschka and H. Abdine, <u>Mikrochim. Acta</u> 657 (1954).
15. H. Flaschka and H. Abdine, <u>Mikrochim. Acta</u> 37 (1955).
16. H. Flaschka, <u>Mikrochim. Acta</u> 55 (1955).

9. 3,3'-DIMETHYLNAPHTHIDINEDISULPHONIC ACID

**Not identified substitution
of two sulphonate groups.**

<u>Reversible indicator</u>: RED: colourless
OX : purple

<u>Transition potential</u> in H_2SO_4 (Ref. 1) for indicator conc. $\sim 10^{-5}$M.

For oxidimetric titrations:

0.1M	0.82 V	2.0M	0.79 V
0.5M	0.81 V	4.0M	0.77 V
1.0M	0.80 V	8.0M	0.75 V

Formal (half-oxidation) potential (Ref. 1)

at pH	0	0.838 V
	0.28	0.796 V
	0.50	0.802 V
	0.79	0.806 V
	1.00	0.784 V

Protolytic reactions ---

Spectrophotometric characteristics ---

Reaction mechanism ---

Purity of indicator ---

Indicator solution. Usually 0.2% or 1% aqueous solution is prepared by dissolving of the acid in small excess of ammonia, expelling excess of it by heating and diluting to the required volume with water (Ref. 2). A few drops are taken for determination.

Conditions of titrations ---

Table of applications

Titrant	Analyte	Remarks	Ref.
Ferrocyanide	Zn(II), Cd(II)	in presence of small amount of $Fe(CN)_6^{3-}$ in 2% $(NH_4)_2SO_4$	2
	Ga(III)	in presence of small amount of $Fe(CN)_6^{3-}$ in 5% ethanol	3

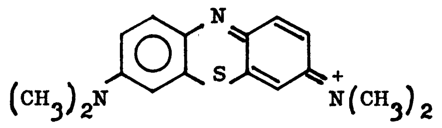
Recommended for titration of Zn^{2+} with $Fe(CN)_6^{4-}$.

REFERENCES

1. R. Belcher, A. J. Nutten and W. I. Stephen, J. Chem. Soc. 3857 (1952).
2. R. Belcher, A. J. Nutten and W. I. Stephen, J. Chem. Soc. 1269 (1952).
3. R. Belcher, A. J. Nutten and W. I. Stephen, J. Chem. Soc. 2438 (1952).

10. METHYLENE BLUE

Bis- 3,9-dimethylamino phenazothionium chloride



Usually as chloride of the oxidized form

Reversible indicator: OX : blue
RED: colourless

Transition potential ---

Formal (half-oxidation) potential

In pH range 1-13 may be described by equation: (Ref. 1)

$$E = 0.532 + 0.0296 \log\left([H^+]^3 + K_{a_1}[H^+]^2 + K_{a_1}K_{a_2}[H^+]\right)$$

where 0.532 is the formal potential at pH = 0 (Refs. 1,2,3) and K_{a_1} and K_{a_2} are the corresponding dissociation constants of the reduced form.

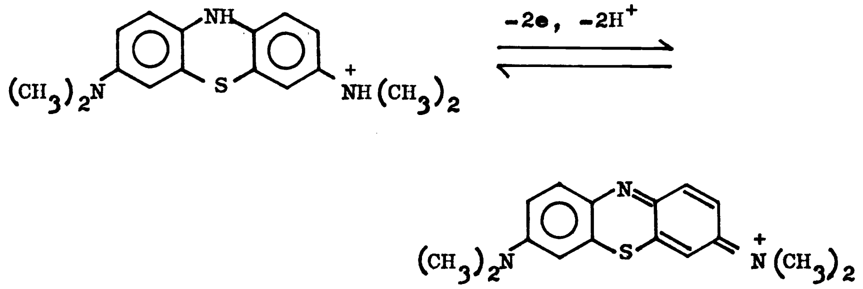
Protolytic reactions:

For reduced form (Refs. 2,3) $pK_{a_1} = 4.52$ (potentiom.)
$pK_{a_2} = 5.85$ (potentiom.)

Spectrophotometric characteristics

The reduced form - no absorption in VIS.
The oxidized form (Ref. 4): $\lambda_{max} = 662$ nm, $\varepsilon_{max} = 2.5 \times 10^4$

Reaction mechanism: One two-electron step



When the redox reaction is carried out in $H_2SO_4 > 10M$ the intermediate semiquinone has been found (Ref. 5).

Purity of indicator ---

Indicator solution may be used as 0.5% or 0.1% (0.015 or 0.003M) aqueous solution of the oxidized form. In titrations usually 2 - 3 drops are sufficient.

Conditions of titrations. Used in a broad range of pH. Depending on titrant - titrate system in room or elevated temperature. Most titrations are carried out in absence of oxygen.

Table of applications

Titrant	Analyte	Remarks	Ref.
Permanganate	Ti(III)	in 0.1M H_2SO_4 at 60°, in mixture with Fe(II) the second end-point with ferroin	6
Cerium(IV)	Ti(III)	as a permanganate titration	7
Iron(III)	V(III)	in 0.2M HCl with Cu^{2+} as catalyst	8
	Ti III	in 25% tartaric acid	9
	U(IV)	in 0.2-0.3M HCl, temp. 98-100°	10
	Sn(II)	in 4-6M HCl, under CO_2	11
Ferrocyanide	U(IV)	in 2.5-4.0M KOH	12
Iron(II)	Mo(V)	in 0.5M HCl in presence of citric acid, temp. ~90°	13
	Mo(VI)	in 11.5-13.0M H_3PO_4	14

Table of applications cont.

Titrant	Analyte	Remarks	Ref.
Iron(II)	V(IV)	in 10.5M H_3PO_4	15
	U(VI)	in 11.6M H_3PO_4	16
Chromium(II)	Fe(III)	in 1.5M H_2SO_4	17
Vanadium(II)	Fe(III)	in 1.0M H_2SO_4	18

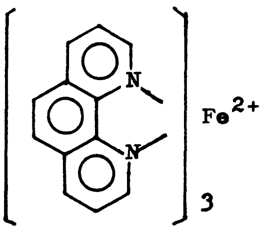
Recommended for titration of Ti(III)in mixture with Fe(II) using permanganate as titrant.

REFERENCES

1. W. M. Clark, B. Cohen and M. D. Gibbs, Public Health Reports (U.S.) 40, 1131 (1925).
2. H. W. Meyer and W. D. Treadwell, Helv. Chim. Acta 35, 1444 (1952).
3. B. P. Nikolskii and V. V. Palchevskii, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. 547 (1957).
4. Z. Marczenko, Spectrophotometric determination of elements,John Wiley New York 1976.
5. L. Michaelis, M. P. Schubert and S. Granick, J. Am. Chem. Soc. 62, 204 (1940).
6. B. A. Shippy, Anal. Chem. 21, 698 (1949).
7. G. F. Smith and L. T. Kurtz, Ind. Eng. Chem. Anal. Ed. 14, 854 (1942).
8. K. L. Chawla and J. P. Tandon, Indian J. Chem. 6, 332 (1968).
9. O. Tomiček, K. Spurný, L. Jerman and V. Holeček, Coll. Czech. Chem. Comms. 18, 757 (1953).
10. S. R. Sagi and G. G. Rao, Z. analyt. Chem. 192, 297 (1962).
11. G. G. Rao and A. M. Mugnier, Anal. Chim. Acta 58, 470 (1972).
12. H. Basińska and W. Wiśniewski, Chem. Anal.(Warsaw) 10, 1007 (1965).
13. S. R. Sagi and G. G. Rao, Acta Chim. Acad. Sci. Hung. 38, 89 (1963).
14. G. G. Rao and S. R. Sagi, Talanta 10, 169 (1963).
15. G. G. Rao and L. S. A. Dikshitulu, Talanta 10, 295 (1963).
16. G. G. Rao and S. R. Sagi, Talanta 9, 715 (1962).
17. J. P. Tandon and R. C. Mehrotra, Z. analyt. Chem. 158, 20 (1957).
18. R. K. Mittal, J. P. Tandon and R. C. Mehrotra, Z. analyt. Chem. 189, 330 (1962).

11. FERROIN

Tris-(1,10-phenanthroline)iron(II) salt



as a solution of sulphate
or perchlorate

Reversible indicator: RED: orange-red
OX : pale-blue

Transition potential: for oxidimetric titrations

in	1.1M H_2SO_4	1.06 V (Ref. 1)
	2.0M HCl	1.065 V (Ref. 2)
	4.0M HCl	1.026 V (Ref. 2)

Formal (half-oxidation) potentials in H_2SO_4

In conc. range 0.25M-6M the potential (accurate to ±5 mV) is given by equation (Refs. 3,4,5,6) : $E = 1.094 - 0.0338\ C$, where C - sulphuric acid molarity. Equivalent to this expression, for range 0.25M-3M is the equation (Ref. 2) for the potential (accurate to ±2 mV) $E = 1.068 + 0.44_2\ H_o$, where H_o - denotes Hammett's acidity function.

Protolytic reactions and related equilibria:

Acid dissociation of 1,10-phenanthroline

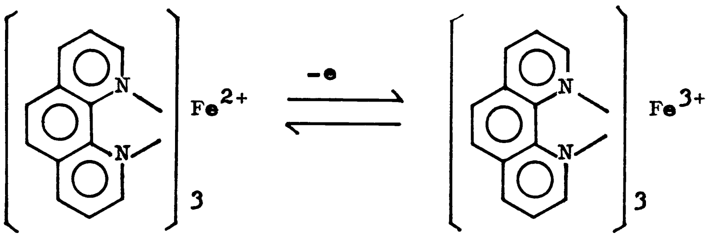
$pK_{a_1} = -1.6$	(spectrophot.)	(Ref. 7)
$pK_{a_2} = 4.92$	(potentiom.)	(Ref. 8)
4.95	(potentiom.)	(Ref. 9)
4.93	(spectrophot.)	(Ref. 10)

Complex stability constants for reduced form: $\log \beta_3 = 21.3$ (potentiom.) (Ref. 9), (spectrophot.)(Ref. 11). For oxidized form: $\log \beta_3 = 14.1$ (potentiom.) (Ref. 11).

Spectrophotometric characteristics:

Reduced form (Ref. 12)	$\lambda_{max} = 510$ nm	$\varepsilon_{max} = 1.11 \times 10^4$
Oxidized form (Ref. 13)	$\lambda_{max} = 590$ nm	$\varepsilon_{max} = 6 \times 10^2$

Reaction mechanism. One one-electron step.



Purity of indicator. The indicator solution prepared from 1,10-phenanthroline and ferrous salt of analytical grade needs no purification.

Indicator solution is usually prepared by dissolution of 1.485 g 1,10-phenanthroline hydrate in 100 cm^3 of water, containing 0.695 g $FeSO_4 \cdot 7H_2O$. This is 0.025M solution of ferroin sulphate. For titrations 1 drop of this solution is sufficient (Ref. 14). The ferroin perchlorate is used as a saturated solution (~0.001M), added in amounts 1-2 cm^3.

Conditions of titrations. Usually in H_2SO_4 solutions from dilute up to 6M. The indicator reaction is rapid at room temperature.

Table of applications

Titrant	Analyte	Remarks	Ref.
Cerium(IV)	Fe(II)	in 1M H_2SO_4	15
		in 1M H_2SO_4, addition of excess of Fe(III) for indirect determination of Nb	16
		Cu(I)	17
	As(III)	in 1M H_2SO_4, OsO_4 as catalyst	15
	H_2O_2	in 1M H_2SO_4	18
	$Fe(CN)_6^{4-}$	in 2M H_2SO_4	19

Table of applications cont.

Titrant	Analyte	Remarks	Ref.
		also used for indirect determination of hydroxylamine	20
		SCN^-	21
		V(IV)	22
	$C_2O_4^{2-}$	in 1M HCl	23
Iron(II)	Ce(IV)	in 1.5M H_2SO_4, addition of excess of Ce(IV) for indirect determination of H_3PO_2, H_3PO_3	24
		reducing sugars	25
		Te(IV)	26
Chromium(VI)	Fe(II)	in 5-6M H_2SO_4 (better results with 5,6-dimethylferroin)	27
	U(IV)	in 5-5.5M H_2SO_4	28
		in 2-4M H_2SO_4	29

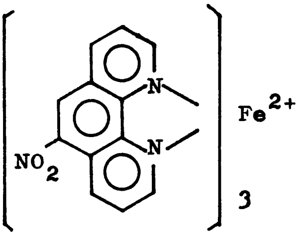
Recommended for titrations of iron(II) and $Fe(CN)_6^{3-}$ with cerium(IV) as titrant.

REFERENCES

1. G. F. Smith and W. M. Banick, Jr. Talanta 2, 348 (1959).
2. J. A. Perez-Bustamante - unpublished data
3. F. P. Dwyer and H. A. McKenzie, J. Proc. Roy. Soc. N. S. Wales 81, 93 (1947).
4. W. W. Brandt and G. F. Smith, Anal. Chem. 21, 1313 (1943).
5. D. N. Hume and I. M. Kolthoff, J. Am. Chem. Soc. 65, 1895 (1943).
6. G. F. Smith and F. P. Richter, Ind. Eng. Chem. Anal. Ed. 16, 580 (1944).
7. R. H. Linell and A. Kaczmarczyk, J. Phys. Chem. 65, 1196 (1961).
8. K. Yamasaki and M. Yasuda, J. Am. Chem. Soc. 78, 1324 (1956).
9. G. Anderegg, Helv. Chim. Acta 46, 2397 (1963).
10. D. A. Brisbin and W. A. E. McBryde, Can. J. Chem. 41, 1135 (1965).
11. T. S. Lee, I. M. Kolthoff and D. L. Leussing, J. Am. Chem. Soc. 70, 2348 (1948).
12. W. B. Fortune and M. G. Mellon, Ind. Eng. Chem. Anal. Ed. 10, 60(1938).
13. A. E. Marvey and D. L. Manning, J. Am. Chem. Soc. 74, 4744 (1952).
14. I. M. Kolthoff and R. Belcher, Volumetric Analysis, Interscience, New York, 1957.
15. R. Belcher, C. L. Chakrabarti and W. I. Stephen, Analyst 94, 20 (1969).
16. O. Tomiček, K. Spurný, L. Jerman and V. Holeček, Coll. Czech. Chem. Comms. 18, 757 (1953).
17. N. Birnbaum and S. M. Edmonds, Ind. Eng. Chem. Anal. Ed. 12, 155(1940).
18. F. P. Greenspan and D. G. McKeller, Anal.Chem. 20, 1061 (1948).
19. R. Belcher, D. I. Rees and W. I. Stephen, Chim. analyt. 41, 397 (1959).
20. B. R. Sant, Z. analyt. Chem. 145, 257 (1955).
21. B. Suseela, Z. analyt. Chem. 145, 175 (1955).
22. B. Suseela, Anal. Chim. Acta 13, 543 (1955).
23. V. P. Rao and G. G. Rao, Talanta 2, 370 (1959).
24. D. N. Bernhart, Anal. Chem. 26, 1788 (1954).
25. G. R. Bhausali and D. L. Mathur and S. P. Rao, Indian J. Chem. 5 454 (1967).
26. G. G. Guilbault and W. H. McCurdy Jr., Anal. Chim. Acta 24, 214 (1961).
27. G. F. Smith and W. W. Brandt, Anal. Chem. 21, 948 (1949).
28. V. Muralikrishne and K. V. Bapanaiach, Z. analyt. Chem. 262, 29 (1972).
29. N. V. Rao, Z. analyt. Chem. 266, 31 (1973).

12. NITROFERROIN

Tris(5-nitro-1,10-phenanthroline) iron(II) sulphate



as solution of sulphate

Reversible indicator: RED: pink
OX : colourless (pale blue)

Transition potential ---

Formal (half-oxidation) potential in H_2SO_4 (Ref. 1)

0.5M	1.26 V
1.0M	1.25 V
2.0M	1.22 V
4.0M	1.12 V

In $HClO_4$ at conc. range 4-8M the potential (accurate to ±4 mV) is given by equation (Ref. 2): $E = 1.239 + 0.055_2H_o$, where H_o - denotes Hammett's acidity function.

Protolytic reaction and related equilibria:

Acid dissociation of 5-nitro-1,10-phenanthroline

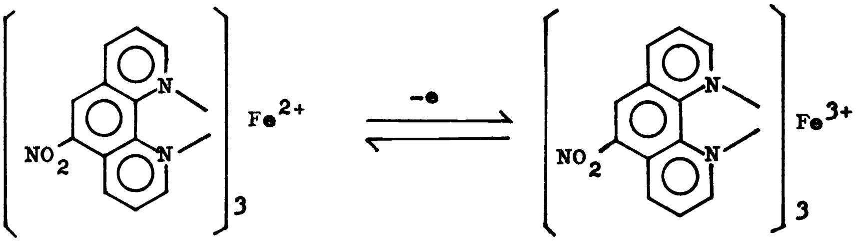
pK_a =	3.57	(potentiom.)	(Ref. 3)
	4.18	(spectrophot.)	(Ref. 4)
	3.23	(spectrophot.)	(Ref. 5)

Complex stability constants for reduced form: $\log \beta_3 = 17.8$ (spectrophot.) (Ref. 3) - for oxidized form: $\log \beta_3 = ?$

Spectrophotometric characteristics:

Reduced form (Ref. 6)	$\lambda_{max} = 510$ nm ;	$\varepsilon_{max} = 1.15 \times 10^4$
Oxidized from	---	---

Reaction mechanism: One one-electron step.



Purity of indicator. The indicator solution prepared from 5-nitro-1,10-phenanthroline and ferrous salt of analytical grade needs no purification.

Indicator solution is usually prepared by dissolution of 1.689 g of 5-nitro-1,10-phenanthroline in 100 cm^3 of water containing 0.695 g $FeSO_4.7H_2O$. This is 0.025M solution of the indicator as sulphate. For titrations 1 drop of this solution is sufficient (Ref. 7).

Conditions of titrations. Usually in HNO_3 or $HClO_4$ media in determination involving cerium(IV).

Table of applications:

Titrant	Analyte	Remarks	Ref.
Cerium(IV)	$C_2O_4^{2-}$	in 2M $HClO_4$	8,9
		in 0.5M HCl, $HClO_4$ or HNO_3	10
		indirect determination of Ba precipitated as BaC_2O_4	11
	As(III)	in 2M $HClO_4$, OsO_4 as catalyst	12
	Fe(II)	in 2M $HClO_4$	
	Hg(I)	in $HClO_4$; Mn(II), Ag(I) as catalyst, temp. 50-60°	13
Oxalate	Ce(IV)	in 0.5M HNO_3 or $HClO_4$	14
		in 4M $HClO_4$ indirect detn. of H_3PO_3	15

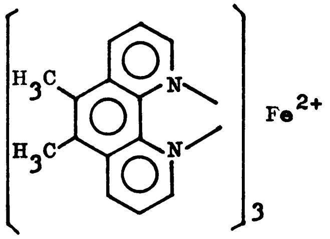
Recommended for titrations of oxalic acid with cerium(IV) in 0.5M hydrochloric or nitric acid.

REFERENCES

1. G. F. Smith and F. P. Richter, *Ind. Eng. Chem. Anal.* Ed. 16, 580(1944).
2. J. A. Perez-Bustamante - unpublished data
3. W. W. Brandt and D. K. Gullstrom, *J. Am. Chem. Soc.* 74, 3532 (1952).
4. C. V. Banks and R. I. Bystroff, *J. Am. Chem. Soc.* 81, 6153 (1959).
5. S. C. Lahiri and S. Aditya, *J. Indian Chem. Soc.* 41, 469 (1964).
6. A. A. Schilt, *Analytical Applications of 1,10-Phenanthroline and Related Compounds*, Pergamon Press, Oxford, 1969.
7. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Interscience, New York, 1957.
8. K. Salomon, B. W. Gabrio and G. F. Smith, *Archiv. Biochem.* 11, 436 (1946).
9. G. H. Koch and F. M. Strong, *Analyt. Biochem.* 27, 162 (1969).
10. K. B. Rao, *Z. analyt. Chem.* 184, 171 (1961).
11. E. Gagliardi and B. Ilmair, *Z. analyt. Chem.* 204, 410 (1964).
12. G. F. Smith and J. S. Fritz, *Anal. Chem.* 20, 874 (1948).
13. G. G. Guilbault, W. H. McCurdy Jr. *Anal. Chim. Acta* 24, 214 (1961).
14. K. B. Rao, *Rec. Trav. Chim. Pays-Bas* 84, 62 (1965).
15. L. R. Martin, M. A. Henry and J. R. Hayes, *Microchem. J.* 13, 525 (1968).

13. 5,6-DIMETHYLFERROIN

Tris(5,6-dimethyl-1,10-phenanthroline) iron(II) sulphate



as solution of sulphate

Reversible indicator: RED: red
OX : yellow-green

Transition potential ---

Formal (half-oxidation) potential in H_2SO_4 (Ref. 1)

0.1M	1.00 V
0.5M	0.97 V

Protolytic reactions and other equilibria:

Acid dissociation of 5,6-dimethyl-1,10-phenanthroline

$pK_a = 5.6$ (spectrophot.) (Refs. 2,3)

Complex stability constants for reduced form

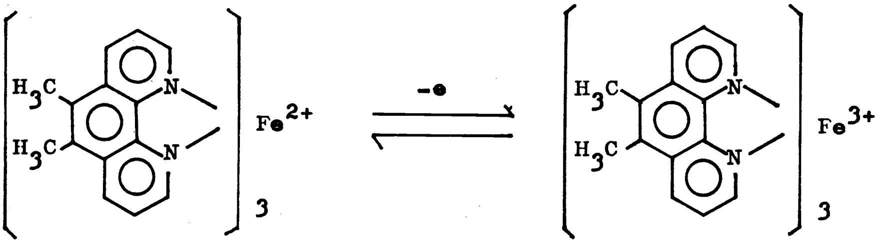
$\log \beta_3 = 23.0$ (partition) (Ref. 2)

Spectrophotometric characteristics

Reduced form (Ref. 4)	$\lambda_{max} = 520$ nm,	$\varepsilon_{max} = 1.26 \times 10^4$
Oxidized form:	---	---

The indicator is very stable in solutions.

Reaction mechanism. One one-electron step.



Purity of indicator. The indicator solution prepared from 5,6-dimethyl-1,10-phenanthroline and ferrous salt of analytical grade needs no purification.

Indicator solution is prepared by mixing 0.06M solution of 5,6-dimethyl-1,10-phenanthroline with equal amount of 0.02M ferrous sulphate (Ref. 5). This solution being 0.01M is used in amount of 1 drop for titration.

Conditions of titrations. Usually in H_2SO_4 or HCl solutions.

Table of applications

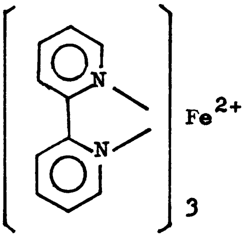
Titrant	Analyte	Remarks	Ref.
Dichromate	Fe(II)	in 1M H_2SO_4 or 1-2M HCl	6
	U(IV)	in 1M HCl	5

Recommended for titration of Fe(II) with dichromate.

REFERENCES

1. W. W. Brandt and G. F. Smith, Anal. Chem. 21, 1313 (1949).
2. D. A. Brisbin and W. A. E. Mc Bryde, Can. J. Chem. 41, 1135 (1965).
3. R. K. Steinhaus and D. W. Margerum, J. Am. Chem. Soc. 88, 441 (1968).
4. A. A. Schilt, Analytical Applications of 1,10-Phenanthroline and Related Compounds, Pergamon Press, Oxford, 1969.
5. I. M. Kolthoff and R. Belcher, Volumetric Analysis(III) Interscience, New York, 1957.
6. G. F. Smith and W. W. Brandt, Anal. Chem. 21, 948 (1949).

14. TRIS-(2,2'-DIPYRIDYL)-IRON(II)- SULPHATE



as solution of sulphate

Reversible indicator: RED: red
OX : faint blue

Transition potential ---

Formal (half-oxidation) potential in H_2SO_4

0.01M	1.086 V	(Ref. 1);	1.069 V	(Ref. 2)
0.11M	1.062 V	(Ref. 2)		
1.0M	1.026 V	(Ref. 2);	1.023 V	(Ref. 3)
2.0M	1.00 V	(Ref. 2)		
4.0M	0.95 V	(Ref. 2)		
6.0M	0.88 V	(Ref. 2)		
10.0M	0.80 V	(Ref. 2)		

Protolytic reaction and related equilibria

Acid dissociation of 2,2'-dipyridyl:

$pK_{a_1} = -0.2$ (spectrophot.) (Ref. 4)
$pK_{a_2} = 4.44$ (potentiom.) (Ref. 5)
4.49 (potentiom.) (Ref. 6)
4.44 (spectrophot.) (Ref. 7)

Complex stability constants for reduced form:

$\log \beta_3 = 17.45$ (pH-metric) (Ref. 6)
17.45 (partition) (Ref. 8)
16.94 (spectrophot.) (Ref. 9)

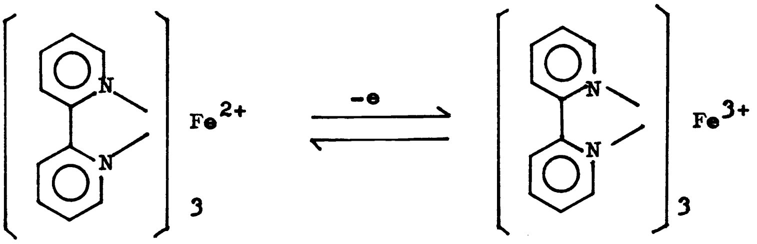
- for oxidized form:

$\log \beta_3 = 12.0$ (potentiom.) (Ref. 9)

Spectrophotometric characteristics

Reduced form (Ref. 10) $\lambda_{max} = 522$ nm ; $\varepsilon_{max} = 8.65\times10^3$
Oxidized form (Ref. 11) $\lambda_{max} = 610$ nm ; $\varepsilon_{max} = 3.3\times10^2$

Reaction mechanism. One one-electron step.



Purity of indicator. The indicator solution prepared from 2,2'-dipyridyl and ferrous salt of analytical grade needs no purification.

Indicator solution is usually prepared by dissolution of 1.17 g of 2,2'-dipyridyl in 100 cm^3 of water containing 0.695 g $FeSO_4.7H_2O$. This is 0.025M solution of the indicator in the sulphate form and 1 drop is needed for titrations (Ref. 12). May be used also as a saturated solution of perchlorate, 1 cm^3 for titration (Ref. 13).

Conditions of titrations. Usually used in titrations which involve cerium IV in acid media.

Table of applications

Titrant	Analyte	Remarks	Ref.
Cerium(IV)	Fe(II)	in 1M H_2SO_4 or HCl	13, 14
	Hydroquinone	in 1M H_2SO_4	15
	V(IV)	in 12M CH_3COOH	16

Recommended for titration of Fe(II) with cerium(IV).

REFERENCES

1. F. P. Dwyer and H. A. McKenzie, *J. Proc. Roy. Soc. N. S. Wales* 81, 93 (1947).
2. A. A. Schilt, *Anal. Chem.* 35, 1599 (1963).
3. R. Belcher, J. N. Brazier and W. I. Stephen, *Talanta* 12, 778 (1965).
4. R. H. Linnell and A. Kaczmarczyk, *J. Phys. Chem.* 65, 1196 (1961).
5. K. Yamasaki and M. Yasuda, *J. Am. Chem. Soc.* 78, 1324 (1956).
6. G. Anderegg, *Helv. Chim. Acta* 46, 2397 (1963).
7. P. Krumholz, *J. Am. Chem. Soc.* 73, 3487 (1951).
8. H. Irving and D. H. Mellor, *J. Chem. Soc.* 5222 (1962).
9. J. H. Baxendale and P. George, *Trans. Faraday Soc.* 46, 55 (1950).
10. M. L. Moss and M. G. Mellon, *Ind. Eng. Chem. Anal. Ed.* 14, 862 (1942).
11. A. A. Schilt, *Analytical Applications of 1,10-Phenanthroline and Related Compounds*, Pergamon Press, Oxford, 1969.
12. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Interscience, New York, 1957.
13. F. W. Cagle, G. F. Smith, *Anal. Chem.* 19, 384 1947 .
14. C. I. Van Nieuwenburg and H. B. Blumental, *Mikrochemie* 18, 39 (1935).
15. T. Sakai, *Nippon Kagaku Zasshi* 83, 1078 (1962).
16. J. S. Gill and G. N. Rao, *Z. analyt. Chem.* 256 201 (1971).

SUBJECT INDEX

The numbers refer to the sequence of indicators in the part II of this report.

According to analytes

Lead(II) - 4, 8
Manganese(II) - 8
Mercury(I) - 4, 12
Mercury(II) - 4
Molybdenum(V) - 1, 3, 10
Oxalate - 11, 12
Rare earths - 8
Silver(I) - 4
Tin(II) - 7, 8, 10
Titanium(III) - 10
Uranium(IV) - 3, 10, 11, 13
Uranium(VI) - 10
Vanadium(III) - 3, 10
Vanadium(IV) - 10, 14
Vanadium(V) - 1, 3, 4
Zinc(II) - 4, 5, 8, 9

<u>According to titrants</u>. Within each titrant the analytes are distinguished and corresponding indicator numbers are given.

Ascorbic acid - Ag(I), Fe(III), Fe(CN)$_6^{3-}$, Hg(II), I$_2$ - 4
Arsenic(III) - Cr(VI) - 1
Cerium(IV) - As(III) - 11, 12; $C_2O_4^{2-}$ - 11, 12; Fe(II) - 3, 11, 12, 14; Fe(CN)$_6^{4-}$ - 3, 11; Hg(I) - 12; H_2O_2 - 11; Hydroquinone - 14; Ti(III) - 10; U(IV) - 14
Chromium(II) - Fe(III) - 10
Chromium(VI) - Fe(II) - 1, 2, 3, 4, 6, 11, 13; U(IV) - 3, 11, 13
EDTA - Cu(II) - 4; Cd(II) - 4; Pb(II) - 4; Zn(II) - 4, 5, 8
Ferricyanide - Sn(II) - 7, 8
Ferrocyanide - Bi(III) - 4, 7; Ca(II) - 8; Cd(II) - 8, 9; Ga(III) - 8, 9; Hg(I) - 4; U(IV) - 4, 10; Zn(II) - 9
Hydroquinone - Au(III) - 7
Iodine(VII) - As(III), Fe(II), Sb(III) - 1
Iron(II) - Ag(I) - 4; Ce(IV) - 11; Cr(VI) - 3; Mo(IV) - 10; Mo(V) - 10; U(VI) - 10; V(IV) - 10; V(V) - 4
Iron(III) - Sn(II), Ti(III), U(IV), V(III) - 10
Manganese(VII) - Ti(III) - 10
Oxalate - Ce(IV) - 12
Silver(I) - I$^-$ - 7
Tin(II) - Cr(VI), V(V) - 1
Vanadium(II) - Fe(III) - 10
Vanadium(III) - Cr(VI), V(V) - 3
Vanadium(V) - Fe(II) - 1, 2, 4, 5; Mo(V) - 1, 3; U(IV) - 3
Zinc(II) - Fe(CN)$_6^{4-}$ - 7, 8.