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REDOX INDICATORS. CHARACTERISTICS AND APPLICATIONS

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REDOX INDICATORS, CHARACTERISTICS AND APPLICATIONS

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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.

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2. Indicator error in redox titration
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2. Diphenylamine-4-sulphonic acid
3. N-Phenylanthranilic acid
4. Variamine Blue
5. 4-Amino-4'-methyl diphenylamine
6. Diphenylbenzidinedisulphonic acid
7. o-Dianisidine
8. 3,3'-Dimethylnaphthidine
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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-empirical basis.
tical basis, partly because of lack of corresponding data and partly be-
cause it was often not sufficiently clear which data should be determined
for analytical purposes. Even the most comprehensive monographs on indica-
tors, which contain all the available data for a very large number of com-
 pounds, 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. Stri-
citely speaking it is not the purpose of such monographs to provide such in-
formation; their main purpose is to collect together all the available in-
formation. Recommendations can only be purely objective when they are the
result of the considered opinion of several experienced investigators. Com-
mession V-1 has examined this problem and has attempted to make suitable re-
commendations 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 doub-
tful results has the work been checked experimentally. For practical reasons
it was not possible to verify the data for all compounds. It is hoped, how-
ever, 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 spe-
cies might be included, according to personal experiences and even preju-
dices.

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 tradi-
tional 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 fo-
llowed 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 represen-
ted 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. An example of
such indicator is N-phenylanthranilic acid.

The indicator may be classified as irreversible when in the cycle of reac-
tions (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 indica-
tor 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, aci-
dity for the species 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 for-
mal redox potential has a precise meaning only for strictly reversible in-
dicators. In the case of other indicators it should be understood as the
potential for half-oxidised indicator. Because of difficulties of determi-
nation corresponding activity coefficient the rigorous definition for for-
mal 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 reductimetric 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 ($25^\circ C$) $pE = 16.9 E$ (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 \text{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 occurring 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 endpoint, is close to the equivalence point potential the effect of above mentioned factors may be diminished.

The indicator consumption error - the systematic error occurring 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 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 non-linearity 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

\[ \text{Ox}_X + n_X e^- = \text{Red}_X \]

and the half-reaction of the titrant

\[ \text{Ox}_T + n_T e^- = \text{Red}_T \]

give the reaction equations for oxidimetric titration:

\[ n_T \text{Red}_X + n_X \text{Ox}_T = n_T \text{Ox}_X + n_X \text{Red}_T \]

and for reductimetric titration:

\[ n_T \text{Ox}_X + n_X \text{Red}_T = n_T \text{Red}_X + n_X \text{Ox}_T \]
which enable the derivation of a general equation (Ref. 1, 2) for the end-
point error \( \Delta V_T \), expressed in the volume units of the titrant:

\[
\Delta V_T = \frac{C_X V_X - C_T V_T}{V_T} \left[ \frac{n_T (E - E^0_X)}{0.06} - 10 \frac{n_X (E - E^0_X)}{0.06} \right] \left[ 1 + 10 \frac{n_X (E - E^0_X)}{0.06} \right]^{-1}
\]

This equation is valid for both indicated reactions, when the number of e-
lectrons of half-reactions indicated above, is taken with the sign prece-
ding when written in the direction of the reaction actually occurring.

The remaining symbols in this equation are:

- \( C_X, C_T \) - molar concentrations of the analyte and titrant, respecti-
vely
- \( V_X, V_T \) - volumes of the analyte and titrant up to the end-point,
respectively
- \( E \) - the end-point potential
- \( E^0_X, E^0_T \) - the formal potentials of the analyte and titrant, respec-
tively

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

\[
\frac{\Delta V_T}{V_T} = \left[ \frac{n_T (E - E^0_X)}{0.06} - 10 \frac{n_X (E - E^0_X)}{0.06} \right] \left[ 1 + 10 \frac{n_X (E - E^0_X)}{0.06} \right]^{-1}
\]

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 pe-
roxide.

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 sys-

tem:

- \( E^0 \) - 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
- \( \varepsilon_R, \varepsilon_O \) - molar absorbivities 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 transi-
tion 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.
- \( I \) - 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

<table>
<thead>
<tr>
<th>Indicator</th>
<th>General equation</th>
<th>Simplified equation for a=b=1</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-colour</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{a^b A^a (1\varepsilon_0)^{b-a}}{(1c_1\varepsilon_0 - a)^b}$</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{A}{1c_1\varepsilon_0 - a}$</td>
</tr>
<tr>
<td>Ox-coloured added as Red.</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{a^b A^a (1\varepsilon_0)^{b-a}}{(1c_1\varepsilon_0 - a)^b}$</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{A}{1c_1\varepsilon_0 - a}$</td>
</tr>
<tr>
<td>One-colour</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{a^b (1\varepsilon_0 - a')^a}{b^a (1\varepsilon_0 - a')^a}$</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{1c_1\varepsilon_0 - a'}{a'}$</td>
</tr>
<tr>
<td>Ox-coloured added as Ox.</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{a^b (1\varepsilon_0 - a')^a}{b^a (1\varepsilon_0 - a')^a}$</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{1c_1\varepsilon_0 - a'}{a'}$</td>
</tr>
<tr>
<td>Red-coloured added as Red</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{a^b (1\varepsilon_0 - a')^a}{b^a (1\varepsilon_0 - a')^a}$</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{1c_1\varepsilon_0 - a'}{a'}$</td>
</tr>
<tr>
<td>One-colour</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{a^b (1\varepsilon_0 - a')^a}{b^a (1\varepsilon_0 - a')^a}$</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{1c_1\varepsilon_0 - a'}{a'}$</td>
</tr>
<tr>
<td>Red-coloured added as Ox.</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{a^b (1\varepsilon_0 - a')^a}{b^a (1\varepsilon_0 - a')^a}$</td>
<td>$E = E_i^0 + \frac{0.06}{n_i} \log \frac{1c_1\varepsilon_0 - a'}{a'}$</td>
</tr>
</tbody>
</table>

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: $n_x (E - E_r^0)/0.06$ and $n_x (E - E_i^0)/0.06$.

![Fig. 1. The diagram indicating the dependece of systematic error of end-point in redox titrations on the potential values of the systems](image-url)
TABLE 2. The transition potentials for redoximetric titrations

<table>
<thead>
<tr>
<th>Indicator</th>
<th>General equation</th>
<th>Simplified equation for $a=b=1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-colour</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{a^{(A')}^{a} (I^e_0)^{b-a}}{(aC_1^e_0 - bA')^b}$</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{A'}{I^e_0}^\frac{A}{A}$</td>
</tr>
<tr>
<td>Ox-coloured</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{b^{(A')}^{a} (I^e_0)^{b-a}}{(bC_1^e_0 - bA')^b}$</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{I^e_0}{I^e_0}^\frac{A}{A}$</td>
</tr>
<tr>
<td>Red-coloured</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{E^R_{a} (aC_1^e_0)^{a-b}}{E^R_{b} (bC_1^e_0)^{a-b}}$</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{E^R_{a}}{E^R_{b}}$</td>
</tr>
<tr>
<td>Ox-coloured</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{E^R_{a} (aC_1^e_0)^{a-b}}{E^R_{b} (bC_1^e_0)^{a-b}}$</td>
<td>$E = E^o + \frac{0.06}{n_I} \log \frac{E^R_{a}}{E^R_{b}}$</td>
</tr>
</tbody>
</table>

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$_2$SO$_4$, $E_m = 0.88$ V and for the titrant $E^o = 1.143$ V, thus $n_r(E-E^o)/0.06 = 4.7$ being not a decisive factor for the error magnitude. Therefore because $n_x(E-E^o)/0.06$ should not be greater than -3, i.e. $E_x < 0.70$ 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$_2$SO$_4$, $E_m = 0.82$ V and for the titrant $E^o = 1.00$ V, thus $n_r(E-E^o)/0.06 = 3.0$ and to keep the error at the level 0.1% the value of $n_x(E-E^o)/0.06 < 3.0$ i.e. $E_x < 0.64$ V.

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

Example 2: When $n_r = n_x = 1$, and $E^o_m = 0.9$ V, $E^o_r = 0.12$ 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 \( n_T \cdot (E - E_0^T)/0.06 \leq -4 \), thus \( E \leq 0.66 \) V.

From the analyte condition \( n_x \cdot (E - E_0^x)/0.06 \leq -4 \), thus \( E \geq 0.36 \) V so finally
\( 0.36 \leq E < 0.66 \) 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

\[
B = \frac{(V_T + V_x)n_T}{C_I n_T}
\]

For pseudoreversible, and so more for irreversible, this correction cannot be estimated precisely. It depends in a great extent 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**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>General equation</th>
<th>Simplified equation for ( a=b=1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-colour</td>
<td>( \Delta V = \frac{BA}{EC_0} )</td>
<td>( \Delta V = \frac{BA}{EC_0} )</td>
</tr>
<tr>
<td>Ox-coloured added as Red.</td>
<td>( \Delta V_1 = \frac{B}{a(1 + \frac{C_I}{EC_0})} )</td>
<td>( \Delta V_1 = B(1 + \frac{C_I}{EC_0}) )</td>
</tr>
<tr>
<td>One-colour</td>
<td>( \Delta V = \frac{B}{a(1 + \frac{C_I}{EC_0})} )</td>
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</tr>
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<td>( \Delta V_1 = B(1 + \frac{C_I}{EC_0}) )</td>
</tr>
<tr>
<td>One-colour</td>
<td>( \Delta V = \frac{B}{a(1 + \frac{C_I}{EC_0})} )</td>
<td>( \Delta V_1 = B(1 + \frac{C_I}{EC_0}) )</td>
</tr>
<tr>
<td>Red-coloured added as Red.</td>
<td>( \Delta V_1 = \frac{B}{a(1 + \frac{C_I}{EC_0})} )</td>
<td>( \Delta V_1 = B(1 + \frac{C_I}{EC_0}) )</td>
</tr>
<tr>
<td>One-colour</td>
<td>( \Delta V = \frac{B}{a(1 + \frac{C_I}{EC_0})} )</td>
<td>( \Delta V_1 = B(1 + \frac{C_I}{EC_0}) )</td>
</tr>
<tr>
<td>Red-coloured added as Ox.</td>
<td>( \Delta V_1 = \frac{B}{a(1 + \frac{C_I}{EC_0})} )</td>
<td>( \Delta V_1 = B(1 + \frac{C_I}{EC_0}) )</td>
</tr>
<tr>
<td>Two-colour</td>
<td>( \Delta V = \frac{BM \cdot C_I}{a \cdot EC_0 + b \cdot EC_R} )</td>
<td>( \Delta V_1 = \frac{BM \cdot C_I}{EC_0 + EC_R} )</td>
</tr>
<tr>
<td>added as Red.</td>
<td>( \Delta V_1 = \frac{BM \cdot C_I}{a \cdot EC_0 + b \cdot EC_R} )</td>
<td>( \Delta V_1 = \frac{BM \cdot C_I}{EC_0 + EC_R} )</td>
</tr>
<tr>
<td>Two-colour</td>
<td>( \Delta V = \frac{BM \cdot C_I}{a \cdot EC_0 + b \cdot EC_R} )</td>
<td>( \Delta V_1 = \frac{BM \cdot C_I}{EC_0 + EC_R} )</td>
</tr>
<tr>
<td>added as Ox.</td>
<td>( \Delta V_1 = \frac{BM \cdot C_I}{a \cdot EC_0 + b \cdot EC_R} )</td>
<td>( \Delta V_1 = \frac{BM \cdot C_I}{EC_0 + EC_R} )</td>
</tr>
</tbody>
</table>
TABLE 4. The reagent consumption error for reductimetric titrations

<table>
<thead>
<tr>
<th>Indicator</th>
<th>General equation</th>
<th>Simplified equation for a=b=1</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-colour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ox-coloured</td>
<td>$\Delta V_I = - \frac{BA'}{al \varepsilon_0}$</td>
<td>$\Delta V_I = - \frac{BA'}{l \varepsilon_0}$</td>
</tr>
<tr>
<td>added as Red.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>One-colour</td>
<td>$\Delta V_I = \frac{B}{l} \left( \frac{A'}{l \varepsilon_R} - C_I \right)$</td>
<td>$\Delta V_I = \frac{B}{l} \left( C_I - \frac{A'}{l \varepsilon_R} \right)$</td>
</tr>
<tr>
<td>Ox-coloured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>added as Ox.</td>
<td>$\Delta V_I = \frac{B}{l} \left( C_I - \frac{A'}{l \varepsilon_R} \right)$</td>
<td>$\Delta V_I = \frac{B}{l} \left( A' - C_I \right)$</td>
</tr>
<tr>
<td>One-colour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red-coloured</td>
<td>$\Delta V_I = \frac{B}{b} \left( \frac{A}{l \varepsilon_R} - C_I \right)$</td>
<td>$\Delta V_I = \frac{B}{b} \left( C_I - \frac{A}{l \varepsilon_R} \right)$</td>
</tr>
<tr>
<td>added as Red.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>One-colour</td>
<td>$\Delta V_I = \frac{B}{b} \left( \frac{A}{l \varepsilon_R} - C_I \right)$</td>
<td>$\Delta V_I = \frac{B}{b} \left( A' - \frac{A}{l \varepsilon_R} \right)$</td>
</tr>
<tr>
<td>Red-coloured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>added as Ox.</td>
<td>$\Delta V_I = \frac{B}{b} \left( \frac{A}{l \varepsilon_R} - C_I \right)$</td>
<td>$\Delta V_I = \frac{B}{b} \left( A' - C_I \right)$</td>
</tr>
<tr>
<td>Two-colour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>added as Red.</td>
<td>$\Delta V_I = \frac{B}{b} \left( \frac{a \varepsilon_0 C_I}{l \varepsilon_R a \varepsilon_0} - C_I \right)$</td>
<td>$\Delta V_I = \frac{B}{b} \left( C_I - \frac{a \varepsilon_0 C_I}{l \varepsilon_R a \varepsilon_0} \right)$</td>
</tr>
<tr>
<td>Two-colour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>added as Ox.</td>
<td>$\Delta V_I = \frac{B}{b} \left( \frac{a \varepsilon_0 C_I}{l \varepsilon_R a \varepsilon_0} \right)$</td>
<td>$\Delta V_I = \frac{B}{b} \left( C_I - \frac{a \varepsilon_0 C_I}{l \varepsilon_R a \varepsilon_0} \right)$</td>
</tr>
</tbody>
</table>

REFERENCES

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

\[ \text{Free base} \]
Pseudoreversible indicator

RED: colourless
OX: violet
RERED: pale greenish

Transition potential (Ref. 1) for indicator conc. \( \sim 5 \times 10^{-5} \text{M} \):

For oxidimetric titrations: in \( 0.5 \text{M } \text{H}_2\text{SO}_4 \) 0.76 V
The value was obtained in titration of \( \text{Fe}^{3+} \) with \( \text{Cr}_2\text{O}_7^{2-} \).

Formal half-oxidation potential for indicator conc. \( 5 \times 10^{-4} \text{M} \):
in \( 1.5 - 9.0 \text{M } \text{H}_2\text{SO}_4 \) 0.766 V (Ref. 2) 0.76 V (Refs. 3, 4)

Protolytic reactions

For reduced form: for \( =\text{NH}_2^+ \) \( pK_a = 0.78 \) spectrophot. (Ref. 2)
0.76 spectrophot. (Ref. 4)
0.79 spectrophot. (Ref. 5)

Spectrophotometric characteristics:

Initial reduced form - no absorption in VIS
Oxidized form: \( \lambda_{\text{max}}^{\text{VIS}} = 565 \text{ nm } \) (violet), \( \lambda_{\text{max}} = 2.25 \times 10^4 \) in \( 2 \text{M } \text{H}_2\text{SO}_4 \) (Ref. 6)
calculated for molarit of the reduced form.

Half-life time (without excess of oxidant) 188 min in \( 2 \text{M } \text{H}_2\text{SO}_4 \) (Ref. 6).
The colour is more stable in more strongly acid solutions.

Reaction mechanism:
The following mechanism, in aqueous solutions of \( \text{H}_2\text{SO}_4 \) 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. \( \text{H}_2\text{SO}_4 \) is diluted and crystallized in the \( \text{CO}_2 \) atmosphere (Ref. 6).

Indicator addition may be achieved using 1% solution in conc. \( \text{H}_2\text{SO}_4 \), not containing \( \text{NO}_3^- \) in amount about 3 drops.

Condition of titrations. Usually titration can be done in 1-4M \( \text{H}_2\text{SO}_4 \) or HCl, at room temperature.

Table of applications

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium(VI)</td>
<td>Fe(II)</td>
<td>1-2M ( \text{H}_2\text{SO}_4 ) in presence of ( \text{H}_3\text{PO}_4 )</td>
<td>1</td>
</tr>
<tr>
<td>Vanadium(V)</td>
<td>Fe(II)</td>
<td>0.5-1M ( \text{H}_2\text{SO}_4 ) in presence of ( \text{H}_3\text{PO}_4 )</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Mo(V)</td>
<td>2-3M HCl</td>
<td>8</td>
</tr>
<tr>
<td>Tin(II)</td>
<td>Cr(VI), V(V)</td>
<td>3-3.5M HCl in carbon dioxide atmosphere</td>
<td>9</td>
</tr>
</tbody>
</table>
Redox indicators. Characteristics and applications

Table of applications Cont.

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic(III)</td>
<td>Cr(VI)</td>
<td>1-2M H₂SO₄</td>
<td>10</td>
</tr>
<tr>
<td>Iodine(VII)</td>
<td>Sb(III), As(III)</td>
<td>0.05M H₂SO₄</td>
<td>11, 12</td>
</tr>
<tr>
<td></td>
<td>Fe(II)</td>
<td>0.5M H₂SO₄</td>
<td></td>
</tr>
</tbody>
</table>

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

REFERENCES

2. A. Hanulicki and S. Giab - unpublished data.

2. DIPHENYLAMINE-4-SULPHONIC ACID

![Structure of DIPhenylamine-4-Sulphonic Acid]

Pseudoreversible indicator

| RED: colourless |
| OX : red-violet |
| HERED: pale greenish |

Transition potential in H₂SO₄ for indicator conc. ~10⁻⁵ M

For oxidimetric titrations:
- 0.1M 0.81 V (Ref. 1)
- 0.5M 0.85 V (Ref. 1)
- 1.0M 0.83 V (Refr. 1, 2, 3)
- 2.0M 0.80 V (Refr. 1, 2)
- 4.0M 0.77 V (Ref. 1)
- 8.0M 0.71 V (Ref. 1)

The values were obtained in titration of Fe²⁺ with Cr₂O₇²⁻.

Formal (half-oxidation) potential for indicator conc. ~10⁻⁵ M.

- in 1M H₂SO₄ 0.85 V (Ref. 4)
- in 0.4-2.5M H₂SO₄ 0.81 V (Ref. 5)

Protoplolytic reactions

For reduced form: \( \text{NH}_2^+ \) \( pK_a = 1.23 \) spectrophot. (Ref. 6)

For oxidized form: \( \text{SO}_3^2- \) \( pK_a = 2.48 \) potentiometric (Ref. 5)

Spectrophotometric characteristics:

Initial reduced form - no absorption in VIS

Oxidized form (Ref. 5) - \( \lambda_{max} = 365 \text{ nm} \), \( \epsilon_{max} = 7.9 \times 10^3 \) in 1M H₂SO₄

\[ \epsilon_{max} = 8.7 \times 10^3 \] in 2M H₂SO₄

\[ \epsilon_{max} = 12.7 \times 10^3 \] in 4M H₂SO₄
calculated for molar concentration of the reduced form.

Half-life time (indicator solution and stoichiometric amount of oxidant) in
1 M H₂SO₄ = 13 min; in 2 M H₂SO₄ = 30 min; in 4 M H₂SO₄ = 220 min.

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

\[
\text{HO}_3\text{S}^+ \text{NH}_2 \rightarrow \rightarrow \frac{1}{2} \text{HO}_3\text{S}^+ \text{NH} \cdots \text{NH} \cdots \text{NH} \cdots \text{SO}_3\text{H}
\]

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

\[
\text{HO}_3\text{S}^+ \text{NH} = \cdots \text{NH} \cdots \text{NH} \cdots \text{SO}_3\text{H}
\]

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 H₂SO₄ in CO₂ 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

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichromate</td>
<td>Fe(II)</td>
<td>0.5-1.75M H₂SO₄ in presence of H₃PO₄</td>
<td>9, 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>indirect determination of Cu⁺,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>after addition of excess of Fe(III)</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>indirect determination of ClO₃⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>after addition of excess of Fe(II)</td>
<td>12</td>
</tr>
<tr>
<td>Vanadium(V)</td>
<td>Fe(II)</td>
<td>0.25-0.5M H₂SO₄ in presence of H₃PO₄</td>
<td>13</td>
</tr>
</tbody>
</table>

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

### REFERENCES

5. A. Hulanicki and S. Gląb - unpublished data

3. N-PHENYLANTHRANILIC ACID
2-carboxy-diphenylamine

![Chemical structure]

Pseudoreversible indicator
- RED: colourless
- OX: purple
- RERED: pale greenish

Transition potential in H₂SO₄ for indicator conc. ~ 10⁻⁵M

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) - unreliable values
- 2M: 0.885 V (Ref. 1)
- 3M: 0.87 V (Ref. 1)

The values were obtained in titration of Fe²⁺ with Cr₂O₇⁻².

Formal (half-oxidation) potential in H₂SO₄ for indicator conc. 5x10⁻⁵M (Ref. 3)
- 3.0M: 0.91 V
- 4.0M: 0.89 V
- 4.9M: 0.87 V

Protolytic reactions:
For reduced form: for =NH⁺₃ pKₐ = -1.41 spectrophot. (Ref. 4)
-1.31 spectrophot. (Ref. 3)
-1.28 solubil. (Ref. 7)
-1.35 spectrophot. (Ref. 7)

for -COOH pKₐ = 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, ε_max = 8.7x10³ in 0.5M H₂SO₄
ε_max = 1.45x10⁴ in 1M H₂SO₄
ε_max = 2.1x10⁴ in 4M H₂SO₄

Re-reduced form (Refs. 1, 3, 8) λ_max = 434 nm, ε_max = 1.2x10⁴ in 2-12M H₂SO₄

calculated for molarity of the reduced form.

Half-life time (Refs. 3, 8) (indicator solution and stoichiometric amount of oxidant) in 0.5M H₂SO₄ - 5 min; in 1M H₂SO₄ - 7 min; in 2M H₂SO₄ - 10 min; in 4M H₂SO₄ - 15 min. The solution is more stable for higher concentrations of H₂SO₄.

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 H₂SO₄ in the atmosphere of CO₂.

Indicator solution may be prepared as 0.1% solution in 0.005M NaOH (Ref. 2). The 0.1% solution in equimolar solution of Na₂CO₃ (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 H₂SO₄ at room temperature.

<table>
<thead>
<tr>
<th>Table of applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titrant</td>
</tr>
<tr>
<td>Cerium(IV)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Chromium(VI)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Vanadium(V)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Iron(II)</td>
</tr>
<tr>
<td>Vanadium(III)</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

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

Recommended for titrations of iron(II) and Fe(CN)₆⁻⁶, with cerium(IV) as titrant.
REFERENCES


4. VARIAMINE BLUE

4-amino-4'-methoxy-diphenylamine

\[ \text{Reversible indicators: RED: colourless} \]
\[ \text{OX : violet blue} \]

Transition potential for oxidimetric titrations

<table>
<thead>
<tr>
<th>Indicator conc.</th>
<th>pH 2</th>
<th>pH 2.1</th>
<th>pH 2.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-4}) M</td>
<td>0.575 V</td>
<td>0.55 V</td>
<td>0.54 V</td>
</tr>
<tr>
<td>(3.5 \times 10^{-4}) M</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values were obtained in titration of \(\text{Fe}^{2+}\) 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 \(=\text{NH}_2^+\) \(pK_a = 0.13\) spectrophot. (Ref. 3)

For oxidized form: for \(=\text{NH}_2^+\) \(pK_a = 5.9\) spectrophot. (Ref. 4)

Spectrophotometric characteristics:

Initial reduced form - no absorption in VIS

Oxidized form: for the oxidant: indicator ratio 1:1

\(\lambda_{\text{max}} = 570-575 \text{ nm (violet blue)}, \quad \varepsilon_{\text{max}} = 6.7 \times 10^3 \), \(\text{pH 2-6 (Refs. 1, 5)}\)

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

\(\lambda_{\text{max}} = 530 \text{ nm (violet red)}, \quad \varepsilon_{\text{max}} = 7 \times 10^3 \), \(\text{pH 2-6 (Refs. 6)}\)

\(\lambda_{\text{max}} = 570-575 \text{ nm (violet blue)}, \quad \varepsilon_{\text{max}} = 6.7 \times 10^3 \), \(\text{pH 2-6 (Refs. 1, 5)}\)

\(\lambda_{\text{max}} = 530 \text{ nm (violet red)}, \quad \varepsilon_{\text{max}} = 7 \times 10^3 \), \(\text{pH 2-6 (Refs. 6)}\)
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 (Ref. 7,8).

\[
\begin{align*}
H_2N^+ & \quad \text{NH} \quad \text{OCH}_3 \\
\text{e}^- & \quad \leftrightarrow \\
H_2N^+ & \quad \text{NH} \quad \text{OCH}_3
\end{align*}
\]

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

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

\[
\begin{align*}
H_2N^+ & \quad \text{NH} \quad \text{OCH}_3 \\
\text{H}_2O, -\text{NH}_4^+ & \quad \leftrightarrow \\
H_2N^+ & \quad \text{NH} \quad \text{OCH}_3
\end{align*}
\]

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).

\[
\begin{align*}
H_2N^+ & \quad \text{NH} \quad \text{OCH}_3 \\
\text{H}_2O & \quad \leftrightarrow \\
H_2N & \quad \text{NH} \quad \text{OCH}_3
\end{align*}
\]

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$_2$S$_2$O$_4$ 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:

<table>
<thead>
<tr>
<th>Indicator form</th>
<th>Addition of the form</th>
<th>Amount needed</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variamine Blue</td>
<td>1% ethanolic soln.</td>
<td>2-3 drops</td>
<td></td>
</tr>
<tr>
<td>Variamine Blue HCl</td>
<td>0.5% aqueous soln.</td>
<td>2-6 drops</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>solid mixture with NaCl (1:300)</td>
<td>20-30 mg</td>
<td></td>
</tr>
<tr>
<td>Variamine Blue 1/2H$_2$SO$_4$</td>
<td>0.2% aqueous soln.</td>
<td>3-6 drops</td>
<td>1 week</td>
</tr>
<tr>
<td></td>
<td>solid mixture with Na$_2$SO$_4$ (1:100)</td>
<td>20-30 mg</td>
<td>stable</td>
</tr>
<tr>
<td>Variamine Blue CH$_3$COOH</td>
<td>1% soln in 20%CH$_3$COOH</td>
<td>3-6 drops</td>
<td>3 weeks</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid</td>
<td>Ag(I)</td>
<td>at pH 4.5</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Hg(II)</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Fe(III), J₂</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Fe(CN)₃⁻/₆</td>
<td>at pH &gt;4.5</td>
<td>14</td>
</tr>
<tr>
<td>Iron(II)</td>
<td>Ag(I)</td>
<td>in presence of fluoride</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>V(V)</td>
<td>in presence of phosphate</td>
<td>16</td>
</tr>
<tr>
<td>Vanadium(V)</td>
<td>Fe(II)</td>
<td>in presence of fluoride</td>
<td>17</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td></td>
<td>or phosphate in acid soln.</td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>Pb(II), Cd(II)</td>
<td>in presence of</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>Fe(CN)₃⁻/₆/Fe(CN)₄⁻/₆</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe(III)</td>
<td>in presence of Fe(II)</td>
<td>19, 20</td>
</tr>
<tr>
<td></td>
<td>Cu(II)</td>
<td>(monochloroacetate buffer)</td>
<td>21, 22</td>
</tr>
<tr>
<td></td>
<td>V(V)</td>
<td>in presence of excess of</td>
<td>23, 24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe(II), pH 1.7-2</td>
<td></td>
</tr>
<tr>
<td>Ferro cyanide</td>
<td>Bi(III)</td>
<td>in presence of Fe(CN)₃⁻/₆</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Hg(I)</td>
<td></td>
<td>27</td>
</tr>
</tbody>
</table>

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

REFERENCES

2. A. Hulanioki and S. Giab, unpublished data.
5. **4-AMINO-4'-METHYLDIPHENYLAMINE**

![Chemical Structure](image)

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 0.34 V
  - For indicator conc., $2.5 \times 10^{-4}$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): $\text{pK}_a^1 = -0.08$ (spectrophot.)
  - For $-\text{NH}_2^+$ $\text{pK}_a^2 = 5.15$ (spectrophot.)
  - $\text{pK}_a^2 = 5.09$ (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), $\xi_{max} = 6060$.

**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):

![Reaction Mechanism](image)

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

**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 $5 \times 10^{-3}$M aqueous solution of hydrochloride (Ref. 1).

**Conditions of titration.**
- In the pH range 1.5-5.5 at room temperature.
### Table of applications

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron(II)</td>
<td>V(V)</td>
<td>in presence of (H_3PO_4) at pH 2-2.6</td>
<td>1</td>
</tr>
<tr>
<td>EDTA</td>
<td>Zn(II)</td>
<td>in presence of (Fe(CN)_6^{3-}/Fe(CN)_6^{4-})</td>
<td>1</td>
</tr>
</tbody>
</table>

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

### REFERENCES


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)**

<table>
<thead>
<tr>
<th>Conc.</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M</td>
<td>0.91 V</td>
</tr>
<tr>
<td>1.5M</td>
<td>0.91 V</td>
</tr>
<tr>
<td>3M</td>
<td>0.86 V</td>
</tr>
<tr>
<td>3.5M</td>
<td>0.82 V</td>
</tr>
</tbody>
</table>

**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: \(\lambda_{max} = 560 \text{ nm}\)

\(\varepsilon_{max} = 2.82 \times 10^4\) in 0.5M \(H_2SO_4\)

\(\varepsilon_{max} = 3.52 \times 10^4\) in 2M \(H_2SO_4\)

\(\varepsilon_{max} = 3.50 \times 10^4\) in 4M \(H_2SO_4\)

\(\varepsilon_{max} = 4.10 \times 10^4\) 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 $\text{H}_2\text{SO}_4$. Titrations at room temperature.

Table of applications

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichromate</td>
<td>Fe(II)</td>
<td>in 1-2M $\text{H}_2\text{SO}_4$, $\text{H}_3\text{PO}_4$ as complexing agent</td>
<td>1, 2</td>
</tr>
</tbody>
</table>

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

REFERENCES

1. A. Hulanioki and S. Głąb - unpublished data

7. o-DIANISIDINE

3,3'-dimethoxybenzidine

\[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{OCH}_3 \\
\text{OCH}_3 \\
\text{NH}_2
\end{array}
\]

Reversible indicator: RED: colourless
OX: red

Transition potential in $\text{H}_2\text{SO}_4$ (Ref. 1) for indicator conc. $\sim 10^{-5}$M.

For oxidimetric titrations:

- 0.1M $\text{H}_2\text{SO}_4$:
  - 0.75 V
  - 0.80 V
- 0.5M $\text{H}_2\text{SO}_4$:
  - 0.79 V
  - 0.81 V
- 4.0M $\text{H}_2\text{SO}_4$:
  - 0.78 V
- 10.0M $\text{H}_2\text{SO}_4$:
  - 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 $\text{H}_2\text{SO}_4$ (Ref. 2)

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

Protolytic reactions (Ref. 3)

For reduced form: $\text{pK}_a = 2.83$
$\text{pK}_{a_2} = 4.05$

Spectrophotometric characteristics (Ref. 4)

Initial reduced form - no absorption in VIS

Oxidized form in 2M $\text{H}_2\text{SO}_4$ has two absorption maxima
- $\lambda_{\text{max}} = 454$ nm
- $\lambda_{\text{max}} = 510$ nm

$\xi_{\text{max}} = 3.1 \times 10^4$
$\xi_{\text{max}} = 2.3 \times 10^4$

Half-life time 190 min in 2M $\text{H}_2\text{SO}_4$.

Reaction mechanism. The following reactions in aqueous solutions of $\text{H}_2\text{SO}_4$ 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

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>Au(III)</td>
<td>neutral or weakly acid</td>
<td>5</td>
</tr>
<tr>
<td>Ferroicyanide</td>
<td>Sn(II)</td>
<td>9M HCl</td>
<td>6</td>
</tr>
<tr>
<td>Ferrocyanide</td>
<td>Bi(III)</td>
<td>in acetic acid media in presence of small amount of ferroicyanide</td>
<td>7</td>
</tr>
<tr>
<td>Zinc(II)</td>
<td>Ferroicyanide</td>
<td>in presence of small amount of ferroicyanide</td>
<td>8</td>
</tr>
<tr>
<td>Silver(I)</td>
<td>I⁻</td>
<td>in presence of small amount of iodine</td>
<td>2</td>
</tr>
</tbody>
</table>

Recommended for titration of Zn²⁺ with Fe(CN)₆⁴⁻.

REFERENCES


8. 3,3'-DIMETHYLNAPHTHIDINE

3,3'-Dimethyl-4,4'-diamino-1,1'-dinaphthyl
Reversible indicator: RED: colourless
OX: purple red

Transition potential in H₂SO₄ solution (Ref. 1) for indicator conc. ~10⁻⁵ M.

For oxidimetric titrations: in 0.1–4.0 M 0.70–0.71 V

The value were determined using dichromate as a titrant. For cerium(IV) titrations in 4.0 M H₂SO₄ = 0.67 V.

Protolytic reactions
For reduced form: pKₐ₁ = 2.62 spectrophot. (Ref. 3)
pKₐ₂ = 3.33 spectrophot. (Ref. 3)

Spectrophotometric characteristics:
Initial reduced form - no absorption in VIS.
Oxidized form: λₘₐₓ=550 nm (purple red), εₘₐₓ=3x10⁴ 1M H₂SO₄ (Ref. 1)
λₘₐₓ=560 nm εₘₐₓ=3x10⁴ 4M H₂SO₄ (Ref. 1)
λₘₐₓ=543 nm εₘₐₓ=3.5x10⁴ 2M H₂SO₄ (Ref. 4)

Half-life time in 2M H₂SO₄ = 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 colorless.

**Condition of titrations.** Solutions should be acidic or weakly acidic. Titration at room temperature.

**Table of applications**

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocyanide</td>
<td>Cd(II), Ca(II)</td>
<td>in presence of Fe(CN)$_6^{3-}$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Ge(III)</td>
<td>$\ddag$ $\ddag$ $\ddag$ $\ddag$</td>
<td>8</td>
</tr>
<tr>
<td>Zinc(II)</td>
<td>In(III)</td>
<td>in presence of Fe(CN)$_6^{3-}$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>after addition of excess of K$_4$Fe(CN)$_6$</td>
<td></td>
</tr>
<tr>
<td>Ferricyanide</td>
<td>Sn(II)</td>
<td>in 9M HCl</td>
<td>10</td>
</tr>
<tr>
<td>EDTA</td>
<td>Zn(II)</td>
<td>in presence of Fe(CN)$_6^{3-}$</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe(CN)$_6^{4-}$ at pH 5</td>
<td></td>
</tr>
<tr>
<td>Zinc(II)</td>
<td>Zn(II), Cd(II)</td>
<td>in presence of Fe(CN)$_6^{3-}$</td>
<td>12</td>
</tr>
<tr>
<td>Pb(II), Fe(III)</td>
<td>Fe(CN)$_6^{4-}$ after addition of</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>Ge(III)</td>
<td>excess EDTA, at pH 5</td>
<td>13</td>
</tr>
<tr>
<td>Al(III)</td>
<td>R.E.</td>
<td></td>
<td>14</td>
</tr>
</tbody>
</table>

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

**REFERENCES**


9. 3,3'-DIMETHYLNAPHTHIDINEDISULPHONIC ACID

Not identified substitution of two sulphonate groups.

**Reversible indicator:** RED: colourless

OX : purple

**Transition potential in H$_2$SO$_4$ (Ref. 1) for indicator conc. $\sim$10$^{-5}$M.
For oximetric titrations:

<table>
<thead>
<tr>
<th>Titration</th>
<th>Analyte</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M</td>
<td>0.82 V</td>
<td>2.0M</td>
</tr>
<tr>
<td>0.5M</td>
<td>0.81 V</td>
<td>4.0M</td>
</tr>
<tr>
<td>1.0M</td>
<td>0.80 V</td>
<td>8.0M</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>pH</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.838 V</td>
</tr>
<tr>
<td>0.28</td>
<td>0.796 V</td>
</tr>
<tr>
<td>0.50</td>
<td>0.802 V</td>
</tr>
<tr>
<td>0.79</td>
<td>0.806 V</td>
</tr>
<tr>
<td>1.00</td>
<td>0.784 V</td>
</tr>
</tbody>
</table>

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**

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocyanide</td>
<td>Zn(II), Cd(II)</td>
<td>in presence of small amount of Fe(CN)₆⁻⁻ in 2% (NH₄)₂SO₄ (or) Ga(III) in presence of small amount of Fe(CN)₆⁻⁻ in 5% ethanol</td>
<td>2</td>
</tr>
</tbody>
</table>

Recommended for titration of Zn²⁺ with Fe(CN)₆⁴⁻.

**REFERENCES**


10. METHYLENE BLUE

Bis-3,9-dimethylamino phenaothionium chloride

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{S} & \\
\text{N} & \\
\text{N(CH}_2\text{)} & \\
\end{align*}
\]

Usually as chloride of the oxidized form

**Reversible indicator:**

OK: blue

RED: colourless

**Transition 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 $\text{pH} = 0$ (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): $\lambda_{\text{max}} = 662$ nm, $\varepsilon_{\text{max}} = 2.5 \times 10^4$

**Reaction mechanism:** One two-electron step

![Reaction mechanism](image)

When the redox reaction is carried out in $\text{H}_2\text{SO}_4 > 10\text{M}$ 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**

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>Ti(III)</td>
<td>in 0.1M $\text{H}_2\text{SO}_4$ at 60°C in mixture with Fe(II) the second end-point with ferroin</td>
<td>6</td>
</tr>
<tr>
<td>Cerium(IV)</td>
<td>Ti(III)</td>
<td>as a permanganate titration</td>
<td>7</td>
</tr>
<tr>
<td>Iron(III)</td>
<td>V(III)</td>
<td>in 0.2M HCl with Cu$^{2+}$ as catalyst</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Ti III</td>
<td>in 25% tartaric acid</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>U(IV)</td>
<td>in 0.2-0.3M HCl, temp. 98-100°C</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Sn(II)</td>
<td>in 4-5M HCl, under CO$_2$</td>
<td>11</td>
</tr>
<tr>
<td>Ferrocyanide</td>
<td>U(IV)</td>
<td>in 2.5-4.0M KOH</td>
<td>12</td>
</tr>
<tr>
<td>Iron(II)</td>
<td>Mo(IV)</td>
<td>in 0.5M HCl in presence of citric acid, temp. ~90°C</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Mo(VI)</td>
<td>in 11.5-13.0M $\text{H}_3\text{PO}_4$</td>
<td>14</td>
</tr>
</tbody>
</table>
### Table of applications cont.

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron(II)</td>
<td>V(IV)</td>
<td>in 10.5M H₃PO₄</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>U(VI)</td>
<td>in 11.6M H₃PO₄</td>
<td>16</td>
</tr>
<tr>
<td>Chromium(II)</td>
<td>Fe(III)</td>
<td>in 1.5M H₂SO₄</td>
<td>17</td>
</tr>
<tr>
<td>Vanadium(II)</td>
<td>Fe(III)</td>
<td>in 1.0M H₂SO₄</td>
<td>18</td>
</tr>
</tbody>
</table>

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

### REFERENCES


### 11. FERROIN

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

![Fe⁡²⁺<br>³<br> as a solution of sulphate or perchlorate](image)

**Reversible indicator:** RED: orange-red  <br>OX : pale-blue  

**Transition potential:** for oxidimetric titrations  

<table>
<thead>
<tr>
<th>pH</th>
<th>Potential (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1M H₂SO₄</td>
<td>1.06 (Ref. 1)</td>
<td></td>
</tr>
<tr>
<td>2.0M HCl</td>
<td>1.065 (Ref. 2)</td>
<td></td>
</tr>
<tr>
<td>4.0M HCl</td>
<td>1.026 (Ref. 2)</td>
<td></td>
</tr>
</tbody>
</table>
Formal (half-oxidation) potentials in \( \text{H}_2\text{SO}_4 \)

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): 
\[
E = 1.068 + 0.442\, H_0
\]
where \( H_0 \) denotes Hammett's acidity function.

Protolytic reactions and related equilibria:

Acid dissociation of 1,10-phenanthroline

\[
\begin{align*}
pK_{a1} &= -1.6 \quad (\text{spectrophot.}) \quad \text{(Ref. 7)} \\
pK_{a2} &= 4.92 \quad (\text{potentiom.}) \quad \text{(Ref. 8)} \\
pK_{a3} &= 4.95 \quad (\text{potentiom.}) \quad \text{(Ref. 9)} \\
pK_{a4} &= 4.93 \quad (\text{spectrophot.}) \quad \text{(Ref. 10)}
\end{align*}
\]

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) \( \lambda_{\text{max}} = 510 \text{ nm} \), \( \varepsilon_{\text{max}} = 1.11 \times 10^4 \)

Oxidized form (Ref. 13) \( \lambda_{\text{max}} = 590 \text{ nm} \), \( \varepsilon_{\text{max}} = 6 \times 10^2 \)

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 of water, containing 0.695 g \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \). 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 cm³.

Conditions of titrations. Usually in \( \text{H}_2\text{SO}_4 \) solutions from dilute up to 6M. The indicator reaction is rapid at room temperature.

Table of applications

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium(IV)</td>
<td>Fe(II)</td>
<td>in 1M ( \text{H}_2\text{SO}_4 )</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in 1M ( \text{H}_2\text{SO}_4 ), addition of excess of Fe(III) for indirect determination of Nb</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu(I)</td>
<td>17</td>
</tr>
<tr>
<td>As(III)</td>
<td></td>
<td>in 1M ( \text{H}_2\text{SO}_4 ), ( \text{OsO}_4 ) as catalyst</td>
<td>15</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td></td>
<td>in 1M ( \text{H}_2\text{SO}_4 )</td>
<td>18</td>
</tr>
<tr>
<td>Fe(CN)(_6)(^{4-})</td>
<td></td>
<td>in 2M ( \text{H}_2\text{SO}_4 )</td>
<td>19</td>
</tr>
</tbody>
</table>
Table of applications cont.

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN</td>
<td>20</td>
<td>also used for indirect determination of hydroxylamine</td>
<td></td>
</tr>
<tr>
<td>V(IV)</td>
<td>21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂O₄²⁻</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>in 1M HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron(II)</td>
<td>Ce(IV)</td>
<td>in 1.5M H₂SO₄, addition of excess of Ce(IV) for indirect determination</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>of H₃PO₂, H₃PO₃ reducing sugars</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te(IV)</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td>Fe(II)</td>
<td>in 5-6M H₂SO₄ (better results with 5,6-dimethylferroin)</td>
<td>25</td>
</tr>
<tr>
<td>U(IV)</td>
<td></td>
<td>in 5-5.5M H₂SO₄</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in 2-4M H₂SO₄</td>
<td>27</td>
</tr>
</tbody>
</table>

Recommended for titrations of iron(II) and Fe(CN)₃⁻ with cerium(IV) as titrant.

REFERENCES

2. J. A. Perez-Bustamante - unpublished data
12. NITROFERROIN

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

\[
\begin{array}{c}
\text{Fe}^{2+} \\
\text{3}
\end{array}
\]  

\[\text{as solution of sulphate}\]

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

Transition potential ---

Formal (half-oxidation) potential in H\(_2\)SO\(_4\) (Ref. 1)

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.26</td>
</tr>
<tr>
<td>1.0</td>
<td>1.25</td>
</tr>
<tr>
<td>2.0</td>
<td>1.22</td>
</tr>
<tr>
<td>4.0</td>
<td>1.12</td>
</tr>
</tbody>
</table>

In HClO\(_4\) at conc. range 4-8M the potential (accurate to \(\pm 4\) mV) is given by equation (Ref. 2):

\[E = 1.239 + 0.0552H_0\]

where \(H_0\) denotes Hammett's acidity function.

Protolytic reaction and related equilibria:

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

\[pK_a = 3.57\]  (potentiometric)  (Ref. 3)  
\[4.18\]  (spectrophotometric)  (Ref. 4)  
\[3.23\]  (spectrophotometric)  (Ref. 5)

Complex stability constants for reduced form: \(\log \beta_3 = 17.8\) (spectrophotometric) (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 form ---

Reaction mechanism: One one-electron step.

\[
\begin{array}{c}
\text{Fe}^{2+} \\
\text{3}
\end{array} \rightarrow_{-e} \begin{array}{c}
\text{Fe}^{3+} \\
\text{3}
\end{array}
\]

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\(_2\)O. 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 HNO₃ or HClO₄ media in determination involving cerium(IV).

Table of applications:

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium(IV)</td>
<td>C₂O₄²⁻</td>
<td>in 2M HClO₄</td>
<td>8, 9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in 0.5M HCl, HClO₄ or HNO₃</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>indirect determination of Ba precipitated as BaC₂O₄</td>
<td>11</td>
</tr>
<tr>
<td>As(III)</td>
<td></td>
<td>in 2M HClO₄, 0.004 as catalyst</td>
<td>12</td>
</tr>
<tr>
<td>Fe(II)</td>
<td></td>
<td>in 2M HClO₄</td>
<td></td>
</tr>
<tr>
<td>Hg(I)</td>
<td></td>
<td>in HClO₄; Mn(II), Ag(I) as catalyst, temp. 50-60°C</td>
<td>13</td>
</tr>
<tr>
<td>Oxalate</td>
<td>Ce(IV)</td>
<td>in 0.5M HNO₃ or HClO₄</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in 4M HClO₄ indirect detn. of H₃PO₄</td>
<td>15</td>
</tr>
</tbody>
</table>

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

REFERENCES

2. J. A. Perez-Bustamante - unpublished data

13. 5,6-DIMETHYLFERROIN

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

\[
\text{Fe}^{2+} \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{N}
\end{array}
\]

as solution of sulphate

Reversible indicator: RED: red
OX: yellow-green

Transition potential ---
Redox indicators. Characteristics and applications

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) \[ \lambda_{\text{max}} = 520 \text{ nm} \]
  \[ \varepsilon_{\text{max}} = 1.26 \times 10^4 \]
- Oxidized form:

The indicator is very stable in solutions.

Reaction mechanism. One one-electron step.

\[
\begin{array}{c}
\text{Fe}^{2+} \\
\text{Fe}^{3+}
\end{array}
\xrightarrow{\text{---}}
\begin{array}{c}
\text{H}_3\text{C} \quad \text{N} \\
\text{H}_3\text{C} \quad \text{N}
\end{array}
\]

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>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichromate</td>
<td>Fe(II)</td>
<td>in 1M $H_2SO_4$ or 1-2M HCl</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>U(IV)</td>
<td>in 1M HCl</td>
<td>5</td>
</tr>
</tbody>
</table>

Recommended for titration of Fe(II) with dichromate.

REFERENCES

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

[Chemical structure of TRIS-(2,2'-DIPYRIDYL)-IRON(II)-SULPHATE]

Reversible indicator: RED: red
OX: faint blue

Transition potential ---

Formal (half-oxidation) potential in H₂SO₄

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M</td>
<td>1.086 V</td>
</tr>
<tr>
<td>0.11M</td>
<td>1.062 V</td>
</tr>
<tr>
<td>1.0M</td>
<td>1.026 V</td>
</tr>
<tr>
<td>2.0M</td>
<td>1.00 V</td>
</tr>
<tr>
<td>4.0M</td>
<td>0.95 V</td>
</tr>
<tr>
<td>6.0M</td>
<td>0.88 V</td>
</tr>
<tr>
<td>10.0M</td>
<td>0.80 V</td>
</tr>
</tbody>
</table>

(Ref. 1); 1.069 V (Ref. 2); 1.023 V (Ref. 3)

Protolytic reaction and related equilibria

Acid dissociation of 2,2'-dipyridyl:

\[ \text{pK}_a^1 = -0.2 \]  
\[ \text{pK}_a^2 = 4.44 \]  
\[ \text{pK}_a^3 = 4.49 \]  
\[ \text{pK}_a^4 = 4.44 \] (spectrophot.)

Complex stability constants for reduced form:

\[ \log \beta_3 = 17.45 \] (pH-metric) (Ref. 6)
\[ \log \beta_3 = 17.45 \] (partition) (Ref. 8)
\[ \log \beta_3 = 16.94 \] (spectrophot.) (Ref. 7)

- for oxidized form:

\[ \log \beta_3 = 12.0 \] (potentiom.) (Ref. 9)

Spectrophotometric characteristics

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

Reaction mechanism. One one-electron step.

[Chemical reaction mechanism]

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 cm³ of water containing 0.695 g FeSO₄·7H₂O. This is 0.025M solution of the indicator in the sulphate form and 1 dpj is needed for titrations (Ref. 12). May be used also as a saturated solution of perchlorate, 1 cm³ for titration (Ref. 13).

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

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium(IV)</td>
<td>Fe(II)</td>
<td>in 1M H₂SO₄ or HCl</td>
<td>13, 14</td>
</tr>
<tr>
<td></td>
<td>Hydroquinone</td>
<td>in 1M H₂SO₄</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>V(IV)</td>
<td>in 12M CH₃COOH</td>
<td>16</td>
</tr>
</tbody>
</table>

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

REFERENCES


SUBJECT INDEX

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

According to analytes

- Aluminium(III) - 8
- Antimony(III) - 1
- Arsenic(III) - 1, 11, 12
- Bismuth(III) - 4, 7
- Cadmium(II) - 4, 8, 9
- Calcium(II) - 8
- Cerium(IV) - 11, 12
- Chromium(VI) - 1, 3
- Copper(II) - 4
- Ferricyanide - 4
- Ferrocyanide - 3, 7, 11
- Gallium(III) - 8, 9
- Gold(III) - 7
- Hydrogen peroxide - 11
- Hydroquinone - 14
- Indium(III) - 8
- Iodide - 7
- Iodine - 4
- Iron(II) - 1, 2, 3, 4, 5, 6, 11, 12, 13, 14
- Iron(III) - 4, 8, 10
According to titrants. Within each titrant the analytes are distinguished and corresponding indicator numbers are given.

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid</td>
<td>Ag(I), Fe(III), Fe(CN)$_6^{3-}$, Hg(II), I$_2$</td>
</tr>
<tr>
<td>Arsenic(III)</td>
<td>Cr(VI)</td>
</tr>
<tr>
<td>Cerium(IV)</td>
<td>As(III) - 11, 12; C$_2$O$_4^{2-}$ - 11, 12; Fe(II) - 3, 11, 12, 14; Fe(CN)$_6^{4-}$ - 3, 11; Hg(I) - 12; H$_2$O$_2$ - 11; Hydroquinone - 14; Ti(III) - 10; U(IV) - 14</td>
</tr>
<tr>
<td>Chromium(II)</td>
<td>Fe(III) - 10</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td>Fe(II) - 1, 2, 3, 4, 6, 11, 13; U(IV) - 3, 11, 13</td>
</tr>
<tr>
<td>EDTA - Cu(II)</td>
<td>Cd(II) - 4; Pb(II) - 4; Zn(II) - 4, 5, 8</td>
</tr>
<tr>
<td>Ferrocyanide</td>
<td>Sn(II) - 7, 8</td>
</tr>
<tr>
<td>Ferrocyanide</td>
<td>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</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>Au(III) - 7</td>
</tr>
<tr>
<td>Iodine(VII)</td>
<td>As(III), Fe(II), Sb(III) - 1</td>
</tr>
<tr>
<td>Iron(II)</td>
<td>Ag(I) - 4; Ce(IV) - 11; Cr(VI) - 3; Mo(IV) - 10; Mo(V) - 10; U(VI) - 10; V(IV) - 10; V(V) - 4</td>
</tr>
<tr>
<td>Iron(III)</td>
<td>Sn(II), Ti(III), U(IV), V(III) - 10</td>
</tr>
<tr>
<td>Manganese(VII)</td>
<td>Ti(III) - 10</td>
</tr>
<tr>
<td>Oxalate</td>
<td>Ce(IV) - 12</td>
</tr>
<tr>
<td>Silver(I)</td>
<td>I - 7</td>
</tr>
<tr>
<td>Tin(II)</td>
<td>Cr(VI), V(V) - 1</td>
</tr>
<tr>
<td>Vanadium(II)</td>
<td>Fe(III) - 10</td>
</tr>
<tr>
<td>Vanadium(V)</td>
<td>Fe(II) - 1, 2, 4, 5; Mo(V) - 1, 3; U(IV) - 3</td>
</tr>
<tr>
<td>Zinc(II)</td>
<td>Fe(CN)$_6^{3-}$ - 7, 8</td>
</tr>
</tbody>
</table>