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**RECOMMENDATIONS FOR PRESENTATION
OF DATA ON COMPLEXIMETRIC
INDICATORS. I. GENERAL**

Prepared for publication by

A. HULANICKI

S. GŁAB

M. GALUS

The University, Warsaw,
Poland

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RECOMMENDATIONS FOR PRESENTATION OF DATA ON COMPLEXIMETRIC INDICATORS. I. GENERAL

Adam Hulanicki, Stanisław Głąb and Małgorzata Galus

Institute of Fundamental Problems in Chemistry, University,
02-093 Warsaw, Poland

Abstract - Principles of analytical application of compleximetric indicators are presented. Relationship between equilibrium constants and the colour change of the indicator used in titrations have been discussed as a basis of a choice of the indicator, and conditions of its use.

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INTRODUCTION

Compleximetric titrations are well established methods of analysis and also serve as standard procedures (Refs. 1,2). The end points are determined, in several instances, instrumentally (e.g. by electroanalytical devices). However chemical indicators are the basis of widely used visual and spectrophotometric titration procedures, which are valued for their simplicity, low cost and rapidity. A large number of chemical substances may be used as indicators, but only a limited number of them finds widespread application and exhibit favourable properties (Refs. 3,4,5). In spite of the large amount of information on indicators, their physicochemical characteristics are in most cases incompletely described and what is worse is that many of the data are unreliable or are presented in such a form that they cannot be used as the basis for further development of new analytical procedures, or for improving existing ones. This situation is to some extent connected with insufficient and variable purity of commercial reagents. Therefore it was decided to specify clearly which characteristics of an indicator it is essential to describe and which should be given when papers on the subject are published.

This report consists of a short description of the general properties of indicators. The characteristics of some common indicators based on data in the literature will be presented in the next part. Such a compilation has a dual purpose - it points out which data can be considered as reliable,

⁺ **Members:** G. Ackermann (GDR), Yu. A. Bankovski (USSR), J. Bartos (France), R. Belcher (UK), G. den Boef (Netherlands), A. Hulanicki (Poland), J. Incezy (Hungary), N. Jordanov (Bulgaria), M. Kapel (UK), E. Lucena-Conde (Spain), F. Pellerin (France), M. Pesez (France), A. T. Pilipenko (USSR), F. J. Reidinger (USA), J. Ruzicka (Denmark), L. Sommer (Czechoslovakia), S. Siggia (USA), W. I. Stephen (UK), D. Thorburn Burns (UK), H. F. Walton (USA), E. Wänninen (Finland), H. Weisz (FRG); **National Representatives:** E. Bishop (UK), G. Duyckaerts (Belgium), S. B. Savvin (USSR);

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and where information is lacking or is presented in an incomplete form. This survey may stimulate other authors to undertake investigations to complete these data and to present information on new indicators in a more suitable form than is done at present. It is the intension to prepare such reports for triphenylmethane dyes, similar reports for azo dyes and some other types of indicators.

1. REMARKS ON THE ANALYTICAL CHARACTERISTICS OF COMPLEXIMETRIC INDICATORS

The action of indicators in visual compleximetric titrations is based on changing a particular optical property (absorption, fluorescence etc.) of the solution titrated in the conditions where the concentration of the free metal aquo ion approaches a defined borderline concentration level. This borderline concentration level should as closely as possible approach the concentration of the free metal aquo ion at the equivalence point of a particular titration reaction. The change of the optical property extends over a metal aquo ion concentration range which is often defined as the transition range.

The mechanism of the indicator reactions are based on several principles:

i - the indicator forms a coloured complex with the metal ion to be titrated. The uncomplexed indicator may be colourless (one-colour indicators) or coloured in its various protonated forms (two-colour indicators). Such indicators are sometimes called metallochromic indicators.

ii - When the complexation reaction of interest proceeds in another liquid phase (usually organic solvent) in equilibrium with the solution being titrated the indicators are described as extraction indicators.

iii - When the indicator is influenced by a redox system, whose equilibrium is controlled by removal of the metal ions being titrated, the indicators are called redox indicators, they are usually one-colour indicators.

The most typical compleximetric indicators are metallochromic indicators. Because the change (or appearance) of colour is based on complex formation reactions the behaviour is usually reversible, unless kinetic factors, mainly connected with the nature of the metal ions are significant.

The reactions in compleximetric titrations are mainly based on chelate formation. The most common and favourable case is when the titrant - analyte reaction proceeds in a stoichiometric ratio of 1:1. Formation of complexes with stepwise ligand attachment may give diffuse end points, unless the formation of the intermediate complexes is well separated. The same considerations apply when more than one metal ion may be bound by a multidentate ligand.

The main reaction of metal ion M, with a titrant L can be represented by the equation:



where the charges are omitted.

When the initial metal concentration equals C_M , then the metal ion concentration at the equivalence point can be calculated from the approximate expression

$$[M]_{eq} = \sqrt{C_M / K_{ML}} \quad (1)$$

which applies when the dilution during titration is neglected. Otherwise C_M should be multiplied by a correction term $V_M / (V_M + V_T)^{-1}$ where V_M and V_T are the initial volume of metal ion solution and the volume of titrant solution respectively. Equation (1) is only valid when the product of the equilibrium constant K and concentration C_M is sufficiently large to neglect dissociation of the complex in the vicinity of the equivalence point.

In the case when side reactions occur in solution titrated, the value of the constant K_{ML} is substituted by a conditional constant

$$K'_{ML} = K_{ML} \frac{\alpha_{ML}}{\alpha_M \alpha_L} \quad (2)$$

where α_M , α_L and α_{ML} represent the side reaction coefficients (Ref. 5) of the metal ion, of the complexing titrant and of the formed complex, respectively. Hence

$$[M']_{eq} = \sqrt{\frac{C_M \alpha_M \alpha_L}{K_{ML} \alpha_{ML}}} \quad (3)$$

Equation (3) indicates that $[M']_{eq}$, being the concentration of all metal species at the equivalence point not bound with the titrant, depends on the total concentration of the metal in solution, the stability of the complex and solution conditions (pH influences α_M , α_L , α_{ML} ; the presence of other metal ions influences α_L).

The free metal ion concentration at the equivalence point should be matched with the metal ion concentration at the transition point ($-\log [M]_{trans} = pM_{trans}$) specific for formation of a given metal-indicator complex. The transition point in the case of a two-colour indicator is conventionally assumed to occur when the total concentration of the indicator not bound with the metal titrated equals the concentration of indicator-metal complex:

$$[I'] = [MI] \quad (4)$$

where the symbol $[I]$ represents all not-metal bound indicator species independent of their protonation. The transition point defined in this manner does not always correspond exactly with the visually observed colour change. This is not only due to the different perception of light at different wavelengths for various observers. The best observable end point is often the more or less clear colour of the uncomplexed indicator persists.

Nevertheless such approximate approach is often justified and useful, because for many metallochromic indicators the molar absorptivities, at different wavelengths, for species involved in the colour change do not differ significantly. For one-colour indicators this treatment is not valid, and the appearance of the end point change is closely related to the molar absorptivity of the coloured form and the total concentration of the indicator.

The value of $[M]_{trans}$ may be calculated from the stability constant ($-s$) of the metal indicator complex ($-es$) and the side reaction coefficients of the indicator and the complex. The side reaction coefficient is related to the conditional constant of the metal indicator complex as follows:

$$\log K_{M'I'}(MI) = pM_{trans} - \log \alpha_M = pM'_{trans} \quad (5)$$

The value of pM'_{trans} is used in calculation of the titration error. Because α_M depends on the solution conditions, pM_{trans} only defines the characteristics of the indicator in those particular conditions, which specify the concentrations of all species influencing the free metal concentration. Those conditions should be strictly defined, otherwise those values have no significance.

The data necessary for calculation of α_M include the concentrations of ligands reacting with the metal and the corresponding stability constants. The α_M values are tabulated in several text-books or tables (Refs. 4,5), usually as a function of pH and total concentration of the ligand. In some instances when the stability constants are not available the values of pM_{trans} were determined experimentally, such data cannot in general be used under other conditions.

The value α_M influences to the same extent the formation of the complex formed in the main titration reaction and the formation of the metal-indicator complex, except if polynuclear complexes are formed. In such case

the value of α_M may depend on the total metal ion concentration.

Most complexes formed with indicators are of 1:1 stoichiometry, sometimes 1:2 complexes occur, rarely 1:3 complexes are formed, but these usually need a significant excess of the indicator ligand. When complexes other than 1:1 are formed pM_{trans} should be given for a specified concentration of the indicator. Sometimes it is sufficient to indicate, that below a given pH and concentration of the reagent there is no need to consider complexes having stoichiometric metal-ligand ratio other than 1:1.

For one-colour indicators the practical pM_{trans} always depends on total indicator concentration, but its value can be used as constant at given indicator concentration.

In rare instances binuclear metal-indicator complexes, M_2I , may be formed. Their formation is a function of the total metal concentration, which therefore should be stated. In compleximetric titrations the concentration of the free metal ions in the vicinity of the equivalence point is usually low, and the formation of binuclear complexes may thus be neglected.

The formation of protonated complexes usually increases the stability of metal-indicator complexes, but some of complexes may be less intensively coloured, or even colourless. Therefore a strictly defined pH range should be employed in titrations.

The calculation of pM_{trans} is based on the following equations:

i. When only 1:1 complex is formed

$$pM_{trans} = \log K_{MI} - \log \alpha_I + \log \alpha_{MI} \quad (6)$$

where

$$\alpha_I = 1 + [H^+]K_{HI} + [H^+]^2 K_{HI} K_{H_2I} + \dots \quad (7)$$

$$\alpha_{MI} = 1 + [H^+]K_{MHI}^H + [H^+]^2 K_{MH_2I}^H K_{MHI}^H + \dots \quad (8)$$

or

$$\alpha_{MI} = 1 + [OH^-]K_{MOHI}^{OH} + \dots \quad (9)$$

ii. When 1:1 and 1:2 complexes are formed:

$$pM_{trans} = \log K_{MI} - \log \alpha_I + \log(1 + 2[I'] K_{MI} K_{MI_2}) \quad (10)$$

which is approximately equal to:

$$pM_{trans} = \log K_{MI} - \log \alpha_I + \log(1 + \frac{C_I K_{MI} K_{MI_2}}{\alpha_L}) \quad (11)$$

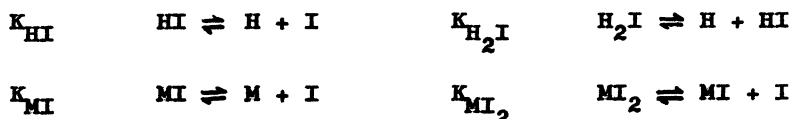
iii. When 2:1 complexes are formed:

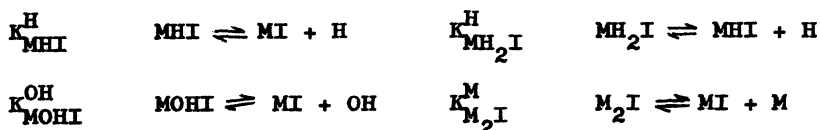
$$pM_{trans} = \log K_{MI} - \log \alpha_I + \log(1 + [M] K_{M_2I}^M) \quad (12)$$

which is approximately equal to:

$$pM_{trans} = \log K_{MI} - \log \alpha_I + \log(1 + \frac{C_M}{\alpha_M} K_{M_2I}^M) \quad (13)$$

In those equations the symbols for equilibrium constants correspond to the following reactions (with charges omitted for simplicity).





In the case when mixed ligand complexes are found (e.g. $ZnNH_3I$, where I stands for Eriochrome Black T) the α_{MI} must contain another term, valid only for a particular concentration of the second ligand, e.g. for 0.1M NH_3 .

The indicator characteristics described should therefore contain the list of equilibrium constants of all the reactions involved in titration with the application of an indicator. These constants must be presented in the notation recommended by IUPAC or otherwise with a clearly defined symbols to avoid any misinterpretation. In general reliable data are scarce, but an analyst may also be interested in evaluated yet approximate values of conditional constants, in spite of the fact, that the complex formulae especially in respect of protonation and exact conditions of complex formation are not always given. In such instances at least total metal concentration to indicator concentration ratio must be given and reaction conditions must be described as exactly as possible. Such data are helpful in choosing the best analytical conditions, however for precise equilibrium calculations such data are unsuitable.

Beside the equilibrium data the characteristics of an indicator should contain at least qualitative information about the reaction rate particularly when titration at normal speed at room temperature is impossible.

The spectral characteristics of the indicator used in visual titrations should include the observed colours, wavelengths of absorption maxima and molar absorptivities of all relevant species, i.e. of the protonated species of the indicator and that of its complexes with the metal being titrated. These data are of concern to the visible range only. A sound system, not however widely used by practical analysts, is the characterisation of colour change by the C.I.E. chromacity indices (Refs. 6,7). Up to the present time only a few indicators have been described by this method.

Several other factors are also of importance for the practical use of an indicator. These are:

Purity of indicator. The indicators may be contaminated by the substances formed or remaining from the synthesis. Other sources of contamination are decomposition or transformation products of the indicator itself, as well as the various isomers formed as by-products in the reagent preparation, added diluents or surfactants. Because of differences of complexation constants of the indicator and accompanying substances (e.g. isomers) their presence may cause the end point to be diffuse and indistinct.

Therefore whenever possible the procedure for assay and purity control of the indicator should be given as well as the permissible contents of various impurities.

Preparation of indicator should be described whether as a solution or solid mixture in the case when the solution is unstable. Depending on the preparation and concentration, the amount of indicator used for titration should be given.

Typical applications of the indicators. This section should point out most common titrations for which the indicator is suitable.

2. ERROR CALCULATION IN COMPLEXIMETRIC TITRATIONS

The indicator error for a compleximetric titration is due to the following factors:

The end point error

The systematic error occurring because under the given conditions of the titration the metal ion concentration at the equivalence point differs from that at the end point, determined from the colour change of the indicator.

The metal ion concentration at the equivalence point depends on the stability constant of the complex formed in the main reaction, the total concentration of the titrated metal and on the side reactions occurring under the conditions of the titration. The transition point depends on the stability constant of the metal-indicator complex, on the side reactions of the species participating in formation of this complex and on the concentration of metal ion or indicator if metal-indicator complex occur with stoichiometric coefficients greater than 1. The end point of titration should be located in the vicinity of the transition point, however it depends on the best observable colour change arbitrarily accepted, on the ability of colour perception for both coloured species, which may be different from analyst to analyst, on the mode of observation and on illumination, on the indicator concentration and sometimes on the colour of the metal ion or metal-titrant complex which may act as a screening component in the solution. Therefore the calculated transition point, expressed as pM_{trans} , for which the concentration of the metal bound and unbound indicator are assumed to be equal, does not correspond exactly with the visually observed end point. In the case of one-colour indicators the transition point characteristics is of less practical value.

The end point error depends on the differences between pM_{eq} calculated from the main titration reaction and the pM_{trans} calculated from the indicator characteristics. In both pM values the side reaction coefficients of the metal ion, α_M , needs not to be taken into consideration because for the same solution conditions the value of α_M is the same, and cancels the difference

$$\Delta pM = pM_{eq} - pM_{trans} \quad (14)$$

The relative end point error of titration $\delta = (C_I - C_M)/C_M$ may be expressed for the case when $C_I \ll C_M$ by the equation (Ref. 4^L)

$$\delta = \frac{1}{[M']_{trans} K'_{ML}} - \frac{[M']_{trans}}{C_M} \quad (15)$$

assuming that in the vicinity of the end point $C_M \gg [M]_{trans}$, where C_M , C_I and C_T represent total concentration of the metal ion, the indicator and the titrant, respectively and K'_{ML} is the conditional stability constant of the main titration reaction. By substituting $[M]_{trans} = [M]_{eq} 10^{-\Delta pM}$, and $[M]_{eq} = (C_M/K'_{ML})^{1/2}$ expression (Ref. 5) relating the error directly to ΔpM is obtained:

$$\delta = (10^{\Delta pM} - 10^{-\Delta pM})(C_M K'_{ML})^{-1/2} \quad (16)$$

For $\Delta pM \geq 0.4$ an approximate expression

$$\delta = 4.6 \Delta pM (C_M K'_{ML})^{-1/2} \quad (17)$$

can be used.

The indicator consumption error

The indicator consumption error is the systematic one occurring because at the end point the fraction of the metal is not bound by the titrant but is present as the metal-indicator complex (-es). This error has a negative value and depends on the amount of indicator present. For indicators exhibiting high colour intensities, which may be used in smaller concentrations, this error decreases. When the end point is close to the transition point the error is equivalent to half of the molar amount of indicator added to titrated solution. In other cases it is smaller because titrations are often carried out to a nearly clear indicator colour. This error can be estimated as equal $10^{-5} - 5 \times 10^{-6}$ mole/dm³, which may play a role for solutions more dilute than 10^{-2} mole/dm³. A significant compensation of this error normally takes place because the standardization of the titrant is carried out in similar conditions to the analysis titration.

In the case of some not very stable indicators (e.g. murexide) which decompose significantly if the titration is carried out slowly, as long as the decomposition products do not contain complexed metal ions the error decrea-

ses as the indicator decomposition proceeds.

3. CONCLUSIONS

On the basis of the foregoing discussion, the following protocol is suggested for the presentation of data on compleximetric indicators:

1. Usual name of indicator
2. Synonyms and colour index
3. Chemical name and formula
4. Equilibrium constants for acid dissociation and metal complexation of indicator
5. Spectral characteristics of indicator and its metal complexes
6. Purity of indicator (purification and tests)
7. Preparation of indicator and amount used in titrations
8. Typical applications

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