6.4 Visual indicators

Visual indicators are widely used for end point detection in the titrimetric analyses. The indicators used normally correspond to the titration reaction and have acid-base or complex-, precipitate formation or oxidation-reduction properties, respectively. There are, however, titrations in which the indicator reaction type is different from that of the titration reaction. E.g. some redox indicators can be used for end point detection in complexometric, some precipitate forming indicators in oxidation-reduction, and some acid-base indicators in the precipitation titrations.

6.4.1 Acid-base indicators

Indicators which exhibit a visual change on neutralization by a base or acid at or near the equivalence point of a titration (See Section 6.2.). For characterization and control of purity of acid-base indicators see PAC 57 (6) 845-848 (1985).

6.4.2 Complexometric indicators

The action of indicators in visual complexometric 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 range of metal aquo ion concentration 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 form (*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 complexometric 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 complexometric 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 consideration 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:

$$M + L \Leftrightarrow ML \tag{6}$$

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

$$[M]_{eq} = \sqrt{c_M / K_{ML}} \tag{7}$$

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

$$K'_{ML} = K_{ML} \frac{a_{ML}}{a_M \cdot a_L} \tag{8}$$

where a_M, a_L and a_{ML} represent the side reaction coefficients of the metal ion, of the complexing titrant and of the formed complex, respectively. Hence

$$[M']_{eq} = \sqrt{\frac{c_M \cdot a_M \cdot a_L}{K_{ML} \cdot a_{ML}}} \tag{9}$$

Equation 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 and 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 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 to the concentration of indicator-metal complex:

$$[I'] = [MI] \tag{10}$$

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.

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:

$$logK_{MI'(MI)} = pM_{trans} - \log \alpha_M = pM'_{trans} \tag{11}$$

The values 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 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.

In the formation of α_L usually the protonation reactions of the ligand *L* have prominent role.

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.

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.

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

The *indicator error* for a complexometric 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 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

$$\Delta pm = pM_{eq} - pM'_{trans} \tag{12}$$

The relative end point error of a titration, $\delta = (C_L - C_M)/C_M$ may be expressed for the case when $C_I \ll C_M$ by the equation

$$\delta = \frac{1}{[M']_{trans} \cdot K'_{ML}} - \frac{[M']_{trans}}{C_M} \tag{13}$$

assuming that in the vicinity of the end point $C_M \gg [M']_{trans}$, where C_M, C_I and C_L represent total concentrations of the metal ion, indicator and titrant, respectively, and K'_{ML} is the conditional stability constant of the product of the main titration reaction.

The indicator consumption error. The indicator consumption error is a systematic error occurring because at the end point a fraction of the metal is not bound by the titrant but is

present as 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. 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.

6.4.3 Redox indicators

The indicator may be classified as *reversible* when the cycle of reactions in redox titration operations (reduction followed by oxidation) gives a product identical with the initial indicator. The relevant 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. Ferroin and related indicators are examples of such indicators.

The indicator may be classified as *pseudoreversible*, when the product from the cycle of reactions (as explained above) is different from the initial compound 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, at the concentrations used in the titration. An 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 Napthyl Blue Black.

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 for 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 of the corresponding activity coefficients 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 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.

Protolytic reaction 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 values. 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.

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.

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.

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 the 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 molar absorptivities of both indicator forms, their 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 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 whose oxidized from is unstable and decomposes slowly. In such cases the electrons lost by the indicator at local oxidant excesses will be not fully replaced by reaction with 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.

6.4.4 Adsorption and precipitation indicators

For *adsorption indicators* see section 6.2. *Precipitation indicators* are indicators precipitating from solution in a readily visible form at or near the equivalence point of a titration.