This characteristic has been elucidated by the mathematical treatment of complexometric titrations with a metal indicator[1]. A similar objection which is presented in the neutralization titration could be overcome by Higuchi, Rehm and Barnstein[2], but their method can not be applied directly to the complexometric titration.

In the titration of a metal with such a reagent as Complexon-III (disodium ethylenediamine tetra-acetate) in an aqueous system, there is the following equilibrium:

$$MI+Y^*=MY+I^* \qquad (1)^{**}$$

The equilibrium constant, K, is given by

$$K=[MY][I^*]/[MI][Y^*]=K^*_Y/K_I^* \qquad (2)$$

where $[MY]$ = concentration of the metal complex with Complexon-III
$[MI]$ = concentration of the metal complex with the indicator
$[Y^*]$ = sum of the concentration of the metal-free Complexon-III
$[I^*]$ = sum of the concentration of the metal-free indicator
K_Y^* = $[MY]/[M][Y^*]$ = apparent stability constant
K_I^* = $[MI]/[M][I^*]$ = apparent indicator constant

When the total concentrations of the metal and of the titrant in the system are m_t and c_t respectively, the following equation is obtained from eq. (2), so far as $m_t \geqq c_t$:

$$K=\frac{[I^*]}{[MI]}K_Y^*(m_t-c_t+[Y^*]) \qquad (3a)$$

Since in the present case $[Y^*]$ is so small that it can be neglected in the course of titration, eq. (3a) is converted into the following:

$$K=\frac{[I^*]}{[MI]}K_Y^*(m_t-c_t) \qquad (3b)$$

By transposing eq. (3b), comes the following equation:

$$c_t=-\frac{K}{K^*_Y}\frac{[MI]}{[I^*]}+m_t \qquad (4)$$

If the factor of titrant is n and the dilution of the solution by titrant can be neglected, there come the following relationships:

Photometric Determinations of Indicator End Points in Complexometric Titrations

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In photometric titrations with indicator, the color does not develop linearly with increasing amount of the added titrant.

1) J. M. H. Fortuin, P. Karsten and H. L. Kies, *Anal. Chim. Acta*, **10**, 365 (1954).
2) T. Higuchi, C. Rehm and C. Barnstein, *Anal. Chem.*, **28**, 1506 (1956).
** In the following equations, ionic charges were omitted for convenience.

$$m_t = nV_{eq} \text{ and } c_t = nV \qquad (5)$$

where V_{eq} is the volume of titrant equivalent to the total amount of metal, m_t, and V is the volume of titrant added.

By substituting eq. (4) with eq. (5), comes the following equation:

$$V = -\frac{K}{nK^*_Y}\frac{[MI]}{[I^*]} + V_{eq} \qquad (6)$$

Values of $[MI]/[I^*]$ can be computed from the absorbancy readings by means of the following equation;

$$[MI]/[I^*] = (A_{S_I} - A_S)/(A_S - A_{S_{MI}}) \qquad (7)$$

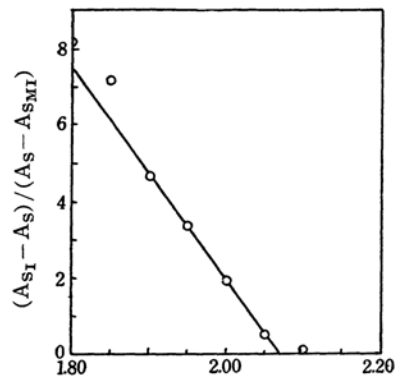
where A_{S_I} =absorbancy of the metal free indicator

$A_{S_{MI}}$ =absorbancy of the metal-indicator complex

A_S =absorbancy during the course of titration

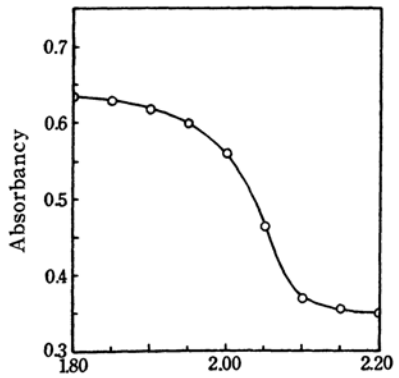
If $(A_{S_I} - A_S)/(A_S - A_{S_{MI}})$ is plotted against V, will result a straight line whose intercept on the V axis is equal to V_{eq}.

This is evident in Fig. 1 where the plot of $(A_{S_I} - A_S)/(A_S - A_{S_{MI}})$ vs. the volume of titrant is shown for the titration of magnesium with Complexon-III using EBT as indicator. About 50 ml. of the solution, which contained the definite amounts of magnesium sulfate, 2 ml. of 1 N ammonium chloride-ammonia buffer solution (pH 10) and 0.3 ml. of 0.5% solution of EBT in ethanol, was titrated with 0.01 M solution of Complexon-III. Absorbancies 545 mμ were recorded at the beginning of the titration and at every 0.05 ml. of added titrant during the titration, until the minimum absorbancy was obtained. The photometric titration curve of the same titration as in Fig. 1 is shown in Fig. 2. Some of the results, obtained from the intercept as shown in Fig. 1, are given in Table I.



0.01 M Complexon-III, ml.

Fig. 1. Plot for titration of 0.504_7 mg. of Mg with Complexon-III using EBT indicator at pH 10.



0.01 M Complexon-III, ml.

Fig. 2. Titration curve of the same titration as in Fig. 1.

TABLE I

RESULTS OF PHOTOMETRIC TITRATION OF MAGNESIUM WITH COMPLEXON-III USING EBT INDICATOR

Mg. taken, mg.	Titrimetric end point, ml.	Mg. found mg.	Error %
0.251_1	1.02_2	0.248_5	−1.0
0.251_1	1.04_5	0.254_1	+1.2
0.504_7	2.07_5	0.504_6	0.0
0.504_7	2.04_5	0.497_3	−1.5
0.504_7	2.07_0	0.503_4	−0.3
0.504_7	2.08_5	0.507_1	+0.5

Further studies on the characteristics of this plot and on its other applications will be reported in subsequent publications.

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