

# COMPLEXOMETRIC ANALYSIS OF MULTICOMPONENT SYSTEMS

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## ABSTRACT

Methods of complexometric analysis are reviewed with particular reference to their improved potential due to recent developments in theory and instrumentation. It is shown how accuracy has been improved and how reactions leading to the formation of compounds with rather low stability constants can be utilized successfully.

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For the analysis of multicomponent systems there are essentially two possibilities: (a) The components are completely separated and determined separately; (b) No separation is performed, and all determinations are made on the same sample solution. In the latter case the determinations may or may not demand appropriate masking procedures.

When several components with very similar properties are present or when the various components require further investigation, complete separation may be necessary. But if only the composition of the sample interests the analyst, methods demanding no separation procedures are simpler and speedier. Therefore, in a symposium on 'Separation Methods' we should not completely forget one essential question: How can separations be avoided? Or, in the terms recently suggested by Dr Chalmers<sup>1</sup>: How can 'literal' separations be replaced by 'figurative' separations?

I think that every analyst is aware of the fact that the introduction of new complexing agents during the recent past has immensely enhanced the possibilities of analysing multicomponent systems—with or without prior separation. May I start with a discussion of analyses without any previous separation.

The theoretical treatment of equilibria is the same for acids and for metal ions. The metal ions can be considered 'Lewis acids', or—if you prefer—acids can be considered hydrogen complexes. In our system the species  $M_I$ ,  $M_{II}$  etc. may represent metal aquo ions or some other Brønsted acids, or some kind of Lewis acids.

Generally speaking, a titrimetric determination of  $M_I$  in the presence of  $M_{II}$  is possible if the difference between the stability constants of the two complexes formed is sufficiently large and if the equivalence point can be detected with sufficient precision. If the difference is too small,  $M_{II}$  has to be masked by means of an appropriate masking agent. However, the masking

should not be treated on a qualitative basis; the stability constants of most common masking reactions are known, and the fundamental equation for all masking procedures is simply<sup>2</sup>

$$K_{M_{II}L'} = K_{M_{II}L} / \alpha_{M_{II}(A)} \alpha_{L(B)} \quad (1)$$

where  $K_{M_{II}L'}$  is the conditional constant when  $M_{II}$  is masked by the masking agent, A. B is usually the hydrogen ion.

The  $\alpha$  coefficients can easily be calculated from the stability constants; collections of  $\alpha$  coefficients can also be found in some textbooks (for instance, ref. 2). If  $\alpha_{M_{II}(A)}$  is sufficiently large,  $M_{II}$  will be completely masked and will not interfere with the titration of  $M_I$ .

However, few masking agents are sufficiently selective. A masking agent, A, eliminating the influence of  $M_{II}$ , usually diminishes also the conditional constant of  $M_I L$  since also the coefficient  $\alpha_{M_I(A)}$  will be relatively high in value. In this connection it may be useful to have a look at the general error diagram<sup>2</sup> in Figure 1 expressing the dependence of the relative error on the stability constant,  $K$ , or, more correctly, the conditional stability constant,

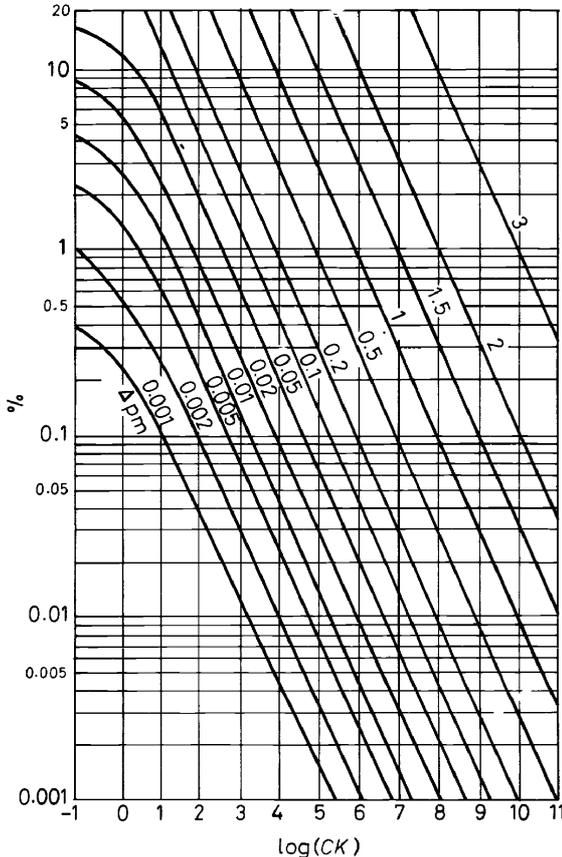


Figure 1. Percentage error as a function of stability constant  $K$  for different values of  $\Delta pM = pM_{\text{end}} - pM_{\text{eq}}$  and for various concentrations,  $C$ , of the metal in the titrated solution

$K'$ , the concentration of the sample solution,  $C$ , and the precision of end point detection,  $\Delta pM$  (or  $\Delta pH$ ).

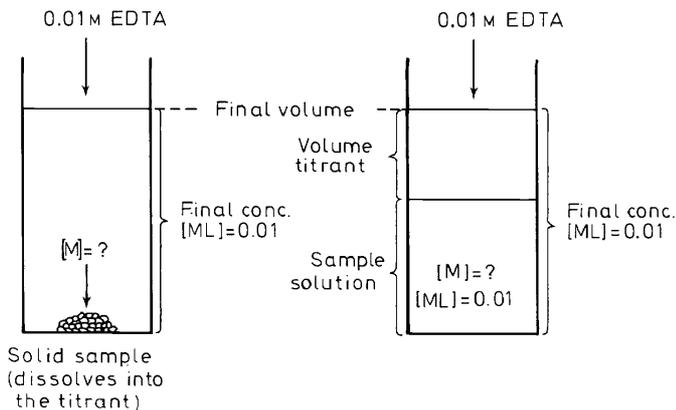
The question arises where the limit of determinability lies. In other words: How large must a conditional constant (or the product  $K'C$ ) be and how precisely (expressed by  $\Delta pM$ ) can the equivalence point be detected?

I am afraid that many chemists consider the scope of this diagram unrealistic, since it includes very small  $\Delta pM$  values—down to  $\Delta pM = 0.001$ —and very small stability constants. If  $\log K'C$  is  $-1$  and the concentration is  $10^{-2}$ , the logarithmic stability constant equals only  $+1$ . I feel that these unusual limits demand some comments.

If visual titration methods are used, the left part of the diagram is, of course, meaningless. The attainable precision is usually considered to be about  $\pm 0.4$  pM (pH) unit; by comparison with a reference solution the precision may be improved to about  $\pm 0.2$ . However, if instrumental methods are used, much higher precision can be attained. Modern potentiometric and photometric instruments are claimed to determine pM and pH values to three places of decimals. I cannot help feeling that, as a rule, analysts do not utilize this high precision sufficiently. For the detection of the end point of a titration about  $\pm 0.2$  pM or pH unit is often considered the attainable limit even if instrumental methods are used, which implies that the stability constant must be larger than about  $10^6$ . This poor utilization of the sensitivity of modern instruments is due to the fact that other factors than the sensitivity of the instrument used affect the detection of the end point. Above all, it is difficult to state the *exact* value of pM (pH) at the equivalence point before a titration since this value depends on the concentration of the sample solution, which is *not* known.

Nevertheless, I want to assert that it is possible to state very accurately—before a titration—the right pM value at the equivalence point in spite of the fact that the concentration of the sample solution is not known. One can use a principle which at our institute is named the ECR principle (Exactly Correct Reference solution).

This principle was suggested as long ago as 1939<sup>3,4</sup> and can best be made clear by means of an example illustrated in *Figure 2*.



*Figure 2.* The ECR principle for exact detection of the equivalence point of a titration

A metal, M, is to be titrated with a 0.01 molar solution of a complexing agent, EDTA, for instance. Before the titration we add to the sample solution an amount of the reaction product, ML, to give a 0.01 molar concentration, i.e. the same concentration as the molarity of the titrant (*Figure 2*, to the right). At the equivalence point we will have an *exactly* 0.01 molar ML solution with a well-defined pM value. The addition of the reaction product to the sample solution will diminish the pM jump. However, if we are able to measure pM values with a precision of a few hundredths or thousandths of a

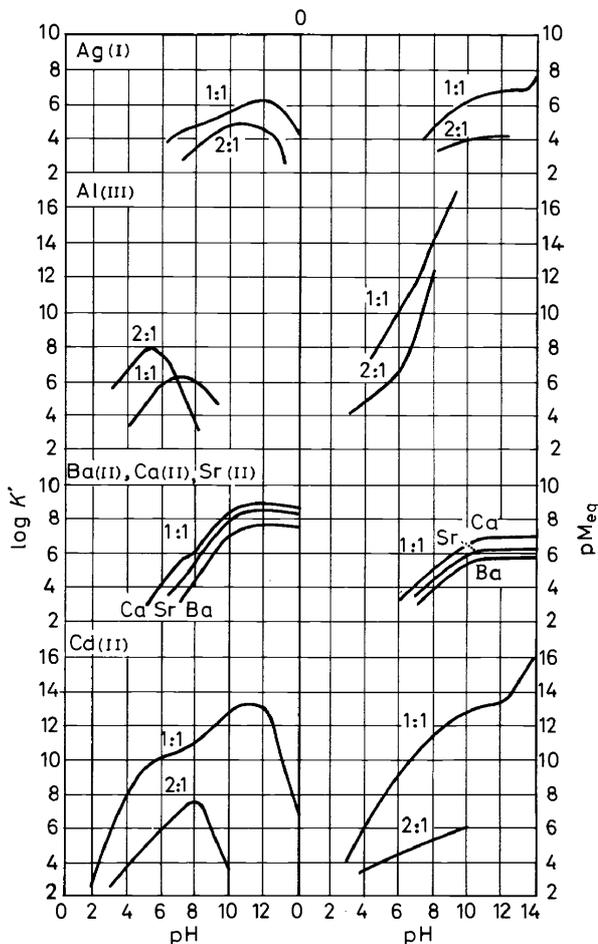


Figure 3. Conditional constants and  $pM_{eq}$  values as functions of pH when titrating Ag, Al, Ba, Ca, Sr and Cd with TTHA to the 2:1 and 1:1 complexes.  $C_M$  is assumed to be  $10^{-3}$  M (From ref. 5)

pM unit, a decrease in the magnitude of the pM jump is of little importance. It is more important to know exactly the true value of pM at the equivalence point.

For a better understanding of the ECR principle, the case where a solid sample is titrated is also illustrated in *Figure 2* (to the left). No addition of the

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reaction product is needed, the sample will dissolve during titration and the concentration of ML is exactly 0.01 molar at the equivalence point.

When applying the ECR principle,  $pM_{eq}$  is always the same as long as the molarity of the titrant is not altered.

ML can be conveniently added to the sample solution if a solution of ML is prepared whose molarity is eleven times the concentration of the titrant and a volume equal to one tenth of the sample solution is added to the latter. Thus, if the titrant is 0.01 molar, a 0.11 molar solution of ML is added. This operation does not require any high degree of precision. In the solution added one can include buffer substances and neutral salts, if needed for the suppression of neutral salt effects.

The ECR principle makes it possible to analyse one-component systems

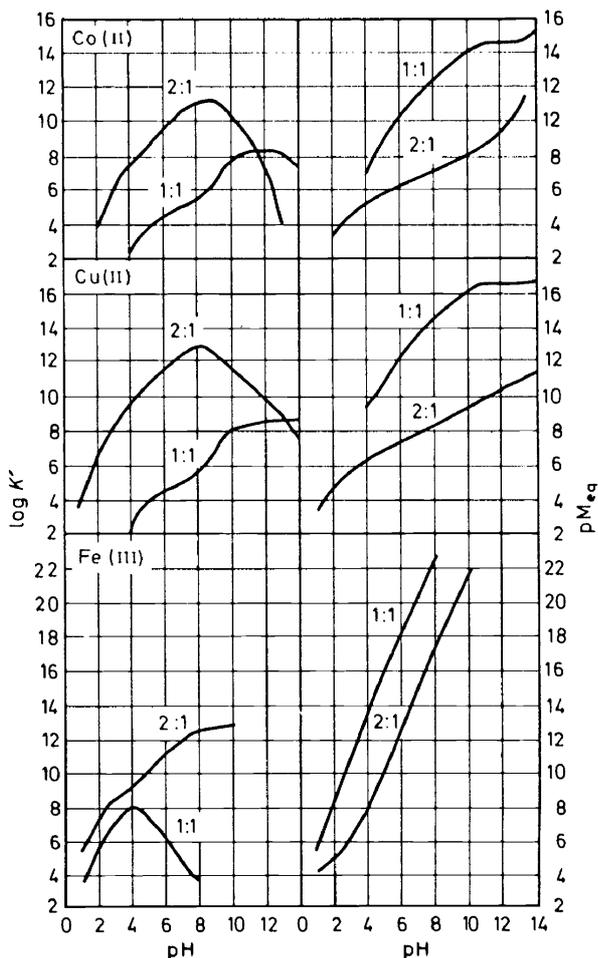


Figure 4. Conditional constants and  $pM_{eq}$  values as functions of pH when titrating Co(II), Cu(II) and Fe(III) with TTHA to the 2:1 and 1:1 complexes.  $C_M$  is assumed to be  $10^{-3}$  M (From ref. 5)

very accurately even when the stability constant is low in value and the solution is very dilute. However, our problem is the analysis of multi-component systems, and it may be asked whether the ECR principle can be applied also to such systems.

No problem exists if complete masking of  $M_{II}$  and other interfering species is possible; you can apply the ECR principle if  $pM_{I,eq}$  is determined in a solution containing the masking agent and  $M_I L$  in the appropriate concentrations. But if the masking is incomplete, problems will arise.

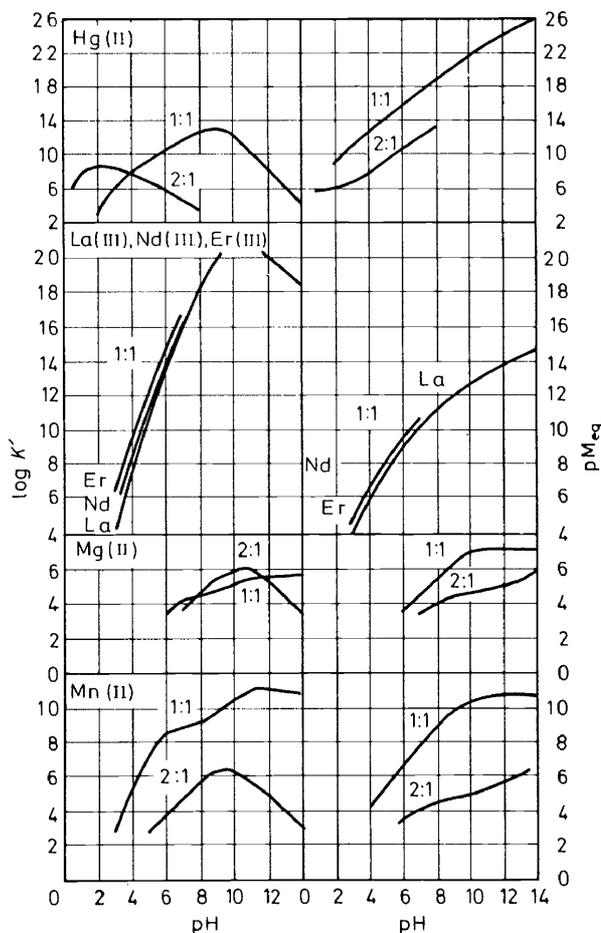


Figure 5. Conditional constants and  $pM_{eq}$  values as functions of pH when titrating Hg(II), La, Nd, Er, Mg and Mn with TTHA to the 2:1 and 1:1 complexes.  $C_M$  is assumed to be  $10^{-3}$  M (From ref. 5)

For a general discussion of the possibilities of analysing multicomponent systems I will write the fundamental equation for the titration of an acid or a metal,  $M_I$ , in the presence of another,  $M_{II}$ .

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$$\log K_{M_I L'} = \log K_{M_I L} - \log K_{M_{II} L} + pM_{II} \quad (2)$$

$$= \Delta \log K + pM_{II} \quad (3)$$

(valid if  $\alpha_{L(M_{II})} > \alpha_{L(H)}$  and  $[M_{II}] K_{M_{II} L} > 1$ )

$K_{M_I L}$  is the conditional constant for the formation of  $M_I L$ . If  $M_I$  and  $M_{II}$  are involved in side reactions,  $\alpha$  coefficients must be considered, i.e. the  $M$  symbols will be primed. (For details the reader should consult ref. 2).

To have a sufficiently high conditional constant, the difference  $\Delta \log K$  must be large enough. For visual titrations about four to five units is usually considered necessary. It should be emphasized that only the difference is important, whereas the absolute values are of minor importance if the above

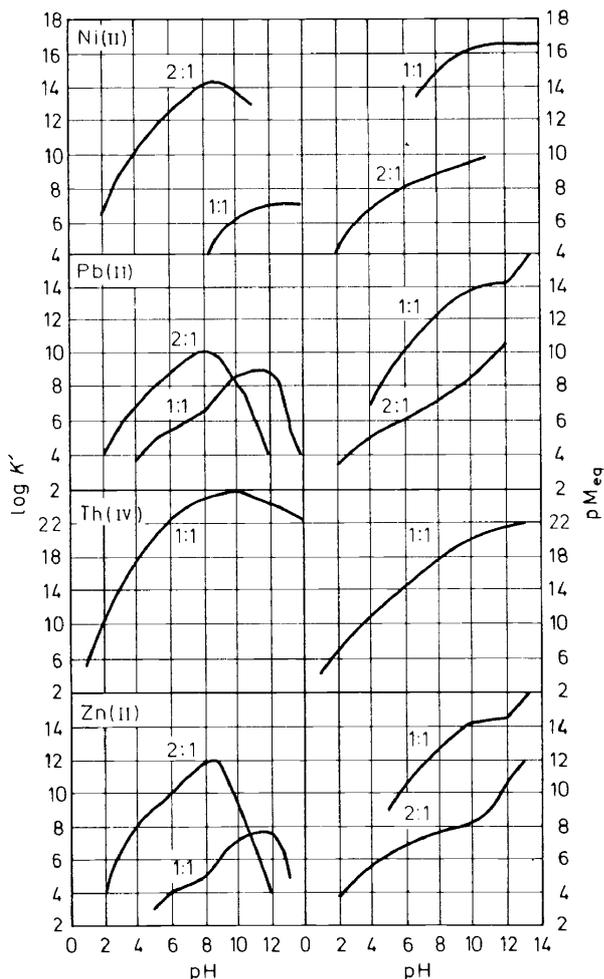


Figure 6. Conditional constants and  $pM_{eq}$  values as functions of pH when titrating Ni, Pb, Th and Zn with TTHA to the 2:1 and 1:1 complexes.  $C_M$  is assumed to be  $10^{-3}$  M (From ref. 5)

conditions for the validity of equation 3 are fulfilled. EDTA is by no means always the best suited complexing agent for the analysis of metal mixtures. The complexing agents investigated during the last decade have opened up many new possibilities. In this connection it is worth while mentioning TTHA (triethylene-tetramine-hexaacetic acid), a reagent that has been investigated particularly by Pribil and co-workers. The usefulness of this reagent is connected with the fact that some metals react with the reagent in a molar ratio of 2:1, whereas others form 1:1 compounds. By appropriate combination of TTHA with other complexing agents, solutions containing several metals can be analysed.

If we want to analyse a system containing several species, the given equation 3 cannot always be applied directly. Particularly complicated are the equilibria of TTHA since an unusually large number of complex compounds are formed: mononuclear, binuclear, acidic and basic complexes. The theoretical treatment of the equilibria is greatly facilitated by a consistent use of conditional constants. This approach is illustrated by *Figures 3 to 6* taken from a recent paper by Harju and Ringbom<sup>5</sup>.

For the way of constructing such curves I have to refer to the original paper<sup>6</sup>. Here are just a few comments on the curves.

The curves to the left give the conditional constants, the curves to the right the pM values at the equivalence points. All side reactions are taken into consideration. On the basis of these curves it is possible to choose the optimum pH and the most suitable indicator. One can also immediately—by means of the error diagram in *Figure 1*—estimate the attainable accuracy expressed as a percentage error. Furthermore, a glance at the curves immediately reveals the effects of various metals on a particular titration and the possibilities for stepwise titration of several metals.

The use of the curves may be illustrated by an example. Pribil<sup>7</sup> recently showed that TTHA is the only appropriate reagent for the titration of aluminium in the presence of manganese. The reason is obvious from the calculations given in *Table 1*.

*Table 1.* Titration of Al in the presence of Mn

Fundamental equation: $\log K_{AlL'} = \Delta \log K + pMn$	
EDTA	$\Delta \log K = \log K_{AlL} - \log K_{MnL} = 16.1 - 14.0 = 2.1$
DCTA	— = 18.3 - 17.4 = 0.9
DTPA	— = 18.5 - 15.5 = 3.0
TTHA	$\Delta \log K' = \log K'_{Al_2L} - \log K'_{Mn_2L} = 7.7 - 2.8 = 4.9$ (from the curves at pH 5.0)
	$\Delta \log K' = \log K'_{AlL} - \log K'_{MnL} = 1 - 10.7 \approx -9.7$ (from the curves at pH = 11)

It can be seen that for the complexes formed by EDTA, DCTA and DTPA the difference between the logarithms of the two constants does not exceed three units. If a titration is performed at pH 5, the differences between the conditional constants are the same because neither acidic nor basic complexes are formed at this acidity. On the other hand, the corresponding values of the conditional constants of the TTHA complexes differ

considerably. From the curves in *Figures 3* and *5* one finds that for the binuclear complexes  $\Delta \log K'$  equals 4.9, which means that it is possible to determine aluminium in the presence of manganese. According to Pribil, good results were obtained by back titration with a copper salt solution using glycinesresol red as indicator.

If we want to mask aluminium and titrate manganese, it can be done in alkaline solution.  $MnL$  and aluminates are formed; the conditional constant of the  $AlL$  complex will be very small.

A study of the curves presenting the conditional constants of the various metal-TTHA complexes reveals many similar possibilities and gives immediate information on the optimum experimental conditions.

It was stated above that the application of the ECR principle to the analysis of multicomponent systems meets difficulties if complete masking is not possible. However, if we are able to detect an equivalence point with great precision, addition of large amounts of the agent masking  $M_{II}$  may be advantageous. I mean that it can be worth while masking  $M_{II}$  completely even if the masking agent at the same time also reduces the conditional constant of  $M_{I}L$  considerably.

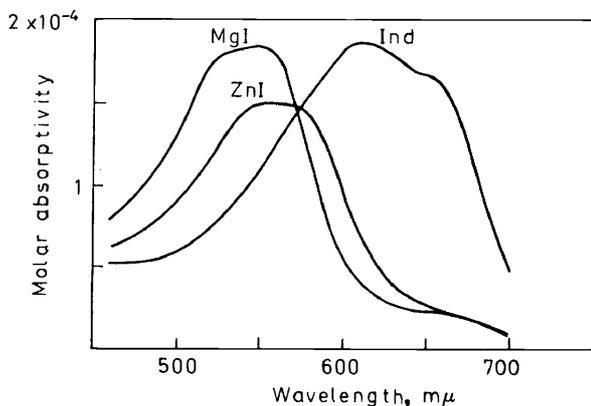
Another way to apply the ECR principle is to add a certain amount of the interfering ion  $M_{II}$  to the sample solution before the titration. If the added amount is considerably larger than the amount initially present,  $pM_{II}$ —and, consequently, also the conditional constant of  $M_{I}L$ —can be kept practically independent of the initial concentration of  $M_{II}$ . On the other hand, this conditional constant will decrease due to the addition of  $M_{II}$ . An estimation of the theoretical error should precede the titration so that the loss in accuracy (caused by the decrease of  $K'_{M,L}$ ) will not exceed the gain in accuracy (resulting from the application of the ECR principle).

For the detection of end points, potentiometric and photometric methods are the most accurate. Potentiometric methods can be conveniently combined with the ECR principle, which thus enables a refinement of the old Müller method with a compensating potential. In this way it is possible to utilize the high sensitivity of modern potentiometers. It may be mentioned that by using the ECR principle, we have succeeded in titrating potentiometrically acids and bases with stability constants between  $10^2$  and  $10^3$ , i.e. dissociation constants of  $10^{-11}$  to  $10^{-12}$ .

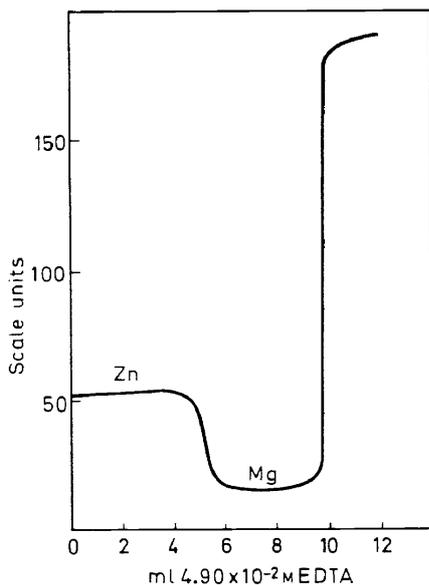
I don't assert that the precision of detecting the end point can be brought to one thousandth of a pM or pH unit, but less than a few hundredths of a unit seems attainable. Of course, it is not a question of measuring absolute values; it is rather a comparison with the value of a reference solution prepared on the basis of the principles presented earlier. The use of modern selective electrodes—membrane or liquid ion-exchanger electrodes, for instance—seems promising in this connection. However, in all potentiometric methods it is important that the reactions are sufficiently fast, i.e. that the equilibrium has been established and the potential has become constant. Moreover, the problem of reproducibility is essential; as a rule, high concentrations of neutral salts affect the reproducibility unfavourably. And if selective electrodes are used in analysing multicomponent systems, it is always important to have an idea of the selectivity of the electrodes used.

When a photometric method is used for the detection of the end point,

problems arise if the indicator forms coloured compounds with several components of the system. Sensitive modern photoelectric instruments enable the performance of titrations even if the difference in colour between the two indicator complexes is rather small. *Figures 7 and 8* taken from a paper by Skrifvars and Ringbom<sup>8</sup> illustrate such possibilities.



*Figure 7.* Molar absorptivities of eriochrome black T and its metal complexes at pH 9.8: free indicator; magnesium complex, MgI; zinc complex, ZnI (From ref. 8)



*Figure 8.* Titration of zinc and magnesium with  $4.90 \times 10^{-2}$  M EDTA at pH 9.7 (ammonia buffer,  $[\text{NH}_3] \approx 0.1$ ). Equivalence points at 5.28 and 9.87 ml. Indicator eriochrome black T. Final volume about 190 ml. Beckman B spectrophotometer, 520 nm (From ref. 8)

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It can be seen that the difference between the absorptivity curves of the magnesium and zinc complexes of eriochrome black T is small. Nevertheless, as can be seen from *Figure 8*, sharp end points are obtained in a consecutive titration.

It can be asked what is the transition point of a metal indicator if the colour change results not from the liberation of the indicator but from the formation of a complex with another metal.

A combination of expressions for the stability constants of the two indicator complexes gives the expression

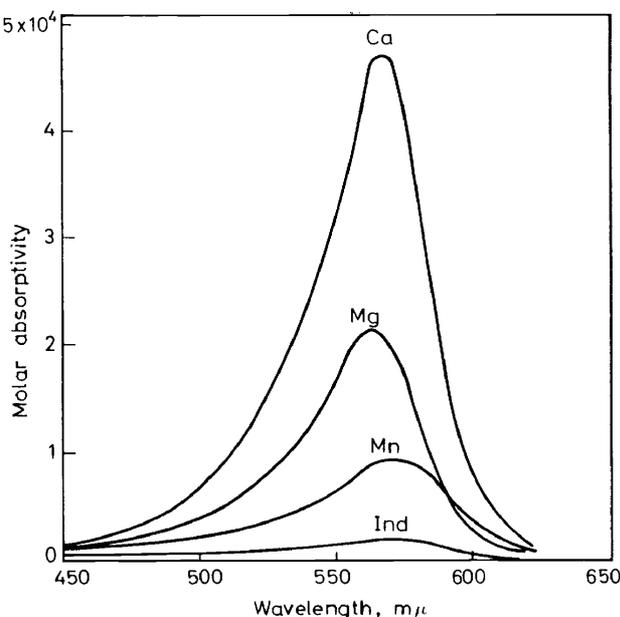
$$\frac{[M_{II}]}{[M_{II}I]} = (K_{M_{II}I}/K_{M_{II}}) [M_I]/[M_{II}] \quad (4)$$

At the transition point  $[M_I I]/[M_{II} I] = 1$  and hence

$$pM_{I \text{ trans}} = \Delta \log K_{MI} + pM_{II} = \log K_{M_{II}I} \quad (5)$$

In other words, we can simply apply the general rule that  $pM_{I \text{ trans}}$  of an indicator equals the logarithmic conditional constant<sup>2</sup>.

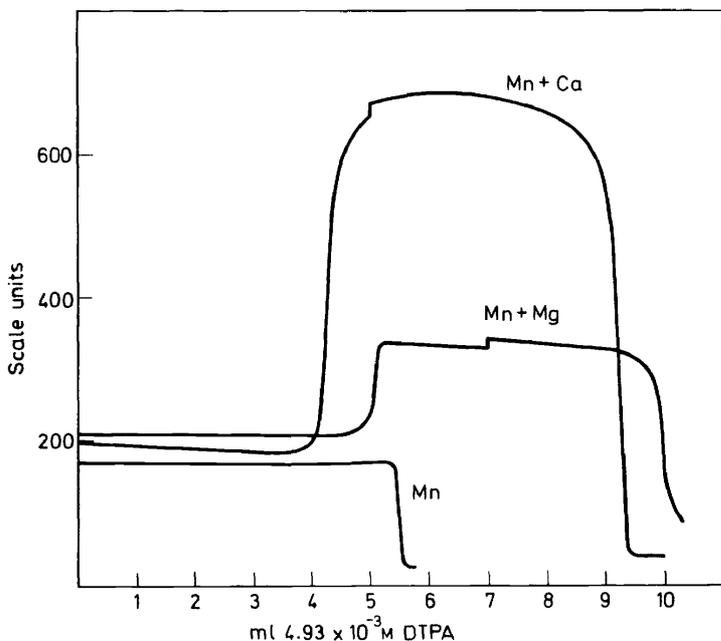
If the metals are involved in any side reactions, for instance with buffer substances, primed quantities must be inserted, i.e.  $\alpha$  coefficients have to be calculated.



*Figure 9.* Molar absorptivities of metalphthalein and its metal complexes: free indicator at pH 9.25; calcium complex at pH 10.0; magnesium complex at pH 9.2; manganese complex at pH 9.1 (From ref. 8)

Another example taken from the paper of Skrifvars and Ringbom<sup>8</sup> is presented in *Figure 9* where the absorptivity curves of the calcium, magnesium and manganese complexes of the metal indicator metalphthalein are plotted. All these metals form red compounds with the indicator, but visual consecutive

titrations are not possible; the human eye cannot distinguish the different red shades of the various metal-indicator complexes. On the other hand, a look at the curves reveals that possibilities for a photoelectric titration exist. Some curves are given in *Figure 10*. The manganese-indicator complex has the faintest colour, and a titration of manganese alone gives the lowermost curve. Titrations of manganese plus calcium and manganese plus magnesium give curves with very pronounced jumps, as can be seen from the figure.



*Figure 10.* Titration of manganese with DTPA at pH 9.3; equivalence point at 5.50 ml. Titration of manganese at pH 9.3 and calcium at pH 10; equivalence points at 4.28 ml and 9.34 ml. Titration of manganese at pH 9.3 and magnesium at pH 9.6; equivalence points at 5.10 and 9.93 ml. Indicator: metalphthalein. Lange colorimeter, green filter (From ref. 8)

In this connection I want to say a few words about the analysis of solutions containing calcium and magnesium. One finds in the literature numerous investigations on the complexometric analysis of such solutions. But it is hard to find a satisfactory method for the *direct* titration of magnesium in the presence of calcium. The reason is that most complexing agents form more stable complexes with calcium than with magnesium. Usually, difference methods are suggested, but if magnesium is the minor component, the accuracy is low. For example, a solution contains  $100 \pm 1$  (mole) parts of Ca + Mg and  $90 \pm 1$  parts of Ca. The amount of Mg is then  $10 \pm 2$  parts, i.e. an error of  $\pm 20$  per cent is possible. There is apparently a need for more accurate methods.

Equilibrium calculations based on known stability constants of various calcium and magnesium complexes show that, if calcium is masked with

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EGTA, titration of magnesium with DTPA is possible. The results of such calculations are given in *Table 2*.

At pH 11.5, the conditional constant  $K_{Mg'L'}$  is about seven, which means that an at least approximate visual titration is possible and that a photometric

*Table 2.* Titration of Mg with DTPA when Ca is masked with EGTA

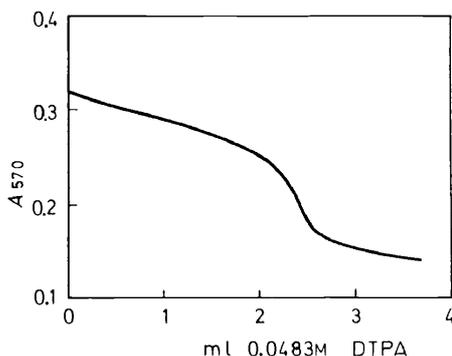
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Constants:	$\log K_{CaEGTA} = 11.0$ ; $\log K_{MgEGTA} = 5.2$
	$\log K_{CaDTPA} = 10.6$ ; $\log K_{MgDTPA} = 9.3$
Assumptions:	$C_{Ca} \approx C_{Mg} \approx 10^{-3}$ ; excess of EGTA = $10^{-3}$
Conditional constants at pH 11.5:	
$\log K_{Ca'DTPA} = 2.6$	
$\log K_{Mg'DTPA} = 7.1$	
$\log K_{Mg'(DTPA)'} = 7.0$ corresponding to $pMg_{eq} = 7.2$	
Indicator:	Calmagite $pMg_{trans}$ at pH 11.5 = 7.4
Errors:	If $\Delta pMg$ is 0.5, the titration error 3%
	If $\Delta pMg$ is 0.2, the titration error is 1%
	If $\Delta pMg$ is 0.05, the titration error is 0.2%

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titration probably will give satisfactory results. An experimental absorbance curve<sup>9</sup> illustrating the titration of magnesium in the presence of an about equimolecular amount of calcium is presented in *Figure 11*. Calmagite was used as indicator.

If the added excess of EGTA is large, the concentration of free EGTA will remain practically constant. Then the conditional constant of the Mg–DTPA



*Figure 11.* Titration of 0.119 mmol Mg in the presence of 0.118 mmol Ca and 0.25 mmol EGTA with DTPA at pH 11.5. Indicator: calmagite; 540 nm; volume ca. 60 ml; equivalence point 2.46 ml

complex will be independent of the amount of calcium present and the ECR principle can be used when determining magnesium.

By the way, the excellence of EGTA as a masking agent for calcium can be utilized also for a complete separation of calcium from magnesium by ion exchange. Theoretical calculations show that if a certain excess of EGTA and a well defined pH is used—usually about seven—all the magnesium will be adsorbed on a short column whereas all the calcium will pass through

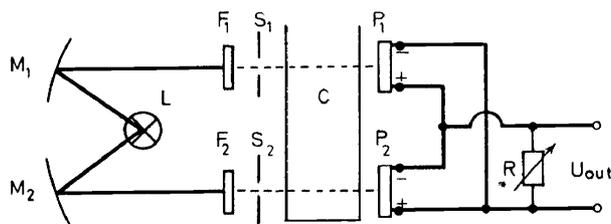
the column. Conducted experiments (ref. 2, p 236) gave results that agreed well with theoretically calculated optimum conditions.

Many similar 'literate' separations are possible, and the right pH range can be calculated on the basis of the conditional constants.

Returning to the photometric titrations, I want to point out one difficulty which arises if the ECR principle is applied to titrations with indicators. Even if it is possible to state exactly the right pM (pH) value at the equivalence point, this does not mean that the correct absorbance value at the equivalence point is known. The reason is that it is not very easy to keep the indicator concentration at a definite value; if very precise measurements are required, even the dilution during a titration may affect the result. It seems therefore desirable to use some method to eliminate the dependence on the indicator concentration. Actually, there exists a method of phototitration which is *independent* of the added amount of indicator. The method requires a special type of photometer named the *dichrotitrator* that has been developed at our laboratory.

The instrument was recently described in the literature<sup>10</sup>. Unfortunately, it is not yet commercially available, but I hope it will appear in the not too distant future. Here I will only say a few words about the underlying principle.

A general scheme of the instrument is presented in *Figure 12*.



*Figure 12.* Diagram of dichrotitrator. L lamp;  $M_1$ ,  $M_2$  mirrors; C titration cell;  $F_1$ ,  $F_2$  monochromators;  $S_1$ ,  $S_2$  shutters;  $P_1$ ,  $P_2$  photocells; R resistor for sensitivity adjustment;  $U_{out}$  = connection to galvanometer, relay or recorder (From ref. 10)

Two light beams of different colours pass through the titration cell and then fall upon a pair of photocells. The photocells are connected in opposition over a load resistor for adjusting the sensitivity. If the wavelengths of the two beams are properly chosen, the net photocurrent changes during titration according to *Figure 13* and will be zero at the end point. In other words, the photocurrents corresponding to the two colours will compensate each other, which means that *the zero point of the photocurrent coincides with the equivalence point regardless of whether the solution contains a high or a low concentration of the indicator* and actually also if no indicator is present.

A titration is performed in the following way.

The titration cell is filled with the colourless sample solution and the monochromators are adjusted to two appropriate—or, as they are called, *corresponding*—wavelengths. The net current is adjusted to zero with shutters or resistors, the indicator is added and the sample solution is

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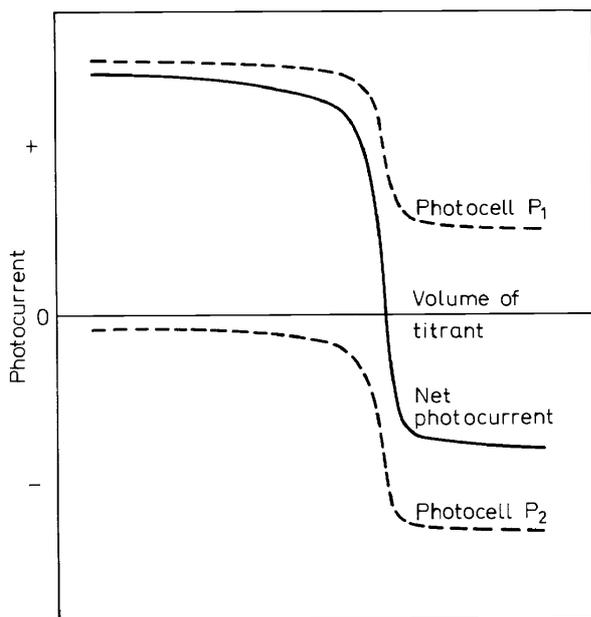


Figure 13. Photocurrents of individual photocells and net photocurrent as functions of titrant volume (From ref. 10)

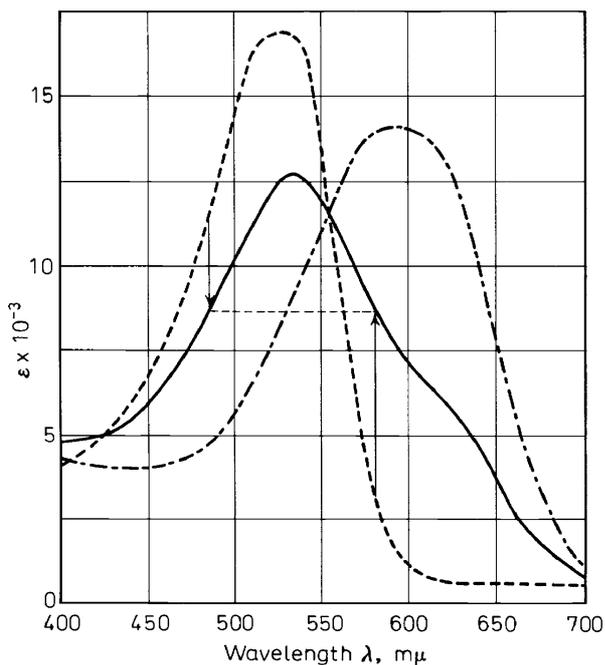


Figure 14. Molar absorptivities at pH 10: - - - - free calmagite; - . - . - magnesium complex of calmagite; ——— calmagite solution of pMg 5.6 (apparent absorptivity) (From ref. 10)

titrated until the galvanometer needle returns to zero. The maximum sensitivity of the galvanometer can be used near the end point.

The determination of the corresponding wavelengths can best be understood from *Figure 14* referring to a titration of magnesium with EDTA using calmagite as indicator. Curves are given which plot the absorptivities of free indicator and its magnesium complex and the average absorptivity of a solution which contains the indicator and has a pMg value of 5.6, i.e. the equivalence point when a  $10^{-3}$  molar magnesium solution is titrated. The two points where a horizontal line intersects the absorptivity curve of an indicator solution of the right pMg<sub>eq</sub> value represents a pair of corresponding wavelengths. The shifts of the average absorptivities during a titration are indicated by the arrows in the figure.

It should be emphasized that a reference solution is not needed for individual titrations but merely for the determination of a suitable pair of corresponding wavelengths. If they are used, the photocurrent of the instrument is always zero at the equivalence point.

Titrations with a dichrotitrator combined with the ECR principle give excellent results when one-component systems or completely masked multicomponent systems are analysed. To give an example, it is possible to titrate sulphate to hydrogen sulphate with a strong acid in spite of the fact that the acidity constant of the hydrogen sulphate ion is only  $10^{1.8}$  (i.e. the dissociation constant of the sulphate base is  $10^{-12.2}$ ).

If no or only moderate masking of interfering species is possible, the same difficulties as discussed above arise. To what extent these difficulties can be eliminated can be calculated fairly accurately if the equilibrium constants are known. In this way it is possible to compare various procedures and choose the best one.

In my review I have tried to point out that the remarkable recent development of instrumentation has markedly improved the potentialities of methods of complexometric analysis. This means that exceptionally accurate analyses are possible, even extremely dilute solutions can be titrated and—above all—even reactions leading to the formation of compounds with rather low stability constants can be utilized for successful analyses.

However, I should like to add a rule expressing the importance of equilibrium calculations. If using the terminology cited in the introduction, I should say that reliable figurative separations demand reliable separation figures.

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