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Selective Titrations of Metal Ions in the Micromolar Range

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With 7 Figures

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The renewed interest in titrimetric analysis in the last two decades can be ascribed to two main factors.

1. The possibility of determining metal ions by titration with complexing agents which form 1:1 complexes with the metal ions.

2. The application of instrumental detection methods other than the traditional potentiometry and conductometry.

A thorough understanding of the principles underlying these two factors has allowed the development of methods for selective titration of metal ions at very low concentrations with the well known advantages of titrimetry, namely speed, good precision and accuracy.

Since most recent developments have occurred in the field of complexometric titrations of metal ions, this type of reaction will be used for illustration.

The Chemical Reaction

The most important reaction to be considered is

$$M + L \rightleftharpoons ML$$

in which $M$ is a metal ion and $L$ is a chelating agent which forms only 1:1 complexes with $M$. The titration curve normally used is
a graph of $pM$ vs $f$, $pM$ being the negative logarithm of the concentration of $M$ and $f$ the fraction titrated. In the titration graphs presented in this paper the effect of dilution during a titration is neglected.

In Fig. 1 two titration curves are given, one for $K=10^{10}$ and $c=10^{-2} M$, the solid curve, and the other for $K=10^{12}$ and $c=10^{-4} M$, the dotted curve. It is obvious that the steep part in both curves is of the same length. It depends only on the product $Kc$, which in both these cases is $10^8$. When this product decreases or increases by a factor of 10, the steep part decreases or increases by one $pM$ unit. This can easily be calculated theoretically. This means that such curves, obtained for example in potentiometric titrations, can only be used if $Kc \geq 10^6$.

This is illustrated in Fig. 2, which shows a titration curve for $K=10^9$ and $c=10^{-6} M$ and hence $Kc=10^3$. No equivalence point can be obtained. However, it is possible to make a titration graph of the concentration $[M]$ itself vs $f$. For the same values of $K$ and $c$ as in Fig. 2 a very useful curve can be obtained, as shown in Fig. 3. Such curves give good equivalence points if $Kc \geq 10^2$.

It is therefore useful to distinguish between logarithmic titration curves, $pM$ vs $f$, which permit the determination of the equivalence

![Fig. 1. Titration curves of $pM$ vs $f$ for $K=10^{12}$ and $c=10^{-4} M$ (— — —) and $K=10^{10}$ and $c=10^{-2} M$ (— — )](image)