A NEW RADIOMETRIC TITRATION METHOD BASED ON SEPARATION
BY MEANS OF ION EXCHANGE, I

MATHEMATICAL EXPRESSIONS FOR THE TITRATION CURVES IN COMPLEXOMETRY AND OXIDIMETRY

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A new radiometric titration procedure is proposed, which is based on phase separation by means of an ion exchanger in the solution. The method can be applied in both complexometry and oxidimetry. A mathematical expression has been derived for the titration curves in both cases. In complexometry, a straight line is possible depending on the concentration, the mass-distribution coefficient and the complex constant, while the titration curve in oxidimetry should always be a straight line.

Introduction

In radiometric titrations it is always necessary to separate the radioactive compound to be determined from the radioactive reactions products in the solution. The end-point of the titration is then determined from the change in activity of the residual solution.

From the excellent monograph on radiometric titrations by BRAUN and TÖLGYESSY¹ it can be learned that a number of methods are available for phase separation, e.g. precipitate formation or dissolution, solvent extraction, and ion exchange. These methods allow the performance of many titrations especially in the case of precipitate formation, where phase separation is achieved by the reaction itself. Radiometric titrations based on complex formation are also well known. Phase separation in this field of titrimetry is mainly achieved by solvent extraction, although the method in which so-called solid indicators are used is also well usable. Both methods have been applied in radiometric titrations based on redox reactions; but only a very limited number of determinations are known.

Another method of determining the end-point is radioactive amalgamating². However, the field of oxidimetry is still far from being exploited.

Up till now only a few publications are known dealing with radiometric titrations by means of ion exchangers as a tool for phase separation. SCHUMACHER and FRIEDEL³ only stated that the theoretical considerations which they derived in their study about the applicability of separation by means of paper chromatography should also hold for ion exchange. STÁRY and RŮŽIČKA⁴,

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developed as a result of studies on substoichiometric isotope dilution analysis, a titration method based on separation by means of ion exchange. However, each point of the titration curve must be found by titrating an aliquot of the solution to be analyzed. Each aliquot has to pass through cation-exchange column after the addition of consecutively increasing, although substoichiometric, amounts of complexing agents.

It is obvious that both methods lack the potential possibility of automation. 
KONEČNY et al. suggested the use of ion exchange membranes. The titration curves obtained under their conditions are not straight lines, therefore they propose to work with calibration curves. This method bears the possibility of automation, as a continuous separation of the phases is possible.

The batch operation technique is not widely used in ion exchange operations, as it is always stated that column operations are much more effective. In complexation reactions, however, this statement is not trustworthy because, when the charges of the ions are altered by complexing agents, excellent separations are possible between the formed anion complex and the cation complexes already present (or vice versa).

The method we want to introduce starts from the principle that, similarly to other normal titration methods, radiometric titration and consequently the necessary phase separation have to be performed in one solution.

This requirement can easily be met when:
1. A batch operation technique is chosen (i.e. during the titration the ion exchanger is in the solution to be analyzed).
2a) The titrant itself forms complexes of opposite charge with the ion to be determined.
b) The titrant forms a compound with the ion to be determined, where after complexation occurs with some complexing agent present in excess in the solution.

Two examples are now given to illustrate the requirements mentioned under 2a and 2b:
1) \( M^{n+} + Y^{4-} \rightleftharpoons MY_{sol}^{n-1} \rightleftharpoons MY_{resin}^{n-1} \)
2) \( M^{n+} \rightleftharpoons M^{m+} + (m-n) e \) followed by a complexation reaction:
\[ M^{m+} + (m + 1) X^{-1} \rightleftharpoons MX_{(m+1)_{sol}}^{-1} \rightleftharpoons MX_{(m+1)_{resin}}^{-1} \]

These two examples also indicate that two important fields of titrimetry, viz. complexometry and oxidimetry, are now open to further investigation.

Concerning the requirement to change the charges of the ions involving the most radical alteration of exchange properties, it is clear that polyaminopolycarboxylic acids are very suited to achieve this purpose in complexometry.

It is obvious from the work of KRAUS and NELSON that many redox reactions can be performed in hydrochloric acid, as in this medium there are very great differences in the distribution coefficients between two valences of a metal ion, owing to the fact that ions with higher valence give stronger chloride complexes.

In both types of titration a strong anion exchanger is the most suitable.