

PROSPECTS OF TITRIMETRIC METHODS IN MODERN ANALYTICAL CHEMISTRY

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ABSTRACT

A survey of possible new applications of titration methods is given. Special attention is paid to redox titrations, in which equilibria among reactants and hence redox potentials can be affected by e.g. complexing agents, suitable selection of the medium etc. It may be assumed that in the future titration methods will be used not only for the determination of substances but also for the study of reaction mechanisms, rates, etc.

Because of their simplicity and rapidity, titration methods are very frequently used in analytical practice. Together with gravimetry they belong among the oldest methods of analytical chemistry; through the years, their development has often been considered completed though their utility has never been questioned. During roughly the last five decades this field experienced several 'impulses' which led to an increase in the prestige of titrimetric methods and paved new ways for broadening their application. The first of these was the introduction of end-point detection techniques other than visual; here only a number of electrometric methods will be mentioned, beginning with potentiometry and including amperometric, biamperometric and coulometric titrations, or, generally speaking, titrations with polarized electrodes, as well as conductometric and high-frequency titrations. These techniques, together with more highly developed instrumentation, have made possible faster and more precise performance of a number of procedures—here let us point out for example fully automated titrators—and have enabled many determinations to be carried out on a semimicro- or microscale. In this group of titrations, where mere visual indication has been replaced by objective end-point detection, can also be classified photometric titrations.

Another stage in the development and application of titrimetric methods involves titrations in non-aqueous media, and, finally, the newest and already well established field employs chelatometric titrations, using EDTA-type titrants and metallochromic indicators. Especially these types of titrations again emphasized the advantages of titrimetric methods.

With the development of functional group analysis methods, titrations have found gradually increasing application in the field of organic chemistry; recently they have been shown to be advantageous in kinetic measurements,

in following reaction rates, etc. Titrations utilizing catalytic reactions are also developing.

Broad development can also be observed in the application of redox titrations. Generally, two main research directions can be traced in this field: one is characterized by an effort to find titrants with reducing or oxidizing properties, which would be more easily prepared than the older ones, be stronger, be more stable in solution or exhibit a particular selectivity. Combination of aqueous and non-aqueous media in some determinations or modification of the redox potential values and shifting of redox equilibria by addition of complexing agents offer very interesting possibilities here. It has been found that titration methods frequently have a greater importance in following the course and rate of chemical reactions, especially those of organic compounds, thus contributing to the elucidation of their mechanism, than in direct determinations.

Since we chiefly studied redox reactions and their use in titrations during the last twenty five years, the present review will deal chiefly with this topic. We shall point out some new titrants and some new potentialities of redox titrations or determinations based on oxidation or reduction from a number of aspects, with special emphasis on those, to the study of which we have contributed¹.

Table 1. A survey of reductometric determinations with hydroquinone

Determined form	Reduced form	Determined form	Reduced form
Cl ₂	→ 2Cl ⁻	Ce ⁴⁺	→ Ce ³⁺
Br ₂	→ 2Br ⁻	Au(III)	→ Au
I ₂	→ 2I ⁻	Ru(VIII)	→ Ru(IV)
BrO ₃ ⁻	→ Br ⁻	Cu(II)	→ Cu(I)
IO ₃ ⁻	→ I ⁻	[Ag(NH ₃) ₂] ⁺	→ Ag
[Fe(CN) ₆] ³⁻	→ [Fe(CN) ₆] ⁴⁻	Mn(III)	→ Mn(II)
Pb(IV)	→ Pb(II)	Mn(IV)	→ Mn(II)
Ir(IV)	→ Ir(III)	S ₂ O ₈ ²⁻	→ SO ₄ ²⁻
Cr ₂ O ₇ ²⁻	→ Cr(III)	Tl ³⁺	→ Tl ⁺
VO ₃ ⁻	→ VO ₂ ⁺		

Two reductometric reagents can be mentioned, namely hydroquinone and hydrazine sulphate, which are both advantageous because of their great stability, even in very dilute solutions. While hydroquinone is a relatively mild reductant (its effect is similar to that of ferrous salts), which can be used especially in acidic and neutral media (in alkaline media it is oxidized not only to quinone with exchange of two electrons but other oxidation products are formed which are not precisely defined, the final products being of the humine acid type), hydrazine sulphate is a compound whose reactivity and reducing properties can be affected by changes in the medium. The reactions of hydrazine are also interesting because nitrogen is generally formed on its oxidation which escapes from the solution, thus shifting the equilibrium in favour of the reaction products. A survey of the applications of the two reagents, including at least the most important reactions, is given in *Tables 1* and *2*.

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Table 2. A survey of reductometric determinations with hydrazine sulphate

Determined form	Reduced form	Determined form	Reduced form
Cl ₂	→ 2Cl ⁻	[Ag(NH ₃) ₂] ⁺	→ Ag
Br ₂	→ 2Br ⁻	Cu(II)	→ Cu(I)
I ₂	→ 2I ⁻	[HgI ₄] ²⁻	→ Hg
ClO ⁻	→ Cl ⁻	[HgBr ₄] ²⁻	→ Hg
BrO ⁻	→ Br ⁻	Tl ³⁺	→ Tl ⁺
BrO ₃ ⁻	→ Br ⁻	Se(VI)	→ Se(IV)
IO ₃ ⁻	→ I ⁻	Se(IV)	→ Se
IO ₄ ⁻	→ IO ₃ ⁻	Mn(IV)	→ Mn(II)
I ⁺	→ I ₂ (I ⁻)	Pb(IV)	→ Pb(II)
[Fe(CN) ₆] ³⁻	→ [Fe(CN) ₆] ⁴⁻	MoO ₄ ²⁻	→ Mo(V)
Cr ₂ O ₇ ²⁻	→ Cr(III)	Mo(V)	→ Mo(III)
VO ₃ ⁻	→ VO ²⁺	NO ₂ ⁻	→ N ₂ O

The effect on the redox potential and shifts in the reaction equilibrium in the presence of complexing agents and with changes in the medium can be demonstrated by titrations with ferrous salts. These titrations belong among reductometric titrations involving an average reducing effect. However, when excess triethanolamine or mannitol and excess alkali hydroxide are present, the trivalent iron formed by the reaction is bound in a stable complex, as has been demonstrated polarographically, and the reaction equilibrium and the reducing effect are shifted to become comparable to the effect of metals or metal amalgams or of chromium(II) and vanadium(II) salts, which, however, are unstable in solution^{2,3}. A survey of titrations of inorganic ions and of some typical organic compounds using this principle and a triethanolamine medium is given in Table 3.

Table 3. A survey of reductometric determinations with ferrous sulphate in a medium of alkaline triethanolamine

Determined form	Reduced form	Determined form*
Mn(IV)	→ Mn(II)	<i>o</i> -Nitrophenol
Cr ₂ O ₇ ²⁻	→ Cr(III)	<i>p</i> -Nitrophenol
Cu(II)	→ Cu	2,4-Dinitrophenol
Bi(III)	→ Bi	Picric acid
TeO ₄ ²⁻	→ TeO ₃ ²⁻	<i>m</i> -Nitrobenzoic acid
Ag(I)	→ Ag	<i>p</i> -Diazobenzenesulphonic acid
[HgI ₄] ²⁻	→ Hg	<i>p</i> -Nitrosodimethylaniline
[Hg(S ₂ O ₃) ₂] ²⁻	→ Hg	Nitroso-R-salts
Pt(IV)	→ Pt(II) (Pt)	2,4-Dihydroxyazobenzene
Pd(II)	→ Pd	Orange II
Os(VIII)	→ Os(VI)	N ₂ O
Ir(IV)	→ Ir(III)	

* With the given compounds, excess reagent is mostly used, its unreacted amount being back-titrated with K₂Cr₂O₇ solution; the reaction scheme is not given since the reaction course varies, depending on the reaction conditions.

Among oxidants, lead tetraacetate can be mentioned¹, the characteristic effect of which, namely the breaking of C—C bonds in α -glycols and related compounds, resembles that of periodic acid. It has been found that lead tetraacetate solutions, which are stable for long periods, are well suited for titrations of many other organic compounds and of inorganic ions, as is shown in *Table 4*, the reaction course being dependent on whether a non-aqueous solution is employed or mineral acids are present etc.

Table 4. A survey of oxidimetric determinations with lead tetraacetate*

Substance		Substance
As(III)	→ As(V)	Organic SH-substances
Sb(III)	→ Sb(V)	Organic sulphides
Sn(II)	→ Sn(IV)	Formic acid
Fe(II)	→ Fe(III)	Tartaric acid
Ti(III)	→ Ti(IV)	Mandelic acid
Cr(II)	→ Cr(III)	Succinic acid [†]
Mo(III)Mo(V)	→ Mo(VI)	Citric acid
U(III)U(IV)	→ U(VI)	1,4-Anhydroerythritol
Ru(VI)	→ Ru(VIII)	Methyl- Δ -D-manofuranoside
Eu(II)	→ Eu(III)	1,4-Anhydromannitol
Peroxidic subst.	→ O ₂	Methyl-2,6-anhydro- Δ -D-altrropyranoside
I ₂ , I ⁻ , I ⁺	→ IO ₃ ⁻	Ethylene glycol
Br ⁻	→ Br ₂	Glycerol
[Fe(CN) ₆] ⁴⁻	→ [Fe(CN) ₆] ³⁻	Mannitol
S ₂ O ₃ ²⁻	→ S ₄ O ₆ ²⁻ (SO ₄ ²⁻)	Glucanans
NO ₂ ⁻	→ NO ₃ ⁻	Hydrazine and its derivatives
		Ascorbic acid
		<i>p</i> -Substituted phenols and their derivatives

* No oxidation scheme is given for the organic compounds, since the reaction course depends on the reaction conditions.

The presence of acetate anions does not permit full utilization of the high redox potential of the Pb(IV)/Pb(II) couple, because of its decrease due to formation of acetate complexes; however, conditions were recently found for coulometric generation of Pb⁴⁺ (i.e. the reagent is in fully ionic form) in perchloric acid medium, thus broadening the application field of oxidations with quadrivalent lead.

Since radical reactions have been assumed in some studies of oxidations with lead(IV) salts, we undertook a study of the compounds of trivalent cobalt for the sake of comparison. These compounds had previously been used for this purpose by a number of authors. In our studies we employed cobalt(III) acetate solutions, where the redox potential of the Co³⁺/Co²⁺ couple is decreased due to formation of acetate complexes, similar to lead tetraacetate. We also studied the titration of some inorganic ions and organic compounds, the oxidations of which were simple, but simultaneously we employed the reagent for the study of more complicated oxidations. We devoted considerable attention to the kinetics of cobalt(III) reactions, catalysed for example by silver salts.

The oxidations of some saccharides, where stepwise oxidation [some of the steps corresponding to oxidations with lead(IV) compounds] occurs in

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Table 5. A survey of oxidimetric determinations with cobalt triacetate

Determined form	Reduced form	Determined substance*
Tl(I)	→ Tl(III)	Hydrazine and its derivatives
Ce(III)	→ Ce(IV)	<i>p</i> -Substituted phenols
Hg(I)	→ Hg(II)	Benzidine
V(III)	→ V(IV)	<i>o</i> -Tolidine
V(IV)	→ V(V)	<i>o</i> -Dianisidine
Fe(II)	→ Fe(III)	Ascorbic acid
Cr(III)	→ Cr(VI)	Cystein
As(III)	→ As(V)	1,4-Dihydroxynaphthalene
Sb(III)	→ Sb(V)	1,5-Dihydroxynaphthalene
Sn(II)	→ Sn(IV)	2,3-Dihydroxynaphthalene
I ⁻	→ I ₂	<i>p</i> -Aminophenol
Br ⁻	→ Br ₂	<i>p</i> -Phenylenediamine
Cl ⁻	→ Cl ₂	Gentisic and homogentisic acids
NO ₂ ⁻	→ NO ⁻	α-Tocopherol
S ₂ O ₃ ²⁻	→ S ₄ O ₆ ²⁻	Glycerol
U(IV)	→ U(VI)	Mannitol
Mo(III)	→ Mo(V)	Glucose
Peroxidic subst.	→ O ₂	D-Galactose
Hydroxylamine	→ NO ₂ ⁻	L-Sorbose
		Saccharose
		Lactose
		Maltose

* No oxidation scheme is given for the organic compounds, since the reaction course is complex (often stepwise) and is affected by the reaction conditions.

dependence on the reaction conditions (reagent action time, temperature, aqueous or non-aqueous medium), have proved interesting. Some examples of oxidations with cobalt(III) acetate, with which we have dealt in recent years⁴, are summarized in Table 5.

A very interesting and simple method of *in situ* preparation of Co³⁺ has been described in the literature; a carbonate complex of the type, Co(NH₃)₆Co(CO₃)₃, which is stable in solutions of pH 7.6, was employed. When certain substances are titrated in acidic media, Co³⁺ ions are 'generated' during decomposition of the carbonate complex and react with the substance to be determined before they can hydrolyse in the aqueous medium⁵.

Among other oxidants, especially suitable for the study of reactions of organic compounds which we have studied, the complexes of copper(III) with tellurate or periodate in alkaline media can be mentioned. Especially solutions of the copper(III) periodate complex offer possibilities for comparison of the roles played in oxidations by various components of the complex⁶.

These few examples have been selected in order to demonstrate the many aspects of this field leading to the increased use of titrimetric methods. It can be assumed that in the future titrations will be used more for the study of reaction mechanisms in addition to their wide use in routine analytical practice as a simple and rapid method. It is probable that mixed media will be studied further, as well as non-aqueous media where some problems are

still not clarified, especially with acid–base reactions. In addition to catalysed reactions, hastened by chemical catalysts, attention will probably be paid to ‘hindered’ reactions at low temperatures, which have so far been investigated little and might contribute to the study of complexes and chelates. ‘Oscillation’ reactions such as the ‘blue-bottle experiment’, frequently used for demonstration purposes, have been investigated very little. Interest in the study of reactions of organic substances and in continuous monitoring of the course of some industrially important reactions is perceptibly increasing; this is true of e.g. diazotization and coupling reactions, followed by ‘diazometric’ titrations using diazonium salt solutions. Coulometric titrations have involved and will still involve the application of generated reagents which would be poorly stable in solution; it is interesting that coulometric oxidation determinations of organic substances with generated compounds of Os(VIII) and Ru(VIII) have recently been studied from the aspect of elucidation of their catalytic effect. It is impossible to mention here the many new redox reagents which have been recently introduced, such as the salts of tervalent manganese for oxidations, hydroxylamine (as a reductant) etc. It is likely that other potentialities in this field will be discovered in the future—notable, for example, is potassium perrhenate, which is still not available in many laboratories, the oxidizing properties of which have been demonstrated, especially in interesting reactions with organic substances. The fact that the reagent is at present relatively difficult to obtain can in a sense be compared with the situation some decades ago, when the possibility of using the oxidizing properties of ceric salts was evident and when it was still rather daring to assume that a rare earth element might be used for the preparation of a common titrant. This example, of course, is not limited to redox processes alone and therefore the future of titrimetric methods can be viewed optimistically when the present state is objectively evaluated. Further, and perhaps even unpredictable development can be expected. For example, the field of ion-selective electrodes was purposely not treated in this article, since their introduction is not based on titrimetry; they can, however, be cited to demonstrate their unexpected and extraordinarily significant contribution to titrimetric and other methods. This is practically the only original analytical method, the development of which is far from complete, which in some respects approaches the ideal of both sensitive and selective sensors. Ion-selective electrodes are just an example of an ‘unexpected’ discovery which probably will also be experienced in the future in titrimetric methods, analogous to various types of electrometric indication or chelatometry in the past. Waiting for these ‘unexpected’ developments is always interesting and is an incentive for further experimenting.

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