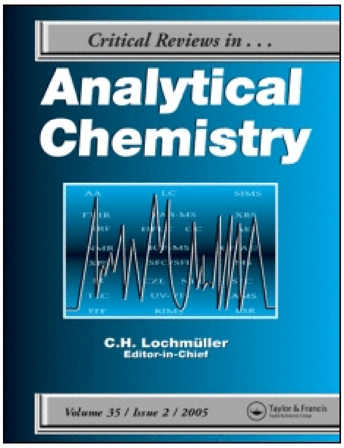

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REDOX TITRANTS IN NONAQUEOUS MEDIA

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I. INTRODUCTION

Titrimetric methods based on redox reactions constitute at present one of the most extensive and most developed fields of analytical chemistry.[1-4] Increased attention recently has been paid to redox titrations in nonaqueous or mixed media.[5-7] Although systematic research of chemical processes in nonaqueous media began in the beginning of this century, it was originally concentrated almost exclusively on acid-base reactions. The theoretical treatment and practical use of redox reactions in nonaqueous media have not yet attained the level common for acid-base reactions. The main reason is that redox reactions are complex processes in which the actual electron transfer is only one of several steps. Especially with organic substances, the overall process involves dissociation and formation of covalent bonds that usually occurs in several steps with formation of variously reactive intermediates. For this reason, it is impossible to use the values of formal redox potentials for prediction of analytical applicability of redox reactions in nonaqueous solutions; moreover, these values are often unknown. The optimum conditions for determinations are found experimentally more often than on the basis of detailed knowledge of the studied systems. The effect of solvent on the formal redox potential has sometimes been studied, but a study of the effect on the kinetics and mechanism of reactions has been exceptional so far. Most of the described methods can be classified in one of the following three groups.

The first group contains methods in which an aqueous solution of the determinand is titrated by a nonaqueous solution of the reagent. This approach is employed when aqueous solutions of the reagent are less stable than a nonaqueous solution, or when an aqueous solution cannot be prepared at all (mostly because of limited solubility of the reagent), or when the nonaqueous solution exhibits better analytical properties than the aqueous solution (the formal redox potential, reactivity, selectivity, etc.).

In the second group are methods in which a nonaqueous solution of the determinand is titrated by an aqueous solution of the reagent. These methods must be used when the substance to be determined is insufficiently soluble in water.

The third group, most interesting theoretically, involves methods in which a nonaqueous solution of the determinand is titrated by a nonaqueous solution of the reagent. These methods enable use of reagents, or determination of substances, which react with water through hydrolysis, oxidation, or reduction. They are used for determinations in which the reaction in the presence of water is incomplete, nonstoichiometric, or too slow, and when elimination of water suppresses undesirable effects of side and subsequent reactions. Practically, these methods are usually most demanding experimentally because even traces of water in the solvents used must be removed, and contamination with atmospheric moisture during the determination must be prevented.

The following review summarizes the preparation, standardization, and stability of many redox reagents in nonaqueous media and their use for titrations of aqueous and nonaqueous solutions of inorganic and organic substances, including the problems of visual or objective end-point detection. The possibilities of coulometric generation of the reagents in nonaqueous and mixed solutions in analytical determinations are also discussed. Redox determinations of water-insoluble substances by titrating them in nonaqueous or mixed solution with an aqueous solution of a suitable reagent are also mentioned.

The selection of solvent and its purity are of decisive importance for a successful determination using a redox reaction in nonaqueous or mixed solution, and thus separate sections are devoted to these problems. The solvents are denoted in the text as follows: acetic acid — AcOH, acetonitrile — MeCN, acetone — Me_2CO, acetanhydride — Ac_2O, dimethylformamide — DMF, dimethylsulfoxide — DMSO, tetrahydrofuran — THF, pyridine — Py, methanol — MeOH, ethanol — EtOH, propanol — PrOH, butanol — BuOH, monochloroacetic acid — $CH_2ClCOOH$, fluorosulphuric acid — HSO_3F.

II. SELECTION OF SOLVENT

The most important properties to be considered in selecting a suitable solvent for a redox reaction are the dielectric constant, basicity, and the accessible potential range. These properties also decide the solubility of the determinand and the stability and/or reactivity of the reagent.

In media with high dielectric constants the ion-pair formation is suppressed; this leads for the most part to an increase in the reaction rate of redox reactions, as at least one reactant or product in homogeneous redox reactions is usually electrically charged. Therefore, the solvent should be able to keep these charged species in solution. However, if ion-pairs are formed on dissolution of ionic compounds due to a low dielectric constant of the solvent, the reaction rates are low. For example, in glacial AcOH the rate of redox reactions is usually low because of small attractive forces between ion aggregates whose overall charge is zero. An addition of CH_3COONa that behaves as a strong base in this solvent often leads to an increase in the reaction rate due to the formation of charged acetate complexes.

The solvent basicity often affects the redox potentials of the reactants, which can affect the selectivity or the equilibrium constant of the reaction and can also influence the reaction rate.

Complex-formation also plays an important role. With decreasing dielectric constant of the solvent, the tendency of the solvent molecules to occupy coordination sites decreases, which facilitates bonding of complexing ions present.[14] Thus nonaqueous solvents can alter the redox behavior of systems compared with that in water as a suitable reference solvent. An example is the strong oxidizing effect of Cu(II) or Fe(III) in MeCN or changes in the relative strengths of redox pairs in various nonaqueous solvents. The order of common redox systems in water is Mn(VII)/Mn(II) — Fe(III)/Fe(II) — I_3^-/I^- — Cu(II)/Cu(I) — Sn(IV)/Sn(II); this order, determined from the half-equivalence potential for several nonaqueous solvents, is as follows:[14] Me_2CO, Fe(III)/Fe(II) — I_3^-/I^- — Mn(VII)/Mn(II) — Cu(II)/Cu(I) — Sn(IV)/Sn(II); acetylacetone, I_3^-/I^- — Sn(IV)/Sn(II) — Fe(III)/Fe(II) — Cu(II)/Cu(I); MeCN, Fe(III)/Fe(II) — I_3^-/I^- — Cu(II)/Cu(I) — Sn(IV)/Sn(II); Py, I_3^-/I^- — Mn(VII)/Mn(II) — Fe(III)/Fe(II) — Cu(II)/Cu(I) — Sn(IV)/Sn(II); AcOH, Mn(VII)/Mn(II) — Fe(III)/Fe(II) — I_3^-/I^- — Cu(II)/Cu(I) — Sn(VI)/Sn(II). In DMF, Cu(II) is a stronger oxidant than Fe(III).

The accessible potential range of a solvent is given by its stability toward oxidation or reduction. Some solvents are highly resistive against oxidation and reduction and thus enable work with strong oxidants and reductants (e.g., AcOH or MeCN). Other solvents (e.g., DMF) permit work with strong reductants, but are readily oxidized by strong oxidants. On the other hand, nitromethane or nitrobenzene are considerably resistive against oxidation, but easily undergo reduction reactions.

Many solvents are advantageous from the point of view of the above characteristics, but their broader use is precluded by practical reasons, such as the availability in the pure form or a possibility of easy purification, sufficiently high boiling point, stability, and low toxicity. These requirements lead to a selection of certain solvents from the great number available that permit easy experimental work and have advantages over other solvents.

Most common organic solvents involve AcOH, MeCN, DMF, and Py; among inorganic solvents H_3PO_4 is most often used. As co-solvents for the reagent or the determinand, MeOH, EtOH, Me_2CO, and glycerol are most commonly used.

III. PURIFICATION OF SOLVENTS

Great attention must be paid to the purity of the solvents, which must not contain any oxidizable or reducible substances and often must not contain even small amounts of water.[5-7] In principle, methods developed for electrochemical measurements[8,9] or for acid-base titrations[10,11] can be used successfully for solvent purification for redox titrations.

AcOH can be freed of reducing impurities by heating with CrO_3 under reflux, followed by column distillation with a high reflux ratio. Traces of water can be removed by heating with Ac_2O.[12,13] Sometimes, the water content is determined according to Fischer and the appropriate amount of Ac_2O is added. In this way, acetic acid with water content below 10^{-3} M can be obtained.[14] To remove last residues of reducing impurities, boiling the acid with $NaMnO_4$, followed by fractionation is recommended.[15] Some less common methods of purification of this solvent are given in the sections describing the preparation of various reagents in this medium.

Commercial MeCN contains H_2O, AcOH, unsaturated nitriles, toluene, various aldehydes, and amines as impurities. For purification of the solvent, boiling successively with P_2O_5 and Na_2CO_3, followed by slow distillation on an efficient column, was originally recommended.[16] Coetzee et al.[17] have described a number of methods of purification of this solvent for polarographic measurements. The most efficient method involves fraction distillation with P_2O_5 and then with CaH_2. This procedures is also most often used for MeCN purification for redox titrations. The water content is then around 10^{-3} M. O'Donell with co-workers[18] recommended for voltammetric measurements slow distillation with a mixture of Na_2CO_3 and $KMnO_4$ in the absence of atmospheric moisture. The distillate is slightly acidified with concentrated H_2SO_4 and distilled again on an efficient column with a high reflux ratio. Thus purified solvent is also suitable for coulometric purposes. A modified procedure has been used[19] for titrations with Fe(III), yielding the solvent with a water content of the order of $1 - 2 \times 10^{-4}$ M. A further decrease in the water content can be attained by adding CaH_2 and filtering it off immediately before use; the water content is then decreased down to 5×10^{-5} M, but MeCN thus dried rapidly absorbs water from the environment, even when working in a dry box. Hence the actual water content in practical work is generally substantially higher than the above minimum value.

The methods applicable for purification of DMF and the tests for its purity are given, together with the corresponding physical properties in Reference 20. This solvent can be purified with anhydrous $MgSO_4$ or Na_2CO_3, followed by distillation on an efficient column.[21] The water content in the solvent thus purified is less than 0.03 M and can be further decreased by using molecular sieves.[22]

Py can be purified by distillation with $KMnO_4$ and NaOH[21] and dried by storage with solid KOH.[14,21,23] The solvent with a water content of 5×10^{-3} M can be obtained by azeotropic distillation with benzene,[21] and the water content can be further decreased below 10^{-3} M by drying with a molecular sieve.[14]

Me_2CO can be dried with anhydrous $CaSO_4$, followed by distillation on an efficient column.[24] After final drying with molecular sieves, the purified solvent contains less than 10^{-3} M water.[14]

Procedures for purification of less common solvents used in redox titrations are given in the sections devoted to the individual reagents. In addition to the monographs[10,11] mentioned above, many references to purification procedures for various solvents can be found in the reviews[5-7,25-30] and in the monograph,[31] in which methods for checking the purity of solvents are also described. To determine water in solvents, the Fischer method[32] or its coulometric modification[33] is most often employed. Spectrophotometric determination of traces of water has also been studied.[34]

IV. OXIDIZING AGENTS

A. Compounds of Divalent Copper

The formal redox potential of the Cu(II)/Cu(I) system in aqueous solution is +0.153 V in acidic and −0.087 V in alkaline media.[35] However, in nonaqueous solution Cu(I) is stabilized by coordination of the solvent molecules and thus the redox potential of the Cu(II)/Cu(I) system substantially increases. For example, the standard redox potential of this system in MeCN is 0.679 V.[37] However, the formal redox potential strongly depends on the anion present.[38] If the Cu(II) solution is prepared from $Cu(ClO_4)_2$, then its formal redox potential equals 0.950 V; with $Cu(NO_3)_2$ it is 0.695 V and with $CuCl_2$ it is only 0.560 V vs. SCE.[38] In solutions prepared from $Cu(NO_3)_2$ or $CuCl_2$, the formal redox potential can be increased by adding $NaClO_4$. With $Cu(NO_3)_2$ the value increases from 0.695 V in the absence of $NaClO_4$ to 0.750 V in 0.01 *M* $NaClO_4$, 0.845 V in 0.1 *M* $NaClO_4$ and 0.860 V in saturated (approximately 2 *M*) $NaClO_4$. With $CuCl_2$ these values are 0.560 V in the absence of $NaClO_4$ and 0.840 V in approximately 2 *M* $NaClO_4$.[38] (All the potentials are given vs. SCE.) Therefore, the potential values approach a certain limiting value with increasing $NaClO_4$ concentration, but this value is about 0.1 V lower than the formal redox potential of the Cu(II)/Cu(I) system in the absence of NO_3^- or Cl^-. This fact has been explained by assuming that anion ClO_4^- replaces anion NO_3^- or Cl^-, so that Cu(II) is present in MeCN in the form, $Cu(ClO_4)_{2-x}(NO_3)_x$ or $Cu(ClO_4)_{2-x}Cl_x$, where x depends on the ratio of the ligand concentrations in the solution.[38] A study of the electrochemical behavior of the Cu(II)/Cu(I) system in MeCN revealed[39] that the system is reversible with a half-wave potential of 1.0 V vs. SCE. The electrochemical behavior of Cu(II) has also been studied in other nitriles and nonaqueous solvents.[40] The formal redox potential of the Cu(II)/Cu(I) system in DMF is 0.710 V in 0.02 *M* HCl, 0.625 V in 0.5 *M* HCl, 0.615 V in 1 *M* HCl, and 0.599 V in 2 *M* HCl. The values for Py are 0.425 V in 0.05 *M* HCl and 0.405 V in 0.5 *M* HCl[21] (all values vs. SCE).

1. *Standard Solutions*

Completely anhydrous 0.07 *M* $Cu(ClO_4)_2$ in MeCN is prepared by dissolving $Cu(MeCN)_4(ClO_4)_2$ in anhydrous MeCN.[42] The initial substance can be prepared either by reaction of $Cu(H_2O)_6(ClO_4)_2$ with P_2O_5,[42] or by reaction of $NOClO_4$ with metallic copper.[43] The solution obtained must be stored in an automatic burette with teflon stopcocks and closed with a drying vent containing $CaSO_4$. A solution of hydrated $Cu(ClO_4)_2$ in MeCN can be prepared by dissolving a required amount of $Cu(H_2O)_6(ClO_4)_2$ in MeCN and filtering off the small amount of white precipitate formed.[42] Kratochvil[44] prepared a 0.03 *M* solution of hydrated $Cu(ClO_4)_2$ from the substance, $Cu(ClO_4)_2.6.1\ H_2O.\ 0.01\ HClO_4$, obtained by reaction of $CuCO_3$ with $HClO_4$. A weighed amount of this substance is dissolved in MeCN and about 1 mℓ of 72% $HClO_4$ is added to 1ℓ of the solution to suppress hydrolysis of Cu(II). The titer of the two solutions can be determined either by potentiometric titration of thiourea in MeCN, or by titration of Cu(II) with an EDTA solution with murexide indicator.[42] Both solutions are sufficiently stable and their titer is virtually constant for 2 weeks. Ferrocene was proposed as a primary standard for the determination of the titer of hydrated $Cu(ClO_4)_2$ in MeCN.[44] Standard solutions of $CuCl_2$, $Cu(NO_3)_2$ or $Cu(ClO_4)_2$ in

MeCN can also be prepared by dissolving weighed amounts of anhydrous or dried substances in the solvent and can be standardized complexometrically.[38]

A 0.1 *M* solution of $CuCl_2$ in DMF is prepared by dissolving a weighed amount of the p.a. substance in the solvent and is standardized iodometrically.[45] The procedures for the preparation of 0.01 *M* $CuCl_2$[46] and 0.1 and 0.01 *M* $Cu(CH_3COO)_2$[47] in DMF are analogous.

A solution of 0.05 *M* $Cu(CH_3COO)_2$ in a 1:1 mixture of EtOH and Py is prepared by dissolving 11 g of $Cu(CH_3COO)_2.H_2O$ in 1ℓ of the mixture and the titer is determined by potentiometric titration of phenylhydrazine hydrochloride.[48]

2. Coulometric Generation of Divalent Copper

Cu(II) can be generated in DMF by anodic dissolution of a Cu electrode in completely anhydrous 0.5 *M* $NaClO_4$.[49] As supporting electrolytes, $LiNO_3$, LiCl, $(C_4H_9)_4NCl$, $(C_4H_9)_4NBr$, and $(C_4H_9)_4NClO_4$ also can be used at concentrations of 0.1 to 0.5 *M*. (The current efficiency decreases at lower concentrations.) A platinum spiral auxiliary electrode is immersed in an aqueous solution of the electrolyte used, which is separated from the anodic solution by a liquid bridge with a DMF solution of the electrolyte. The current density must be higher than 8 mA/cm^2, as only Cu(I) is formed at lower values. (At a current density of 2 to 4 mA/cm^2 Cu(I) is even produced with a 100% current efficiency.) The presence of water also leads to a decrease in the generation current efficiency for Cu(II), so that with a content of water as low as 5% only Cu(I) is formed.

In the coulometric generation of Cu(II) in MeCN, 0.1 *M* $(C_2H_5)_4NBF_4$ and 0.04 *M* $CuBF_4$ is used as the catolyte, and 0.1 *M* $(C_2H_5)_4$ NBF_4 and 0.004 *M* $CuBF_4$ as anolyte in this solvent.[50] The oxidation takes place on a Pt electrode with a surface area of 0.75 cm^2 at a current of 1 to 10 mA. The authors have not studied the current efficiency and its dependence on the concentrations of the components of the generation solution, but the results obtained in the determination of ferrocene and its derivatives suggest that under the given conditions the generation of Cu(II) proceeds with a 100% current efficiency. In coulometric generation of Cu(II) in MeCN,[51] 0.14 *M* CH_3COOH and 0.04 *M* $LiClO_4$ were used as the catolyte and 0.02 *M* $CuClO_4.4$ MeCN in the solvent as the anolyte. The cathode and anode compartments were separated by an anion-exchanger membrane and a Pt gauze was used as the anode. Cu(II) with coordinated MeCN is sufficiently stable and can be isolated as ClO_4^- or BF_4^-.[52]

3. Determination of Inorganic Substances

In nonaqueous media, Cu(II) is reduced to Cu(I); reduction to Cu(0) does not occur because of the too low potential of the Cu(I)/Cu(0) system, whose value is, e.g., −0.05 V (SCE) in MeCN.[42] Titrations of inorganic systems have been carried out in DMF,[46,47,49,53] MeCN,[38,42,54] and Py.[21,47] The most common method of end-point detection is potentiometry (Pt-SCE). As a reference electrode, Ag/0.01 *M* $AgNO_3$ in MeCN,[43] or DMF[46,55] is also used and is connected with the solution titrated by a bridge packed with a column of methylcellulose saturated with a 0.1 *M* NH_4NO_3 in DMF.[46] A system of a platinum indicator and a glass reference electrode was used in MeCN[54] and about 30 combinations of Pt with other metallic electrodes,[56] as well as biamperometry with 2 Cu electrodes, were used in DMF.[49]

During potentiometric titration of I^- in completely anhydrous MeCN, using $Cu(ClO_4)_2$ as the titrant, two breaks appear, corresponding to the oxidation of I^- to I_3^- and then to I_2,[42] as the formal redox potentials are 0.396 V for the reaction, $3\ I_2 + 2\ e^- \rightleftharpoons 2\ I_3^-$, and −0.248 V for the reaction, $I_3^- + 2\ e^- \rightleftharpoons 3\ I^-$ (vs. the Ag/0.01 *M* $AgNO_3$ reference electrode in MeCN). When using $CuCl_2$ or $Cu(NO_3)_2$ as the titrant, only one break is obtained, corresponding to the oxidation to I_3^-, and the other break appears only on addition of ClO_4^-. This fact is in agreement with the dependence of the redox potential of the Cu(II)/Cu(I) system on the presence of various anions discussed above.[38] Analogous results have been obtained when titrating NaI, KI, and alkylammonium iodides with $Cu(ClO_4)_2$ and $Cu(NO_3)_2$ in MeCN.[42,54]

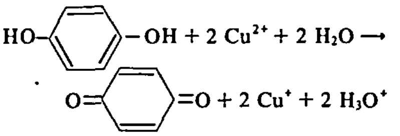
Fe(II), Cr(II), and Ti(III) can be potentiometrically titrated with 0.1 *M* $CuCl_2$ in DMF.[21] The titration of Ti(III) can also be performed on microscale.[46] Methylene blue can be used in the visual titration of Ti(III).[53] A coulometric titration of Fe(II) and Ti(III) with Cu(II) in DMF[49] and a titration of V(III) with 0.1 to 0.01 *M* $CuCl_2$ or $Cu(CH_3COO)_2$ in DMF and Py[47] have also been described. Sn(II) was coulometrically titrated with Cu(II) in DMF with biamperometric end-point detection[49] and was potentiometrically titrated in DMF and Py.[47] The reaction of Cr(II) with Sn(II) was also studied in Me_2CO, AcOH, MeCN, and Py;[14] however, only the reaction in MeCN seems to be analytically useful.

Further, coulometric titration of $Na_2S_2O_3$ with Cu(II) in DMF, involving the oxidation of thiosulfate to tetrathionate, and titration of S^{2-}, complicated by the formation of insoluble CuS, have been studied.[49] These titrations employed biamperometric end-point detection.

4. *Determination of Organic Substances*

The oxidation of organic substances by Cu(II) compounds in nonaqueous media has so far been used for the determination of hydroquinone,[42] ascorbic acid,[45,46,49,63] ferrocene and its derivatives,[44,57] various arylamines,[43] thiourea,[42,49,54,58,65] xanthates and thiocarbamates,[54,59] hydroxylamine, phenylhydrazine and its derivatives,[48] and many substances containing the –SH group.[45,46,49,53,60-62,64,66] The most common media are MeCN[42-44,54,57-59,64-66] or DMF,[45,46,49,53,60-62] and mixtures EtOH-Py (*1:1*)[48] and AcOH-MeCN[63] also have been used.

In potentiometric titration of hydroquinone with 0.07 *M* $Cu(ClO_4)_2$ in MeCN,[42] hydroquinone is oxidized according to Equation 1.



(1)

No potential break is observed in a completely anhydrous medium, but on addition of as little as 0.2% H_2O a well-developed titration curve is obtained. The positive effect of water is explained by its ability to bind the protons formed. The nonstoichiometric reaction and a small change of the potential at the equivalence in the titration of hydroquinone and of a number of thiols in MeCN by coulometrically generated Cu(II) are also explained by the absence of a suitable proton acceptor.[51]

Potentiometric titration of ascorbic acid with 0.01 *M* $CuCl_2$ in DMF yields two poorly developed and reproducible breaks,[46] the overall reagent consumption corresponding to Equation 2.

$$2\ Cu^{2+} + C_6H_8O_6 \longrightarrow 2\ Cu^+ + C_6H_6O_6 + 2\ H^+ \qquad (2)$$

However, the reverse titration of Cu(II) with ascorbic acid is characterized by a single, sharp, and reproducible break corresponding to the above stoichiometry. In spectrophotometric titration of ascorbic acid with 0.1 *M* $CuCl_2$ in DMF the same stoichiometry was found,[45] but a Cu:ascorbic acid ratio of 1:0.2 was found in the reverse titration. The absorbance of the solution titrated was measured at 435 nm, where Cu(II) has an absorption maximum. The results obtained were rather imprecise; the authors explained this fact by low stability of ascorbic acid in this solvent. A solution of hydrated $Cu(ClO_4)_2$ was used for potentiometric and visual titrations of ascorbic acid in a mixture of MeCN and AcOH.[63] Dehydroascorbic acid is the oxidation product. A Pt indicator and modified calomel or antimony reference electrodes are used. Diphenylamine or diphenylbenzidine can be employed for visual end-point detection. The reverse titration also yields reliable results and can be used for back-titration of unreacted Cu(II) in indirect determinations.

In potentiometric titration of ferrocene in MeCN the potentials stabilize rapidly and the break at the end point is so sharp that the precision of the end-point determination is 0.1%. In view of easy availability, possibility of purification, sufficient stability, and a great molecular weight, ferrocene has been proposed as a primary standard for the determination of the titer of Cu(II) standard solutions in MeCN.[44] The oxidation of ferrocene obeys Equation 3.

$$Fc + Cu^{2+} \rightleftharpoons Fc^{+} + Cu^{+} \qquad (3)$$

where Fc is ferrocene and Fc^+ is the ferrocenium cation.

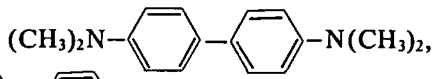
In the same way as ferrocene, many of its derivatives, namely, carboxyl-, acetyl-, amyl-, benzoyl-, butyryl-, *n*-butyl-, 1,1′-dibutyl-, 1,1′-dimethyl-, and dimethylaminomethylferrocene, can be potentiometrically titrated with Cu(II) in MeCN.[57] Ferrocene substituted with two carboxyl or acetyl groups is not oxidized under these conditions.

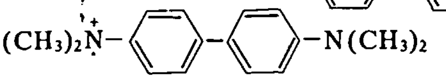
Ferrocene and its derivatives can also be determined by coulometric titration with Cu(II) in MeCN, with biamperometric[50] or potentiometric[51] end-point detection.

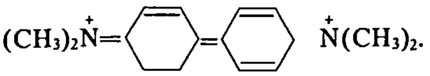
Two breaks are obtained in potentiometric titration of tetramethylbenzidine with anhydrous 0.07 *M* $Cu(ClO_4)_2$ in MeCN.[43] The oxidation, accompanied by pronounced changes in the solution color, can be described by Equations 4 and 5 in anhydrous medium,

$$TMB + Cu^{2+} \rightleftharpoons TMB^{+} + Cu^{+} \qquad (4)$$

$$TMB^{+} + Cu^{2+} \rightleftharpoons TMB^{2+} + Cu^{+} \qquad (5)$$

where TMB is 

, TMB^+ is green radical cation 

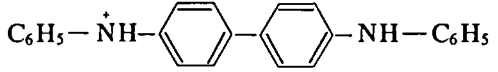
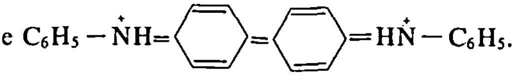
and TMB^{2+} is yellow quinoid dication 

. Both steps are reversible. In the presence of about 1% H_2O the titration curve exhibits three breaks, which is explained by partial protonation of tetramethylbenzidine by H^+ ions supplied by H_2O molecules. Unprotonated tetramethylbenzidine is then oxidized in two steps, followed by the oxidation of the protonated TMB (denoted below as $TMBH^+$), according to Equations 6 and 7.

$$2\,TMBH^{+} + Cu^{2+} \longrightarrow TMB^{+} + Cu^{+} + TMBH_2^{2+} \qquad (6)$$

$$TMB^{+} + Cu^{2+} \longrightarrow TMB^{2+} + Cu^{+} \qquad (7)$$

These two reactions take place at very similar potentials and thus appear as a single potential break. TMB protonated with two protons ($TMBH_2^{2+}$) does not react with

Cu(II) under the given conditions, as no potential break is obtained in the presence of 2 *M* $HClO_4$. In the titration of diphenylbenzidine two breaks are obtained at Cu:diphenylbenzidine molar ratios of 1:1 and 2:1, the proposed reaction mechanism being analogous to that given above. The titration curve of diphenylamine exhibits a single break at the molar ratio of Cu(II) to the substance oxidized equal to unity.[43] The mechanism proposed can be described by Equations 8 to 10, where DPA is diphenylamine, $DPAH^+$ is its protonated form, DPB is diphenylbenzidine, DPB^+ is a radical cation of the type  and DPB^{2+} is a quinoid dication of the type .

$$2\,Cu^{2+} + 4\,DPA \longrightarrow 2\,Cu^{+} + DPB + 2\,DPAH^{+} \qquad (8)$$

$$Cu^{2+} + DPB \longrightarrow Cu^{+} + DPB^{+} \qquad (9)$$

$$Cu^{2+} + DPB^{+} \longrightarrow Cu^{+} + DPB^{2+} \qquad (10)$$

The overall reaction is thus described by Equation 11, as it must be assumed that $DPAH^+$ does not react with Cu(II) under the given conditions.

$$4\,Cu^{2+} + 4\,DPA \longrightarrow 4\,Cu^{+} + DPB^{2+} + 2\,DPAH^{+} \qquad (11)$$

The oxidation of DPA, DPB, and DPB^+ must occur at the same potential, because only one potential break is observed. In the presence of H_2O, two potential breaks appear at Cu(II):DPA molar ratios of about 0.5 and 2.0 and hence Equation 12 was proposed for the first and Equations 13 and 14 for the second break.

$$2\,Cu^{2+} + 4\,DPA \longrightarrow 2\,Cu^{+} + DPB + 2\,DPAH^{+} \qquad (12)$$

$$4\,Cu^{2+} + 2\,DPAH^{+} + 4\,H_2O \longrightarrow 4\,Cu^{+} + DPB^{2+} + 4\,H_3O^{+} \qquad (13)$$

$$2\,Cu^{2+} + DPB \longrightarrow 2\,Cu^{+} + DPB^{2+} \qquad (14)$$

In these reactions, H_2O acts as a base binding the protons liberated in the oxidation of DPB; this oxidation is not complete (to DPB^{2+}), because of partial protonation of DPB.

Further amines that yield well-developed titration curves in titration with Cu(II) in MeCN in the presence of H_2O involve [the molar ratio of Cu(II) to the substance oxidized is given in the parentheses]: dithizone (2 breaks, 1.0 and 2.5), triphenylamine (1 break, 2.0), tetraphenylpyrrol (2 breaks, 1.0 and 1.5), and diphenylcarbazole (1 break, 6.0). The following compounds do react with Cu(II), but do not yield well-developed titration curves: benzidine, aniline, *o*-phenylenediamine, *p*nitrophenol, *p*-nitrophenylhydrazine, and crystal violet. Carbazole and *N*-phenylcarbazole are not oxidized under these conditions.[43]

Considerable attention has been paid to the oxidation of thiourea and its derivatives with Cu(II) in MeCN.[42,49,54,58] In aqueous solutions Cu(II) is reduced to Cu(I) and thioures is oxidized to formamidinedisulfide. Cu(I) then forms a stable complex with thiourea which is not further oxidized. The overall reaction can thus be described by Equation 15,

$$2\,Cu^{2+} + 8\,NH_2CSNH_2 \longrightarrow NH_2C(NH){-}SS{-}C(NH)NH_2 + 2[Cu(S{=}C(NH_2)_2)_3]^{+} + 2\,H^{+} \qquad (15)$$

However, the redox potential of the Cu(II)/Cu(I) system is sufficiently high in MeCN, so that even the complex of Cu(I) with thiourea is oxidized.[58] This fact was utilized for the determination of three complexes of Cu(I) with thiourea. The corresponding reactions are described by Equations 16 to 18.

$$\begin{aligned} &2[\mathrm{Cu(SC(NH_2)_2)_3]Cl} + 6\ \mathrm{Cu(ClO_4)_2} \longrightarrow \\ &\quad 3\ \mathrm{NH_2C(NH)SSC(NH)NH_2} + \\ &\quad 8\ \mathrm{CuClO_4} + 4\ \mathrm{HClO_4} + 2\ \mathrm{HCl} \end{aligned} \tag{16}$$

$$\begin{aligned} &[\mathrm{Cu(SC(NH_2)_2)_3]_2SO_4.2\ H_2O} + 6\ \mathrm{Cu(ClO_4)_2} \longrightarrow \\ &\quad 3\ \mathrm{NH_2C(NH)SSC(NH)NH_2} + 8\ \mathrm{CuClO_4} + \\ &\quad \mathrm{H_2SO_4} + 4\ \mathrm{HClO_4} + 2\ \mathrm{H_2O} \end{aligned} \tag{17}$$

$$\begin{aligned} &2\,[\mathrm{Cu(SC(NH_2)_2)_5](NO_3)_2.3\ H_2O} + 10\ \mathrm{Cu(ClO_4)_2} \longrightarrow \\ &\quad 5\ \mathrm{NH_2C(NH)SSC(NH)NH_2} + 14\ \mathrm{CuClO_4} + \\ &\quad 6\ \mathrm{HClO_4} + 4\ \mathrm{HNO_3} + 6\ \mathrm{H_2O} \end{aligned} \tag{18}$$

The reaction of thiourea itself with Cu(II) is sufficiently rapid even in completely anhydrous media and obeys Equation 19.[42]

$$\begin{aligned} &2\ \mathrm{(H_2N)_2CS} + 2\ \mathrm{Cu^{2+}} \longrightarrow \ \mathrm{NH_2C(NH)SSC(NH)NH_2} + \\ &\quad 2\ \mathrm{Cu^+} + 2\ \mathrm{H^+} \end{aligned} \tag{19}$$

This indicates that the disulfide formed can, under the given conditions, binds the protons liberated, i.e., act as a base, with the formation of the $[\mathrm{(NH_2)_2CS}]_2^{2+}$ ion. This reaction was utilized for potentiometric titration of thiourea with $\mathrm{Cu(ClO_4)_2}$ or $\mathrm{Cu(NO_3)_2}$ in MeCN with a Pt indicator and a glass reference electrode[54] and for coulometric titration of this substance in this solvent with Cu(II), detecting the end point potentiometrically or biamperometrically.[49]

Titrations of many thiourea derivatives were also studied (*N*-methyl-, *N,N*-dimethyl-, *N,N'*-diethyl-, *N,N'*-diisopropyl-, *N,N'*-di-*n*-butyl-, *N,N'*-di-*n*-octyl-, tetramethyl-, *N,N*-diphenyl-, *N,N*-di-*o*-tolyl-, *N,N*-di-tert-butyl-, *N,N*-dimethyl-*N'*-*o*-tolyl-, *N,N*-dimethyl-*N'*-*m*-tolyl, and *N,N*-diethyl-*N'*-*p*-tolylthiourea).[65] With the last six substances, the formation of red complexes with Cu(II) was observed on addition of a small amount of the reagent, as reaction intermediates. In contrast to the other derivatives, with these six substances the potentials stabilize slowly and elemental sulfur is sometimes formed, which complicates analytical use of these reactions.

Many works[45,46,49,53,60-62] have been devoted to the determination of substances containing the —SH group in DMF, where their oxidation with Cu(II) obeys Equation 20,

$$2\ \mathrm{R{-}SH} + 2\ \mathrm{Cu^{2+}} \longrightarrow \mathrm{RSSR} + 2\ \mathrm{Cu^+} + 2\ \mathrm{H^+} \tag{20}$$

Using a standard solution of $\mathrm{CuCl_2}$ in DMF, thiophenol, benzylmercaptan, 4-octylmercaptan, and 5-dodecylmercaptan[61] as well as thioglycolic and thiolactic acids, thiophenol, pentachlorothiophenol, and *o*-thiocresol[60] were potentiometrically titrated. Thiolactic acid and cystein can also be determined on a microscale.[46] Other — SH compounds have also been studied.[62] Thioglycolic and thiolactic acids, mercaptoethanol and cysteine were spectrophotometrically titrated with 0.1 *M* $CuCl_2$ in DMF.[45] Cysteine can also be visually titrated using KSCN indicator.[53] Thioglycolic acid, *n*-amylmercaptane, and benzylmercaptane can be coulometrically titrated with Cu(II) in DMF, with biamperometric end-point detection.[49] Many mercaptanes (*n*-butyl-, isobutyl-, benzyl-, and dodecylmercaptane, 2-mercaptoethanol, thiophenol, and 2-mercaptobenzothiazole) can be determined indirectly, by oxidation with hydrated $Cu(ClO_4)_2$ in MeCN and back-titration of the unreacted oxidant with an ascorbic acid standard solution in a mixture of MeCN and AcOH, with potentiometric (Pt-SCE) or visual (diphenylamine or *N,N'*-diphenylbenzidine) indication.[64] Titration of mercaptopyridines with 0.1 *M* $Cu(ClO_4)_2$ in MeCN was also studied.[66] Ethylxanthate can be determined by potentiometric titration with $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ (a platinum indicator and a glass reference electrode).[54] Xanthates and trithiocarbonates can be visually titrated with $Cu(NO_3)_2$ in MeCN, using *N,N*-diphenylbenzidine indicator.[59]

Phenylhydrazine is oxidized by Cu(II) in a mixture of EtOH and Py(1:1) according to Equation 21, while the oxidation of hydroxylamine is described by Equation 22.

$$C_6H_5NH-NH_2 + 2\ Cu^{2+} + 2\ OH^- \longrightarrow C_6H_6 + 2\ Cu^+ + N_2 + 2\ H_2O \qquad (21)$$

$$2NH_2OH + 4\ Cu^{2+} + 4\ OH^- \longrightarrow N_2O + 4\ Cu^+ + 5\ H_2O \qquad (22)$$

This fact was utilized in potentiometric titration of the two substances with a solution of 0.05 *M* $Cu(CH_3COO)_2$ in the above mixture; this method can also be used for an indirect determination of a number of carbonyl compounds on the basis of their reaction with phenylhydrazine.[48] The phenylhydrazones formed resist oxidation with Cu(II).[67,68] The formation of cation radicals in the oxidation of N-substituted anilines with $CuCl_2$ in Me_2CO was verified by ESR.[69] However, these reactions have not been used for analytical purposes.

B. Compounds of Trivalent Iron

The electrochemical behavior of the Fe(III)/Fe(II) system in many nonaqueous solvents is discussed in detail in the chapter on compounds of Fe(II); therefore, it only should be mentioned here that the redox potential of this system in MeCN is 1.57 V vs. the reference electrode, Ag/0.01 *M* $AgNO_3$ in MeCN, provided that both Fe(II) and Fe(III) are not hydrated. However, both forms are rapidly hydrated due to absorption of atmospheric moisture and consequently the redox potential decreases. For hydrated system of Fe(III)/Fe(II), a formal redox potential of +1.1 V vs. the above reference electrode was found from the potentiometric titration curves of hydroquinone, iodide, and thiourea.[19] A study of the spectrophotometric behavior of this system has shown that a solution of Fe(III) in MeCN exhibits absorption maxima at 218, 252, 278, and 366 nm, whereas a solution of Fe(II) has a broad absorption band in the region, 205 to 215 nm.[19] Hydrolysis of Fe(III) in a mixture of MeOH and H_2O was also followed spectrophotometrically.[70]

1. Standard Solutions

A solution of $Fe(ClO_4)_3$ in completely anhydrous MeCN can only be prepared by electrochemical oxidation of a completely anhydrous solution of $Fe(ClO_4)_2$.[19] An attempt to prepare $Fe(ClO_4)_3$ with MeCN coordinated instead of H_2O was not successful.[19] Therefore, solutions of hydrated Fe(III) ions in this solvent are used for analytical purposes. A 0.1 *M* solution of this reagent can be prepared by dissolving a weighed amount of $Fe(ClO_4)_2.6\ H_2O$ in MeCN purified by the procedure of O'Donnell et al.[18] The titer of the solution can be determined by titration with I^-, ferrocene or tetrachlorohydroquinone. During storage and use of this solution in a dry box, the titer decreases by about 0.1%/day; in the presence of atmospheric moisture, this decrease amounts to about 1%. This decrease is apparently caused by slow hydrolysis of Fe(III), rather than by the reduction to Fe(II). This assumption is also supported by the fact that the titer of a solution which is several days old is almost restored on addition of a small amount of $HClO_4$. Another demonstration of the hydrolysis is the UV spectrum of the solution, exhibiting a pronounced absorption maximum at 259 nm, which is analogous to the maximum observed with a Fe(III) solution in a $MeOH$-H_2O mixture attributed to the $FeOH^{2+}$ ion.[70] Due to this absorption, solutions of hydrated Fe(III) in MeCN are yellow-red.[19]

Mergens and Ewing[14] prepared standard solutions of 0.02 *M* $FeCl_3$ in MeCN, AcOH, Me_2CO, Py, and acetylacetone by dissolving an accurately weighed amount of the predried substance in the solvent and checking the titer using a standard solution of $SnCl_2$ in the same solvent. They concluded that $FeCl_3$ can serve as a primary standard in these cases. Solutions of 0.1 to 0.01 *M* $FeCl_3$ in DMF,[21,46,47] Py,[21,47] and MeOH[72] were prepared by dissolving the anhydrous substance in the appropriate solvent. The same holds for 0.1 *M* $FeCl_3$ in 0.5 *M* HCl in Py.[60] A standard solution of ferricenium trichloroacetate in CCl_3COOH was also prepared.[138]

2. Determination of Inorganic Substances

Mergens and Ewing[14] studied the possibilities of potentiometric titration of Sn(II) with Fe(III) in a number of nonaqueous media. They obtained well-shaped titration curves in Py, whereas no break was obtained in Me_2CO and MeCN. This is probably caused by the formation of a complex of Fe(III) with Cl^- ions liberated from $SnCl_2$. Good titration curves also have not been obtained in AcOH and acetylacetone.

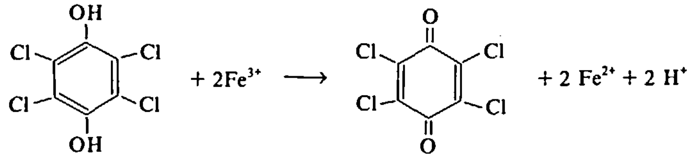
In potentiometric titration of KSCN with Fe(III) in MeCN, two breaks were observed at Fe(III):SCN^- ratios of 0.19 and 1.0.[19] It follows from a spectrophotometric study of this reaction that the first break corresponds to the formation of the $[Fe(SCN)_6]^{3-}$ or $[Fe(SCN)_5OH]^{3-}$ complexes and only a further addition of Fe(III) does lead to the oxidation of SCN^- to $(SCN)_2$. A well-developed curve was also obtained in the titration of $(C_4H_9)_4NI$.

The determination of some inorganic systems with 0.1 to 0.01 *M* $FeCl_3$ in DMF was further studied.[46,53] In potentiometric titration of Ti(III), drawn-out and poorly reproducible curves were obtained; the reverse titration gave better results.[46] No potential break was observed in the titration of Co(II). The electrode system in these titrations consisted of a Pt indicator and an Ag/0.01 *M* $AgNO_3$ in DMF reference electrode.[46] Visual titration using SCN^- indicator can also be used, but has a poorer precision.[53]

A solution of 0.1 *M* $FeCl_3$ in Py was employed for potentiometric titration of Ti(III), V(II), and Cu(I) in this medium[21] and a standard solution of $FeCl_3$ in MeCN for potentiometric titration of I^-.[73]

3. Determination of Organic Substances

A standard solution of hydrated Fe(III) in MeCN was used for titration of many substances.[19] Ferrocene is oxidized with this reagent more deeply than to the ferricenium ion, but this nonstoichiometric deeper oxidation can be suppressed by decreasing the redox potential of Fe(III) by adding a little water. Tetrachlorohydroquinone is oxidized by this reagent according to Equation 23, whereas two single-electron reversible breaks corresponding to Equations 24 and 25 were observed in titration of water-insoluble *N,N*-diphenyl-*p*-phenylenediamine.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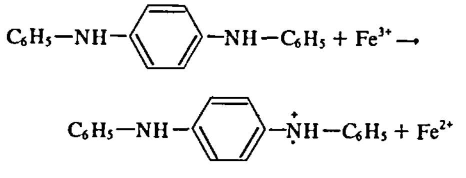
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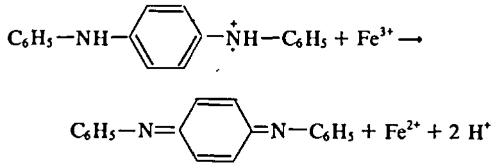
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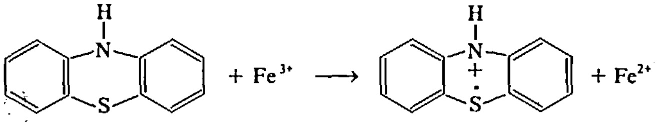
In titration of phenothiazine, which is also insoluble in water but readily soluble in MeCN, two breaks can be observed corresponding to Equations 26 and 27.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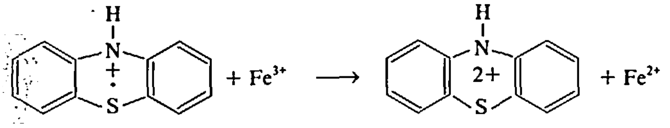

(27)

Compounds formed by substitution of hydrogen by an alkyl are more difficult to oxidize than phenothiazine itself. Some of them can be titrated, but the reaction is too slow for practical purposes. All the organic compounds studied are surveyed below, the values in the parentheses specifying the number of electrons exchanged and the potential break at the end point, defined as the difference in the potentials coresponding to the degrees of titration, 0.9 and 1.1. Benzidine (2e$^-$; 150 mV), carbazole (2e$^-$; 170 mV), dimethoxybenzidine (0.5e$^-$; 100 mV and 2e$^-$; 100 mV), diphenylbenzidine (0.5e$^-$; 50 mV and 2e$^-$; 350 mV), diphenylquanidine (0.25e$^-$; 900 mV), *N,N'*-diphenyl-*p*-phenylenediamine (1e$^-$; 120 mV and 2e$^-$; 250 mV), ferrocene (1e$^-$; 700 mV), hydroquinone (2e$^-$; 400 mV), 2-mercaptobenzothiazole (1e$^-$; 600 mV), 2-naphthalenethiol (1e$^-$; 550 mV), phenothiazine (1e$^-$; 150 mV and 2e$^-$; 175 mV), *N*-phenylcarbazole (2e$^-$; 50 mV), *N*-phenyl-phenothiazine (1e$^-$; 300 mV and 2.5e$^-$; 50 mV), promazine (1e$^-$; 150 mV and 2e$^-$; 100 mV), tetrachlorohydroquinone (2e$^-$; 250 mV), tetramethylbenzidine (2e$^-$, 250 mV), tetramethylurea (1e$^-$; 700 mV), tetraphenylpyrrole (2e$^-$; 200 mV), thioacetamide (1e$^-$; 600 mV), thioacetanilide (2e$^-$; 120 mV), thiocarbanilide (1e$^-$; 600 mV), thiourea (1e$^-$; 500 mV).

Because of hydrolysis of Fe(III), the titer of the reagent is sometimes different with respect to compounds with different redox potentials. Thus to obtain optimal results, it is recommended to use always a fresh reagent and to determine its titer with a substance with a redox potential as close as possible to that of the system to be titrated. Under these conditions the titration error does not exceed 1%.[19]

Potentiometric titration of ascorbic acid with 0.1 to 0.01 *M* $FeCl_3$ in DMF takes a long time because of slow potential stabilization, and the results are imprecise.[46] However, on addition of three drops of a 25% solution of $(C_4H_9)_4NOH$ in MeOH, the solution titrated turns red after the addition of the first few drops of the reagent, apparently due to the formation of a complex of Fe(III) with ascorbic acid. When the end point is determined as the instant of disappearance of this coloration, precise results can be obtained.[53] No potential break has been observed in potentiometric titration of cystein and thiolactic acid with this reagent and in the reverse titration.[46]

Standard $FeCl_3$ solutions in DMF and Py were used for potentiometric titrations of compounds containing —SH groups.[21,47,60] A standard solution of this reagent in MeOH was used for potentiometric titrations of 1,1′-diethylferrocene, butylferrocene, hydroxymethylferrocene, hydroxyethylferrocene, pentylferrocene, hexylferrocene, and 1,1′-dibutylferrocene. Ferrocenes substituted by carboxy or acyl, namely, ferrocene-1,1′-dicarboxylic acid, ferrocenoylpropionic acid, acetylferrocene, 1,1′-diacetylferrocene, 1,1′-dibutanoylferrocene, and hexanoylferrocene, do not react under these conditions, which can be used for analyses of their mixtures with ferrocene alkylderivatives.[72]

$K_3[Fe(CN)_6]$ was used for potentiometric titration of ascorbic acid and of hydrazine derivatives and thiourea in fused $CH_2ClCOOH$,[75] for amperometric titration of ferrocene in a mixture of AcOH and Me_2CO,[405] and for potentiometric titration of 4-aminodiphenylamine and its *N*-alkyl derivatives in a mixture of AcOH, Me_2CO, and H_2O.[74] A solution of ferricenium trichloroacetate in CCl_3COOH was employed for titration and spectrophotometric determination of ascorbic acid in a $CHCl_3$-H_2O two-phase system.[138,402]

C. Compounds of Trivalent Cobalt

In aqueous media, Co(III) compounds are very strong, but unstable oxidants with values of the redox potential of the Co(III)/Co(II) system of about 1.8 V vs. NHE.[76] The chief cause of this instability is the reaction of Co(III) with water.[77] On the other hand, solutions of Co(III) in anhydrous AcOH are relatively stable[78,79] and can be used for determination of many inorganic and organic systems. The reactivity of Co(III) with respect to organic[80] and inorganic[81] substances and the use in titrimetric analysis[2,77] have been reviewed.

The similarity between the UV and visible absorption spectra of Co(III) in glacial AcOH and those of $Co_2(SO_4)_3$ or $Co(ClO_4)_3$ in aqueous media indicates that Co(III) is present in AcOH in the form, $Co(CH_3COO)_3$ and not in the form, $H_3Co(CH_3COO)_6$.[82] It follows from conductance measurements[83] that in glacial AcOH only a small fraction of the $Co(CH_3COO)_3$ molecules is dissociated, in contrast to aqueous solutions. The behavior of the Co(III)/Co(II) system in alkaline triethanolamine was also studied.[97]

1. Standard Solutions

Sharp and White[83] prepared solutions of $Co(CH_3COO)_3$ in glacial AcOH, EtOH and *n*-BuOH by dissolving the electrochemically prepared substance in the given solvent and determined the titer iodometrically in aqueous solution. Minczewski and Pszonicka[78] prepared a 0.1 *M* $Co(CH_3COO)_3$ in glacial AcOH by dissolving Co_2O_3 in this solvent at 70 to 75°C, determining its titer by titration of Fe(II) or NaI,[78] or As(III)[79] in aqueous solution. The titer of this reagent decreases by 2% within the first 3 days and by 1% during the next 10 days.

A great attention has been paid to the electrochemical preparation of Co(III) in glacial AcOH.[76,83,84] The effect of H_2O, the concentrations of $Co(CH_3COO)_2$ and CH_3COONa

and of other parameters on the value of the current efficiency and on the stability of the solution obtained was followed, the amount of the Co(III) formed being monitored by titration or spectrophotometrically.[84] The required electrolysis time amounts to tens of hours and the current efficiency never attains the value of 100%.

The most stable solution was prepared by complete electrolysis of 0.005 to 0.1 *M* $Co(CH_3COO)_2$, adding 10 g of CH_3COONa per liter of the solution. The titer of a 0.05 *M* solution of Co(III), which did not contain any Co(II), decreased by less than 5% during 40 days. The unfavorable effect of H_2O on the stability of the reagent appears only at H_2O concentrations greater than 2%. Co(III) can also be electrochemically generated in the absence of CH_3COONa, but the resultant solution is less stable.

2. *Determination of Inorganic Substances*

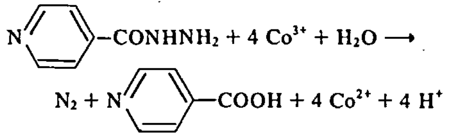
A standard solution of Co(III) in glacial AcOH was used for potentiometric titration (Pt-SCE) of Fe(II) in 2 *M* HCl and As(III) in 8 *M* HCl,[79] Mo(V) in 5 *M* HCl,[85] U(IV) in 4 *M* H_2SO_4,[86] Sn(II) and Sb(III) in 2 *M* HCl[87] and Ru(III),[88] Two breaks were observed in potentiometric titration of I^- with this reagent in 2 *M* HCl,[87] the first corresponding to the oxidation of I^- to I_2 and the second to the oxidation of I_2 to I^+. The reaction of As(III) with Co(III) can be catalyzed by Os(VIII)[79] or $AgNO_3$.[89] A standard solution of Co(III) in glacial AcOH, prepared electrochemically, was used for potentiometric titration (Pt-SCE) of S^{2-} and SO_3^{2-},[90] I^- in the presence of Br^- and Cl^-, NO_2^- in the presence of NO_3^- and thiosulfate, peroxides, hydrazine and hydroxylamine.[91] The behavior of Co(III) in $CHCl_3$ was also studied.[217]

3. *Determination of Organic Substances*

Direct potentiometric titration of phenylhydrazine, *p*-nitrophenylhydrazine, isonicotinic acid hydrazide, semicarbazide, ascorbic acid, and cysteine with a standard solution of Co(III) in glacial AcOH yields, according to the authors, reliable results only in media containing HCl at concentrations greater than 4 *M*. The oxidation of the above hydrazine derivatives is described by Equations 28 to 31.

$$C_6H_5{-}NH{-}NH_2 + 4\,Co^{3+} + HCl \longrightarrow N_2 + C_6H_5Cl + 4\,Co^{2+} + 4\,H^+ \tag{28}$$

$$O_2N{-}C_6H_4{-}NH{-}NH_2 + 4\,Co^{3+} + H_2O \longrightarrow N_2 + O_2N{-}C_6H_4{-}OH + 4\,Co^{2+} + 4\,H^+ \tag{29}$$



(30)

$$NH_2NHCONH_2 + 4\,Co^{3+} + H_2O \longrightarrow N_2 + CO_2 + NH_4^+ + 4\,Co^{2+} + 3\,H^+ \tag{31}$$

Ascorbic acid is oxidized to dehydroascorbic acid with the exchange of two electrons; in the oxidation of cysteine, an unusual exchange of six electrons was observed.[92] The oxidation of hydroxylamine by Co(III) in mineral acids and in AcOH is very slow and reproducible results have been obtained only in H_2SO_4. The reagent consumption corresponds to the oxidation of NH_2OH to HNO_3. The titration of hydrazine with this reagent also yields reliable results only within a narrow acidity range given by 1 *M* H_2SO_4, the reagent consumption corresponding to the oxidation to N_2. These titrations cannot be recommended for practical use, because of a long time required for completion of the reaction.[91]

An attempt to directly titrate benzidine, *o,o'*-tolidine and *o,o'*-dianisidine with Co(III) in glacial AcOH was unsuccessful; the dependence of the consumption of the oxidant on time in an indirect determination indicated a slow and deeper oxidation of the primary products, quinonediimines. The total number of electrons exchanged is roughly 8 for benzidine, 12 for *o,o'*-tolidine and 14 for *o,o'*-dianisidine.[93] However, these reactions cannot be utilized analytically, because of, among other things, a low stability of the solutions of the oxidized substances in glacial AcOH.

1,4-dihydroxynaphthalene is quantitatively oxidized with Co(III) in glacial AcOH to 1,4-naphthoquinone. This reaction can be used for direct potentiometric titration of the substance or for its direct determination, based on back-titration of unreacted excess of the reagent with $FeSO_4$. The oxidation of 2,3-dihydroxynaphthalene and 1,5-dihydroxynaphthalene with this reagent is nonstoichiometric and thus cannot be utilized analytically,[94] in contrast to the two-electron oxidation of gentisic acid and to the oxidation of α-tocopherol to the corresponding quinone.[95] The reagent has further been used for potentiometric titration of hydroquinone, *p*-tetrachlorohydroquinone, ascorbic acid, *p*-aminophenol, and *p*-phenylenediamine[96] and many other substances.[98] Glucose, D-galactose and L-sorbose are oxidized in 95% AcOH with an exchange of 8 electrons, mannitol with an exchange of 10 electrons, and glycerol with a stepwise exchange of 2, 4, and 6 electrons. Saccharose has been reported to resist the oxidation, in contrast to lactose and maltose.[104]

The oxidation of alkanes,[99] cyclic hydrocarbons,[100] *p*-cymene,[101] alkylarenes,[102] and phenol derivatives[103] with various forms of Co(III) has been studied from the point of view of preparation or physical chemistry, but these reactions are generally unsuitable for analytical purposes.

D. Compounds of Trivalent Manganese

Compounds of Mn(III) belong among less common but interesting oxidants, whose analytical use in aqueous solutions has been reviewed.[105,106] Recently, an increased attention has been paid to the use of Mn(III) in AcOH and propionic acid.

The formal redox potential of the Mn(III)/Mn(II) system in 0.9 *M* CH_3COONa in glacial AcOH is 0.930 V[107] and in 1.5 *M* CH_3COOK in propionic acid equals 0.900 V[397] vs. a mercuroacetate electrode. A kinetic study of the oxidation of organic substances with this reagent[106,109,111] has shown that Mn(III) is present as an acetate complex in AcOH.

1. Standard Solutions

A standard solution of Mn(III) in glacial AcOH can be prepared by dissolving $Mn(CH_3COO)_3$ prepared by reaction of $Mn(NO_3)_2$ with an excess of Ac_2O, during which the HNO_3 formed oxidizes Mn(II) to Mn(III).[109] A simpler method of preparation of 0.01 to 0.001 *M* $Mn(CH_3COO)_3$ in glacial AcOH involves the reaction between $Mn(CH_3COO)_2$ and $KMnO_4$ in this medium.[110] The titer of the solution can be determined iodometrically or with $FeSO_4$ and is virtually constant within several days. Treindl[111] prepared a solution of this reagent by electrochemical oxidation of 0.01 *M* $MnSO_4$ or $Mn(CH_3COO)_2$ in 70% AcOH, using a large-area Pt electrode; the solution was then standardized by amperometric titration with oxalic acid.

A 0.1 *N* solution of Mn(III) in anhydrous H_3PO_4 was prepared by dissolving a weighed amount of $KMnO_4$ in the solvent and heating to 50 to 60°C after 2 to 3 hr.[411]

2. *Coulometric Generation of Trivalent Manganese*

A 100% current efficiency can be attained using 0.6 *M* CH_3COOK in glacial AcOH saturated with $Mn(CH_3COO)_2$.[112] The presence of CH_3COOK leads to a decrease in the electrolyte resistance and to an increase in the solubility of $Mn(CH_3COO)_2$ in glacial AcOH. Even small amounts of H_2O decrease the current efficiency, and thus traces of water must be removed by Ac_2O.[113] Under these conditions a 100% current efficiency can be attained with current densities from 0.2 to 1.0 mA/cm^2. The current efficiency decreases with decreasing concentration of Mn(II), so that, e.g., in 0.01 *M* $Mn(CH_3COO)_2$ a 100% current efficiency can only be attained at current densities lower than 0.6 mA/cm^2. The dependence of the current efficiency on the concentrations of H_2O and Mn(II) and on the current density is also discussed.[113]

In coulometric generation of Mn(III) in propionic acid, the catolyte consisted of 1 to 2 *M* CH_3COOK in this solvent or in its mixture with propioneanhydride, and the anolyte was prepared by saturating the catolyte with $Mn(CH_3COO)_2$.[397]

3. *Determination of Inorganic Systems*

In spite of a relatively high formal redox potential of the Mn(III)/Mn(II) system in glacial AcOH, Mn(III) has not been used for direct titrations of common inorganic systems in this medium. This is evidently caused by the fact that more common reagents are available for the determination of these systems, although Mn(III) can undoubtedly be used for these purposes.

4. *Determination of Organic Systems*

Mn(III) has so far been used for studying the kinetics of the oxidation of the many organic substances in glacial AcOH.[106,109,111] It follows from this study that the rate of the oxidation of organic substances with this reagent is lower than with Mn(III) in aqueous solution. The requirement of the stability of the reagent necessitates the work in media with high concentrations of AcOH, which acts as a complexing agent decreasing the reactivity of Mn(III).[106] The main advantage of this reagent will thus be the possibility of determining organic substances insoluble in water, but soluble in AcOH.

Wadhwa and Bose[108] used Mn(III) in AcOH for indirect determination of oxalic, malonic, citric, mandelic, *p*-hydroxy-benzoic, and pyruvic acids; an Mn(III) solution in anhydrous H_3PO_4 was employed for potentiometric titration of terpenes in DMF.[411]

In direct coulometric titration of hydroquinone, the presence of water in the anolyte does not affect the accuracy of the results obtained, provided that the hydroquinone is present in the anolyte from the beginning of the generation of Mn(III). However, if it is added only after the generation of a certain amount of the reagent, the results are lower when more than 1% H_2O is present in the anolyte.[112] This phenomenon indicates a difference between the titration and generation current efficiencies, the generation current efficiency decreasing with increasing content of H_2O in the anolyte. This is in agreement with the results of a later study[113] devoted to the dependence of the current efficiency on the anolyte composition. In this titration, visual end-point detection with benzidine[112] was compared with potentiometric, bipotentiometric, and biamperometric detection,[113] and bipotentiometry was found to give the best results.

In direct or indirect coulometric titration of hydrazine it has been found[167] that the reagent consumption is about 1.3 mol per mol of hydrazine. This fact is explained by the simultaneous occurrence of reactions in Equations 32 and 33, the total reagent consumption depending on the relative extent of these two reactions.

$$N_2H_4 + Mn(CH_3COO)_3 \longrightarrow 1/2\ N_2 + CH_3COONH_4 + Mn(CH_3COO)_2 \qquad (32)$$

$$N_2H_4 + 4\ Mn(CH_3COO)_3 \longrightarrow N_2 + 4\ CH_3COOH + 4\ Mn(CH_3COO)_2 \qquad (33)$$

Quantitative reaction according to Equation 33 is attained when using excess reagent at 140° C for 95 min. The oxidation of isonicotinic acid hydrazide is also nonstoichiometric at laboratory temperature, with the consumption of about 3 mol of the reagent per mole of the substance. The quantitative oxidation to elemental nitrogen is attained only by the action of excess reagent at 140°C for 2 hr. On the other hand, phenylhydrazine can be readily determined at laboratory temperature, either by direct coulometric titration, or indirectly, using excess reagent. Biamperometric end point was always used, and the unreacted reagent was determined by adding excess hydroquinone, which was back-titrated coulometrically with Mn(III).[167] Coulometric titration of thiols is based on their oxidation to the corresponding disulfides.[107] It has been found that thiomalic acid can be determined by direct coulometric titration, whereas thioglycolic and thiosalicylic acids must be determined indirectly. The unreacted excess of the reagent is titrated using hydroquinone, as described above. In determination of *n*-heptylmercaptane and ethylthioglycolate, excess reagent must be used at an elevated temperature. Biamperometric-end-point detection gave the best results. Coulometric titration of hydroquinone, methylhydroquinone, 2-aminophenol and thiomalic acid in propionic acid, with biamperometric or potentiometric end-point detection, was also described. Thiomalic acid and 2-aminophenol can also be determined indirectly. The studied substances react with 2 mol of Mn(III), except for thiomalic acid which exchanges one electron.[397]

The oxidation of *p*-cymene,[101] *p*-methoxytoluene,[114] flavones,[115] and other organic compounds[103,106] with Mn(III) in AcOH, and of saturated hydrocarbons with the complex of Mn(III) with CF_3COOH[99] was studied from the point of view of preparation, but it has not been used for analytical purposes.

E. Compounds of Tetravalent Cerium

The use of Ce(IV) compounds in aqueous media was reviewed.[36,116,117] In nonaqueous solutions, compounds of Ce(IV) have been studied in glacial AcOH,[118-120] MeCN,[121-130,132-135] or in mixtures of the two solvents.[121-123,127-129] Mixtures of CCl_4-tributylphosphate[131] and AcOH-H_2SO_4[136] have also been used. The formal redox potential of the Ce(IV)/Ce(III) system in MeCN is 1.056 V vs. SCE or 0.755 V vs. the Ag/0.01 *M* $AgNO_3$ in MeCN reference electrode.[122] The presence of AcOH increases the formal redox potential of this system up to a 1000-fold excess of this substance over Ce(IV). At higher AcOH concentrations the formal redox potential remains constant, equal to 1.174 V vs. SCE. This fact is explained by the formation of an acetate complex of Ce(III), which has also been confirmed spectrophotometrically and is in agreement with the results of a kinetic study of the reaction of Ce(III) with Pb(IV) in glacial AcOH.[137] The formal redox potential of the Ce(IV)/Ce(III) system in glacial AcOH increases from 0.990 V in 0.25 N $HClO_4$ to 1.06 V in 2.5 *N* $HClO_4$, whereas in 2.5 *N* H_2SO_4 it equals 0.810 V.[118] A silver chloride reference electrode was used, whose potential in this medium is not known, and thus the values given above have only a relative significance.

1. Standard Solutions

Because of limited solubility of $Ce(SO_4)_2$ or $Ce(OH)_4$ in glacial AcOH it has been recommended a standard solution be prepared of Ce(IV) in this medium from

$(NH_4)_2Ce(NO_3)_6$, whose solubility is sufficient for the preparation of up to 0.05 N solutions. The solutions can be standardized by potentiometric or biamperometric titration of sodium oxalate.[118] The titer of a 0.05 M $(NH_4)_2Ce(NO_3)_6$ in AcOH containing 1 M H_2O can be determined by its titration with a sodium oxalate standard solution to the disappearance of the yellow coloration of Ce(IV) or with biamperometric indication.[119] The titer of a 0.025 M reagent decreases by about 10%/day in the light, and the decomposition rate gradually increases. When the solution is stored in a dark glass bottle, the titer decreases by 1 to 2%/day; consequently, the reagent must be standardized daily. The presence of $HClO_4$ accelerates the oxidation of many substances, but adversely affects the reagent stability. The titer decreases by 25% within 2 hr in 0.5 N $HClO_4$ and by 50% in 1 N $HClO_4$; therefore this decomposition cannot be compensated by carrying out the blank determination. A solution of 0.05 M $(NH_4)_2Ce(NO_3)_6$ in MeCN is prepared[130] by dissolving a weighed amount of the substance in the solvent and standardized iodometrically or by titration of Fe(III) in aqueous[124] or of thiourea in nonaqueous[132] medium. If the solution is protected against light and atmospheric moisture, then its titer remains virtually constant within 15 days. A 0.02 M $(NH_4)_2Ce(NO_3)_6$ in a mixture of CCl_4 and tributylphosphate can be prepared and standardized analogously.[131]

In indirect determinations, excess Ce(IV) in MeCN can be titrated with hydroquinone in AcOH,[121,129] with sodium oxalate in a mixture of CCl_4 and tributylphosphate[119] and with a hydroquinone solution in AcOH, or a mixture of $CHCl_3$ and tributylphosphate.[131] A standard solution of $Fe(ClO_4)_2$ in glacial AcOH, which has been proposed as a suitable reductant in this medium,[343] cannot be used for back-titration of $(NH_4)_2Ce(NO_3)_6$ because of the danger of reduction of NO_3^-.

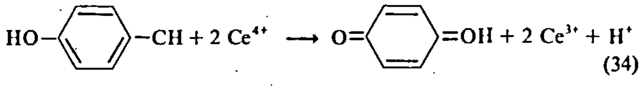
2. *Determination of Inorganic Substances*

Two breaks were observed in the titration of I^- in MeCN,[129] the first corresponding to the oxidation of I^- to I_3^- and the second to the oxidation of I_3^- to I_2. The potential stabilization is rather slow in MeCN alone, but is substantially hastened by addition of AcOH.

Fe(II) can be titrated in MeCN with a standard solution of $(NH_4)_2Ce(NO_3)_6$, using potentiometric[126] and biamperometric[120] end-point detection. An aqueous solution of $Ce(SO_4)_2$ was used for analysis of binary mixtures of Fe(II) with Sn(II), Ti(III), V(IV), Mo(V), and Fe(III) in concentrated H_3PO_4.[139]

3. *Determination of Organic Substances*

In direct titration of hydroquinone with Ce(IV) in MeCN, using a platinum indicator and a glass or antimony reference electrode, the potential stabilization is slow.[129] On addition of AcOH the potential stabilization is improved, but the consumption of the reagent is lower than corresponds to Equation 34.

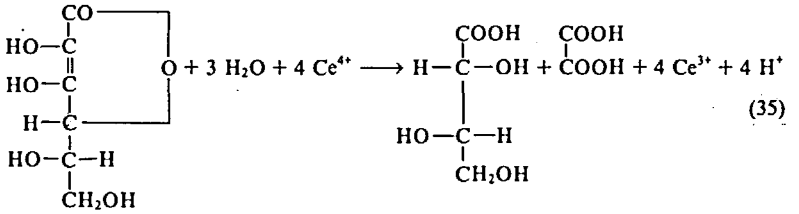


(34)

This phenomenon has been explained by the authors by a reaction of hydroquinone with the Pt indicator electrode. The reverse titration of Ce(IV) with hydroquinone yields, however, accurate and precise results and the end point can be determined even visually using ferroin. Visual titration of hydroquinone with Ce(IV) in MeCN can also be carried out using ferroin, diphenylamine, methyl red, or Janus green. Phenosafranin and neutral red yielded poor results.[128] The substance to be determined can be dissolved both in

MeCN and in glacial AcOH. Kratochvil and co-workers[123] studied the slow potential stabilization of a Pt electrode in the titration of hydroquinone with Ce(IV) in MeCN. The authors have found that the potential stabilizes most rapidly in 1 *M* AcOH. The same effect was achieved with 0.1 *M* CH_3COONa and even with picric acid and its salts at a concentration of 0.025 *M*. In contrast, an addition of $NaNO_3$ decelerated the reaction and made the potential stabilization worse. This fact has been explained by the authors by the formation of an acetate or picrate complex of Ce(IV). Thus it seems that electron transfer from hydroquinone to Ce(IV) is faster through the acetate or picrate ligand than through the nitrate ligand.

The reaction of ascorbic acid with Ce(IV) in MeCN is analytically utilizable provided that Ce(IV) is titrated with a solution of ascorbic acid in AcOH, determining the end point potentiometrically with a Pt indicator and a glass or antimony reference electrode.[127] The end point can also be detected visually using malachite green, methyl red, or methyl blue.[135] Under these conditions, 4 mol of the reagent were consumed per mole of ascorbic acid, so that the assumed reaction is described by Equation 35.



(35)

However, this mechanism seems to be improbable when compared with the data on the oxidation of oxalic acid given below.

The oxidation of oxalic acid with Ce(IV) in AcOH[118] is rapid and quantitative, with the consumption of two equivalents of the reagent per mole of the substance oxidized. The reaction mechanism is apparently very complex and has not yet been clarified. The reaction can be used for direct potentiometric or biamperometric titration of oxalic acid. No interference from HCOOH, Ac_2O, EtOH, isoPrOH, Me_2CO, formaldehyde, and benzaldehyde has been encountered. Ethyleneglycol and glycerol can be masked with Ac_2O. Tartaric acid and carbohydrates interfere.[118] Oxalic acid can also be determined with a $(NH_4)_2Ce(NO_3)_6$ standard solution in MeCN.[121] In the determination of a completely anhydrous sample, the sparingly soluble Ce(IV) oxalate is formed first, which is gradually decomposed with formation of Ce(III) oxalate and CO_2. Thus it is necessary to use excess reagent in the determination, back-titrating the unreacted portion with hydroquinone. Oxalic acid can then be dissolved in MeCN or AcOH. Analyses of oxalic acid samples containing the water of crystallization yield results by 1 to 2% lower than requested by the theory, and this error cannot be removed even by adding Ac_2O in the amount corresponding to the amount of water of crystallization.

Interesting data have been obtained in a study of the oxidation of α-ketoacids, α-hydroxyacids and polyhydroxyacids with Ce(IV) in AcOH.[119] The studied substances were dissolved in AcOH containing 1 *M* $HClO_4$ and treated with excess reagent; the unreacted portion of the reagent was then determined after a certain time by biamperometric titration with sodium oxalate.

It has been found that glycolic, lactic, and phenyl-lactic acids are oxidized according to Equations 36 and 37, the latter reaction being substantially slower. Its quantitative course would require the action of the excess reagent for several tens of hours; however, the stability of the reagent is insufficient for this purpose. Even at short times the reagent consumption exceeds a value of 2 mol/mol of the substance oxidized. Therefore, these reactions cannot be used analytically.

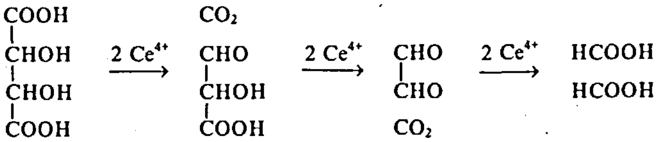
$$\mathrm{RCHOHCOOH + 2\,Ce^{4+} \longrightarrow RCHO + 2\,Ce^{3+} + 2\,H^{+} + CO_2} \qquad (36)$$

$$\mathrm{RCHO + 2\,Ce^{4+} + H_2O \longrightarrow RCOOH + 2\,Ce^{3+} + 2\,H^{+}} \qquad (37)$$

Mandelic acid is rapidly and quantitatively oxidized under these conditions according to Equation 38, which can be employed for its indirect titration determination.

$$\mathrm{C_6H_5CHOHCOOH + 2\,Ce^{4+} \longrightarrow C_6H_5CHO + CO_2 + 2\,Ce^{3+} + 2\,H^{+}} \qquad (38)$$

In the oxidation of tartaric acid, which is not only an α-hydroxyacid but also a diol, it has been found that Ce(IV) reacts faster with the α-hydroxycarboxylic group than with the glycolic group. The reaction mechanism is described by Scheme 39.



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{CHOH}\\|\\\mathrm{CHOH}\\|\\\mathrm{COOH}\end{array} \xrightarrow{2\,\mathrm{Ce^{4+}}} \begin{array}{c}\mathrm{CO_2}\\\\\mathrm{CHO}\\|\\\mathrm{CHOH}\\|\\\mathrm{COOH}\end{array} \xrightarrow{2\,\mathrm{Ce^{4+}}} \begin{array}{c}\mathrm{CHO}\\|\\\mathrm{CHO}\\\\\mathrm{CO_2}\end{array} \xrightarrow{2\,\mathrm{Ce^{4+}}} \begin{array}{c}\mathrm{HCOOH}\\\mathrm{HCOOH}\end{array} \qquad (39)$$

However, the low rate of this reaction, together with the reagent instability, precludes analytical application. Phenylcyclopentylglycolic acid is oxidized according to Equation 40; this reaction can be used analytically, because the ketone formed does not undergo any further oxidation to a perceptible degree.

$$\mathrm{C_6H_5(C_5H_9)COHCOOH + 2\,Ce^{4+} \longrightarrow C_6H_5COC_5H_9 + 2\,Ce^{3+} + CO_2 + 2\,H^{+}} \qquad (40)$$

In the oxidation of citric acid, acetone dicarboxylic acid is apparently first formed that undergoes a further nonstoichiometric oxidation; hence the reaction cannot be used analytically. Pyruvic, glyoxylic, and benzoylformic acids react according to Equations 41 and 42 and these reactions can be used for an indirect titration determination of these substances.

$$\mathrm{RCOCOOH + H_2O \longrightarrow RC(OH)_2COOH} \qquad (41)$$

$$\mathrm{RC(OH)_2COOH + 2\,Ce^{4+} \longrightarrow RCOOH + 2\,Ce^{3+} + CO_2 + 2\,H^{+}} \qquad (42)$$

The oxidation of mesitoylformic acid is described by Equation 43 and cannot be used in analysis.

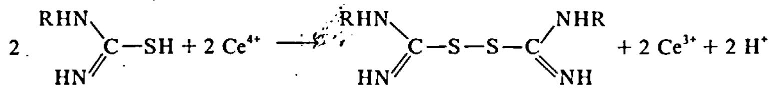
$$\mathrm{C_6H_2(CH_3)_3COCOOH + 2\,H_2O + 4\,Ce^{4+} \longrightarrow C_6H_2(CH_3)_3OH + 2\,CO_2 + 4\,Ce^{3+} + 4\,H^{+}} \qquad (43)$$

Thus it follows from work[119] that the oxidation of α-keto- and α-hydroxyacids with the α-phenyl group is rapid and stoichiometric and can become a basis of titration determinations. The oxidation of aliphatic α-hydroxyacids is slower and nonstoichiometric and polycarboxylic hydroxyacids are oxidized rapidly, but also nonstoichiometrically; therefore, these reactions cannot be utilized analytically.

p-Aminophenol and *p*-phenylenediamine can be titrated with 0.05 N $\mathrm{(NH_4)_2Ce(NO_3)_6}$ in MeCN, using malachite green, methyl red, or methyl blue as visual indicators.[135]

A great attention has been paid to the determination of thiourea and its derivatives with Ce(IV) standard solutions in nonaqueous media.[124,125,129,131]

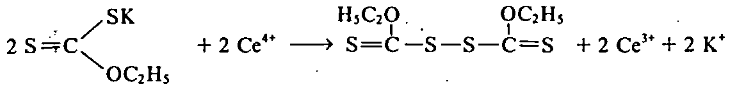
The oxidation of thiourea and its derivatives with Ce(IV) in MeCN obeys Equation 44.[124]


(44)

This reaction has been used for direct visual or potentiometric titration of thiourea, methylthiourea, ethylthiourea, isopropylthiourea, *n*-propylthiourea, and *n*-butylthiourea. As the potentials fluctuated when a common SCE type was used, a modified SCE containing a saturated solution of KCl in MeOH was employed. For visual indication, the coloration produced by the first drop of excess reagent can be used, or, fuchsine, ferroin, gentian violet, light green, methyl red, and quinalizarine indicators can be employed.[125] Organic thiocyanates, isothiocyanates, and isocyanates do not interfere, whereas ammonium thiocyanate, amines, urea, thiosemicarbazide, and cyanamide interfere.

The oxidation of thiourea with Ce(IV) in a mixture of CCl_4 and tributylphosphate can be applied to its indirect titration determination involving back-titration of the unreacted reagent with a standard solution of hydroquinone in AcOH or in a $CHCl_3$-tributylphosphate mixture with potentiometric indication (a Pt indicator and a glass reference electrode).[131]

Potassium ethylxanthate reacts with Ce(IV) in MeCN according to Equation 45, and the dixanthogenate formed is not further oxidized. The end point is indicated by the yellow coloration produced by the reagent excess,[130] or using ferroin, fuchsine, gentian violet, or quinalizarine.[125] A sparingly soluble precipitate of Ce(III) is formed in this titration and complicates the determination of the end point when present in a greater amount. Therefore, 20 to 100 μmol of potassium ethylxanthate can be determined with a precision better than ±2%, whereas the error in the determination of 300 to 600 μmol is as large as 5 to 10%. In the potentiometric titration the consumptions were lower than predicted by the theory, which has been explained by the effect of the Pt indicator electrode that causes a catalytic oxidation of the substance titrated.[129]


(45)

Organotrithiocarbonates are oxidized with Ce(IV) in MeCN according to Equation 46,

$$2\ \text{RS-CSS}^- + 2\ \text{Ce}^{4+} \longrightarrow \text{RS-CS-S-S-CS-SR} + 2\ \text{Ce}^{3+} \qquad (46)$$

This reaction can be utilized for direct potentiometric (a Pt indicator and an antimony or a modified calomel reference electrode) or visual (fuchsine, ferroin, methyl red, diphenylamine, diphenylbenzidine, methyl blue, malachite green, etc.) titration. Organic isothiocyanates, cyanates, thiocyanates, and isocyanates do not interfere, in contrast to urea, thiourea, ammonium thiocyanate, thioacetamide, thiosemicarbazide, and amines.[133] An attention has also been paid to potentiometric titration of pyrrazolinedithiocarbonates with Ce(IV) in MeCN.[134] An aqueous solution of $Ce(SO_4)_2$ was also used for an indirect determination of propionaldehyde in an AcOH-H_2SO_4 mixture[136] and rhodamine in MeOH.[140]

F. Compounds of Tetravalent Lead

Compounds of Pb(IV) belong among strong oxidants often used in preparative organic chemistry.[80] $Pb(CH_3COO)_4$ is most common, as it can readily be prepared and is easily soluble in glacial AcOH, $CHCl_3$, CCl_4, benzene, nitrobenzene, and others. The original papers[141-143] have shown that this reagent is more selective than PbO_2 used previously. Further works[144-150] have pointed out the characteristic effect of the reagent on glycolic substances and these properties were also reviewed.[151] The analytical use of $Pb(CH_3COO)_4$ is discussed in several monographs.[2-4,36] Attention has also been paid to standard solutions of $PbCl_4$ in DMF,[152] lead tetraformamide and trilead octaformamide in formamide,[153] and $Pb(CH_3COO)_4$ in fused $CH_2ClCOOH$.[179] The oxidation of hydrocarbons with a Pb(IV) complex in CF_3COOH has only been studied from the point of view of preparation.[99] In glacial AcOH, the formal redox potential of the Pb(IV)/Pb(II) system decreases from 1.08 V in 0.001 *M* to 0.91 in 1 *M* CH_3COONa and increases from 1.22 V in 0.001 *M* to 1.28 in 0.1 *M* $HClO_4$ (all the values vs. SCE). The two dependencies are roughly linear over the range, 0.001 to 0.1 *M* with a slope of 0.029 V per concentration order of CH_3COONa or $HClO_4$.[154] The effect of other mineral acids on the redox potential of the system in 30 to 100% AcOH,[155] and the polarographic behavior of Pb(IV)[164] in this medium have also been studied. The redox potential of this system in DMF decreases from 0.90 V in the solvent alone to 0.76 V in the presence of 1.5 *M* HCl.[152]

1. *Standard Solutions*

Standard solutions of $Pb(CH_3COO)_4$ in glacial AcOH can be prepared in two ways. Either an amount of Pb_3O_4 about 30% greater than required for the preparation of the solution of the required molarity is added to glacial AcOH, the mixture is filtered, and a solution of $Pb(CH_3COO)_4$ is obtained that contains $Pb(CH_3COO)_2$. The titer is determined and the required molarity is adjusted by adding a calculated amount of AcOH.[143] By the second method, a solution of $Pb(CH_3COO)_4$ that does not contain any $Pb(CH_3COO)_2$ is obtained by adding Pb_3O_4 to AcOH to the appearance of less soluble $Pb(CH_3COO)_4$ which is filtered off, recrystallized, and dissolved in AcOH.[156] In earlier works it was recommended that $Pb(CH_3COO)_4$ be prepared at temperatures below 65°C. Our experience indicates that higher temperatures can also be used without Pb(IV) being reduced. The reduction at higher temperatures described in older works can be explained by the reaction of Pb(IV) with Ac_2O that was added to attain absolutely anhydrous medium. However, the presence of Ac_2O is not necessary, because very small amounts of water do not interfere with the preparation. Weighing of $Pb(CH_3COO)_4$, which requires special care to avoid hydrolysis due to atmospheric moisture, can be circumvented by diluting a saturated solution, in which the crystals prepared can also be stored for a very long time.[156]

The titer of a $Pb(CH_3COO)_4$ solution in glacial AcOH can be determined iodometrically or using AsO_3^-,[157] hydrazinium sulfate,[158] or hydroquinone;[154] for more dilute solutions, potentiometric titration of Tl(I) can be used.[160] In a glacial AcOH medium, the reagent can be titrated with aqueous solutions of HSO_3^-,[161] $S_2O_3^-$ or $S_2O_7^{2-}$,[162] and tri- or tetrathionate.[163] When the solution is stored in the dark, then its titer remains constant for several months. The presence of Ac_2O and alkali acetates causes a considerable decrease in the solution stability.

A standard solution of $PbCl_4$ in DMF can be prepared by dissolving a weighed amount of the substance in the solvent and standardized iodometrically in an aqueous medium. The titer decreases by about 10%/month.[152]

Standard solutions of lead tetraformamide and trilead octaformamide in formamide can be obtained by dissolving $Pb(HCONH)_4$ and $Pb_3(HCONH)_8$, prepared by solvolysis of PbO_2 or Pb_3O_4, in the solvent.[153] Solutions of lead tetraformamide must be prepared daily; those of trilead octaformamide are somewhat more stable. A standard solution of $Pb(CH_3COO)_4$ in fused $CH_2ClCOOH$ can be prepared by dissolving the substance in this solvent.[179]

2. *Coulometric Generation of Tetravalent Lead*

Agasyan and co-workers[159] first attempted coulometric generation of Pb(IV). They claim a 100% current efficiency at a Ni anode electrolytically coated with PbO_2, during an electrolysis in glacial AcOH containing at least 0.5 *M* $Pb(CH_3COO)_2$ and 0.6 *M* CH_3COONa with a current density of 0.025 to 0.25 mA/cm^2. A similar procedure was employed earlier for an electrochemical preparation of a $Pb(CH_3COO)_4$ solution.[165] However, Pastor et al.[112] state that in this method the PbO_2 is dissolved from the anode surface, leading to an apparent current efficiency greater than 100%. The authors therefore studied coulometric generation of the reagent at a Pt anode. They concluded that in 0.6 *M* CH_3COOK and 0.5 *M* $Pb(CH_3COO)_2$ a 100% current efficiency can only be attained when the medium is absolutely anhydrous; even traces of H_2O decrease the efficiency because of hydrolysis of the product formed. Moreover, prolonged electrolysis in the presence of water leads to deposition of PbO_2 at the anode. In spite of these difficulties, a number of coulometric titrations with Pb(IV) in AcOH have been described.[107,112,159,166,167]

3. *Determination of Inorganic Substances*

$Pb(CH_3COO)_4$ has been used for potentiometric or amperometric titration of Fe(II), As(III), SO_3^{2-} and SCN^- in AcOH containing 1 *M* CH_3COONa.[164,168] Further, CN^- has also been titrated in this solvent.[412] The kinetics of the oxidation of Ce(III) with this reagent were also studied.[137] Cu(I), Cr(III), Fe(II), Ti(III), and I^- can be potentiometrically (Pt-SCE) titrated with a $PbCl_4$ solution in DMF.[152] Sn(II), As(III), and Sb(III) can be determined by potentiometric titration (Pt-modified SCE) with a lead tetraformamide solution or with a trilead octaformamide solution.[153] As the presence of H_2O causes acceleration of the oxidations with Pb(IV), many determinations are carried out in AcOH aqueous solutions of various dilutions.[2] The conditions must be such that the oxidation of the substance to be determined is faster than hydrolysis of Pb(IV). Potentiometric titration of Fe(II), As(III), Sb(III), and Ce(III) with $Pb(CH_3COO)_4$ in fused $CH_2ClCOOH$ has also been described.[179]

4. *Determination of Organic Substances*

A solution of $Pb(CH_3COO)_4$ was used for direct potentiometric titration (Pt-SCE) of hydroquinone, tetrachlorohydroquinone, pyrocatechol, 2-naphthol, and ascorbic acid in glacial AcOH.[154,169] The reaction with ascorbic acid is rather slow at laboratory temperature and thus titration at 60°C is recommended, using *N,N'*-bis[4-(4-methoxyphenylamine)-phenyl] thiourea indicator.[169]

Using a Pb indicator electrode, erythritol anhydride (also in the presence of methyl-α-glucoside) and 1,4-anhydromannitol were potentiometrically titrated in glacial AcOH.[170] Other cis-glycols were titrated in 25 and 50% AcOH.[170] The reactivity of cis-glycols is often so much greater than that of other substances of glycolic character that the end point of direct titration is almost unaffected by less reactive glycols. Many substances of glycolic character can be determined indirectly, by iodometrically determining excess Pb(IV) in glacial AcOH.[2] In determination of mandelic acid, the unconsumed reagent was back-titrated with hydroquinone.[154] The reaction with $Pb(CH_3COO)_4$ in glacial AcOH was also used for kinetic analysis of binary mixtures of ethanediol, propane-1,2-diol, and butane-2,3-diol[171] and for the determination of the structure of some pentoses and hexoses on the basis of the reagent consumption and the amount of formic acid and formaldehyde formed.[172] In the determination of a number of other glycolic substances, the presence of H_2O in the reaction mixture is desirable.[177,178]

Mercaptans can be titrated with Pb(IV) in glacial AcOH with potentiometric or visual indication using quinalizarine.[154,173] The corresponding disulfides are formed. In this way, thioglycolic acid, *n*-butylmercaptan, *sec*-butylmercaptan, and benzylmercaptan can be determined. Using thioglycolic acid, cysteine, thiourea, and thiosemicarbazide as model substances, it has been found taht – SH substances can be oxidized in the presence of water to various oxidation states, depending on the concentration of AcOH which may also contain a mineral acid.[173] Di-*n*-butyl-, di-*sec*-butyl-, and *n*-butylsulfide can be amperometrically titrated on the basis of their oxidation according to Equation 47.[174]

$$R_2S + Pb(CH_3COO)_4 + H_2O \longrightarrow R_2SO + Pb(CH_3COO)_2 + 2\,CH_3COOOH \qquad (47)$$

Direct titration of phenylthiourea using quinalizarine indicator,[176] an indirect determination of methylketone peroxide,[175] and a determination of hydrazine and its derivatives in the presence of a small amount of H_2O[158] have been described.

Pb(IV) generated coulometrically in glacial AcOH was used for the determination of hydroquinone,[112,159] hydrazine and its derivatives,[167] and a number of thiols.[107] The precise determinations of sulfur-containing organic compounds have been utilized for checking the purity of various reagents (thionalide, thioacetic acid, *p*-allylthiourea, thioacetamide, 4-benzil-2-thiouracil, bismutol I, bismutol II, thioglycolic acid anilide), and for analyses of pharmacological preparations. The end point of coulometric titrations in glacial AcOH is determined potentiometrically or biamperometrically with automatic recording of the titration curve. This method can also be used for the determination of some metals after their precipitation with some of the above reagents.[166]

Thioglycolic acid, amylmercaptan, dodecylmercaptan, benzylmercaptan, *o*-thiocresol, pentachlorothiophenol, and glutathione can be directly potentiometrically titrated with $PbCl_4$ in DMF, whereas the determination of phenylhydrazine and 2,4-dinitrophenylhydrazine requires the addition of excess reagent and its back-titration with $TiCl_3$.[152]

G. Compounds of Hexavalent Chromium

So far, solutions of Cr(VI) in AcOH,[15,180] or in a mixture of AcOH with trimethylamine,[181] in DMF[46,53] and in fused $CH_2ClCOOH$[75,179] have been studied. The formal redox potential of the Cr(VI)/Cr(III) system in glacial AcOH is 1.15 V in the presence of 1 *M* $HClO_4$ and 1.02 in the presence of 0.001 *M* $HClO_4$ (vs. SCE).[15] The formal potentials in other solvents are not known.

1. Standard Solutions

A 0.1 *M* solution of Cr(VI) in glacial AcOH was prepared by dissolving a weighed amount of CrO_3 in the solvent and standardized iodometrically or ferrometrically in an aqueous medium.[15] When using commercial AcOH, the reagent titer decreased by about 20% within a single day; with the p.a. solvent the decrease amounted to about 5% within 10 days, and with AcOH previously distilled with CrO_3 to less than 2% within 10 days. A 0.01 *M* $K_2Cr_2O_7$ in an AcOH-trimethanolamine mixture[181] and in fused $CH_2ClCOOH$,[75,179] and a 0.1 *M* $(NH_4)_2Cr_2O_7$ in DMF,[46] and 0.2 *M* $K_2Cr_2O_7$ in formamide[153] can be prepared by dissolving appropriate amounts of the substances in the solvents.

2. *Determination of Inorganic Substances*

A 0.1 *M* Cr(VI) solution in glacial AcOH was used for potentiometric titration of Fe(II), Sb(III), Ti(III), H_2O_2, and I^-.[15] The titration medium must be acidified with H_2SO_4 or $HClO_4$ to prevent precipitation of insoluble $Cr(CH_3COO)_3$. Hg(I) can also be titrated, but the potentials stabilize rather slowly. The reaction of As(III) with the reagent is so slow that Sb(III) can be titrated even in the presence of small amounts of As(III).

A solution of 0.1 *M* $(NH_4)_2Cr_2O_7$ in DMF was used for potentiometric titration of Ti(III) (a Pt indicator and Ag/0.01 *M* $AgNO_3$ in DMF reference electrode).[46] Large standard deviations obtained are evidently caused by a poor stability of dilute Ti(III) solutions in this solvent. Methylene blue can also be used for the end-point detection.[53] No potential break was obtained in the titration of Co(II) with this reagent. Titrations of Fe(II), Sn(II), and As(III) with 0.2 *M* $K_2Cr_2O_7$ in formamide have also been described.[153]

A 0.01 *M* solution of $K_2Cr_2O_7$ in an AcOH-trimethylamine mixture was employed for direct potentiometric titration of $SnCl_2$.[181] The reagent reaction with hydrazine is nonstoichiometric and thus cannot be analytically utilized, even if the titration curves are well developed. A 0.01 *M* $K_2Cr_2O_7$ solution in fused $CH_2ClCOOH$ was used for direct potentiometric titration of Sn(II),Fe(II), As(III), and Sb(III).[179]

3. *Determination of Organic Substances*

A Cr(VI) standard solution in glacial AcOH was used for direct potentiometric titration (Pt-SCE) of pyrocatechol, resorcinol, hydroquinone, *p*-aminophenol, and metol.[15] The medium must be acidified with H_2SO_4; in some cases (resorcinol, *p*-aminophenol, and metol) the potentials slowly stabilize and the potential break is small, which limits practical usefulness of the method. A high-frequency end-point detection was employed in the titration of phenazine derivatives with 0.1 N $K_2Cr_2O_7$ in glacial AcOH.[180]

Good results were obtained in direct potentiometric titration (Pt indicator and Ag/0.01 *M* $AgNO_3$ in DMF reference electrode) of ascorbic acid with 0.1 *M* $(NH_4)_2Cr_2O_7$ in DMF.[46] Methylene blue can also be used for the end-point detection.[53]

A standard solution of $K_2Cr_2O_7$ in fused $CH_2ClCOOH$ was employed for direct potentiometric titration of ascorbic acid and of thiourea and hydrazine derivatives.[75]

H. Compounds of Heptavalent Manganese

In aqueous media, MnO_4^- belongs among most common titration agents.[1-4,36] It can be reduced to Mn(VI), Mn(IV), Mn(III), and Mn(II), depending on the experimental conditions. In nonaqueous media, only the reduction to Mn(II) and Mn(IV) has been utilized.

1. *Standard Solutions*

Solutions of 0.1 or 0.05 *N* $NaMnO_4$ in glacial AcOH were prepared by dissolving weighed amounts of $NaMnO_4$, which has a higher solubility than $KMnO_4$, in AcOH purified by distillation with CrO_3 and boiling with $KMnO_4$.[15] It has been found that the titer of this solution, which can be determined using $(COOH)_2$ or $FeSO_4$ in aqueous solution, somewhat decreases during the first few days and then remains constant. A 0.01 *N* solution of $KMnO_4$ in glacial AcOH was prepared by dissolving a weighed amount of the substance in the solvent and standardized before use employing $(COOH)_2$.[182]

Solutions of 0.01 *N* $KMnO_4$ in fused $CH_2ClCOOH$[179] and in concentrated H_3PO_4[183] were prepared by dissolving weighed amounts of the substance in the solvents. Solutions of $KMnO_4$ in Me_2CO and Py are prepared analogously. These solutions are stable for about 24 hr and then a precipitate is formed, which is probably MnO_2. This precipitate appears almost immediately during dissolution of $KMnO_4$ in MeCN or in acetylacetone.[14]

The preparation of 0.02 *M* $KMnO_4$ in chloro- or bromobenzene[184] involved addition of a certain volume of the organic solvent to the same volume of aqueous 0.02 *M* $KMnO_4$, followed by the addition of a 1.5-fold molar excess of a halide or hydroxide of tetrabutylammonium. The permanganate was then transferred into the organic phase by 1 min of shaking. The titer of the solution was determined by the photometric titration of an accurately weighed amount of *trans*-stilbene. The titer decreased by 5%/week at 10°C. The spectrum of this solution is similar to that of an aqueous solution, the molar absorption coefficient at 530 nm being 1.85×10^3 mol^{-1} l cm^{-1}. This fact was utilized for spectrophotometric indication of titrations with this reagent.[184]

In nonpolar solvents, $KMnO_4$ alone is insoluble, but its dissolution can be achieved by adding crown polyethers[185] or tetrabutylammonium ions.[186] For example, 0.06 *M* $KMnO_4$ in benzene can be prepared by dissolving the substance in the solvent, to which dicyclohexyl-18-crown-6 is added.[185] This reagent has not yet been used for analytical purposes.

2. *Determination of Inorganic Substances*

A solution of $NaMnO_4$ in glacial AcOH can be used for determination of Fe(II) and Ti(III), whereas the determination of As(III) and Sb(III) does not yield reliable results.[15]

In concentrated H_3PO_4, Mn(II), Ce(III), V(IV), Se(IV), and Te(IV) were potentiometrically or spectrophotometrically titrated with $KMnO_4$.[183] In the titration of Sn(II) in AcOH, Me_2CO and Py, both potentiometry and the coloration caused by the first excess drop of the reagent can be used for the end-point detection.[14] Potentiometric titration of As(III), Sb(III), P(III), Ce(III), Sn(II), and Fe(II) with $KMnO_4$ in fused $CH_2ClCOOH$ in an inert atmosphere has been described,[179] using a Pt indicator and an SCE reference electrode provided with a capillary with an asbestos plug preventing penetration of water into the solution titrated.

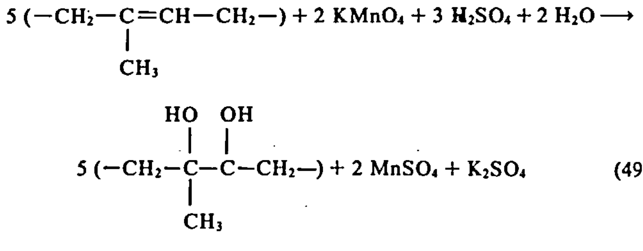
3. *Determination of Organic Substances*

A $KMnO_4$ solution in chlorobenzene was used for the determination of substances with a double bond (styrene and its derivatives, stilbene and 1-dodecene), which react with this reagent according to Equation 48.

$$3\ R{-}CH{=}CH{-}R + 8\ KMnO_4 \longrightarrow 6\ RCOOK + 8\ MnO_2 + 2\ KOH + 2\ H_2O \qquad (48)$$

In this determination, the solution is heated after each titrant addition, the MnO_2 formed is filtered off and the filtrate absorbance is measured at 530 nm.[184]

The determination of rubber after its extraction with CCl_4 by titration with a $KMnO_4$ standard solution in glacial AcOH is based on the oxidation of the double bonds according to Equation 49 and is made possible by the good miscibility of CCl_4 with AcOH. Concentrated H_2SO_4 and AcOH must be used for acidification, because an emulsion is formed on addition of H_2O. For end-point detection, the coloration caused by the first drop of excess titrant is employed.[182]



$$5\,({-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}) + 2\ KMnO_4 + 3\ H_2SO_4 + 2\ H_2O \longrightarrow 5\,({-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle HO}{\overset{|}{C}}}}{-}\overset{\displaystyle OH}{\overset{|}{C}}{-}CH_2{-}) + 2\ MnSO_4 + K_2SO_4 \qquad (49)$$

This reagent was further used for potentiometric titration of hydroquinone and pyrocatechol[15] and for the determination of reducing impurities in AcOH.[187] Ascorbic acid, thiourea, hydrazine and its derivatives were titrated with 0.01 *N* $KMnO_4$ in fused $CH_2ClCOOH$.[75]

Trans-stilbene, benzylalcohol, and benzaldehyde are stoichiometrically and quantitatively oxidized to benzoic acid, cyclohexene, and adipic acid, respectively, by $KMnO_4$ in benzene, while benzhydrol is oxidized to benzophenone and *p*-xylene to toluylic acid. However, these reactions have so far been used only for preparative purposes.[185] The same holds for the oxidation of 1- and 2-propanol, propylaldehyde, 1-octane, 4-heptanol, 1- and 2-nitropropane, and formic acid by a solution of triphenylmethylarsonium permanganate in $CHCl_3$ or nitrobenzene,[189] of olephines to α-diketones with $KMnO_4$ in Ac_2O[190] or benzene,[191] and for the oxidation of primary and secondary alcohols in benzene with $KMnO_4$ bound on silica gel or on some clays.[188]

I. Chlorine and its Compounds

In nonaqueous media, solutions of chlorine in Ac_2O,[192] chloramine T in MeOH[41] and EtOH,[71] chloramine B in AcOH and in an AcOH-EtOH mixture with H_2O,[193] dichloramine T,[194-196,214] dichloraminu B,[197] *tert*-butylhypochlorite[12] and ClO_2[198,199] in AcOH, have so far been used. Coulometric generation of elemental chlorine in AcOH[200,201] and its mixture with MeOH[202] or EtOH[203] had also been studied. Solutions of chlorine in liquid hydrogen chloride[204,205] and HSO_3F[206] also have been prepared.

Only the formal redox potentials of the ClO_2/Cl^- system in glacial AcOH (0.48 V) and in AcOH containing 0.1 *M* CH_3COONa (0.75 V)[199] and of the dichloramine T/sulphonamide system in glacial AcOH (1.2 V)[194] are known (vs. SCE). From an electrochemical study of chloramine T and dichloramine T in MeCN, it follows that dichloramine T remains a strong oxidant in the medium, whereas chloramine T behaves rather as a weak reductant.[207]

1. Standard Solutions

A standard solution of chlorine in Ac_2O can be prepared[192] by dissolving the gaseous substance in the solvent purified according to Malhotra and Katoch.[208]

A 0.05 *N* solution of chloramine T in MeOH, in which it is supposed to be more stable than in glacial AcOH, can be prepared by dissolving a weighed amount of the substance in the solvent and standardized iodometrically.[41] The same holds for 0.01 *M* dichloramine T in glacial AcOH containing 10% v/v Ac_2O.[194-196] During storage in the absence of light and atmospheric moisture, the titer remains constant for 3 days and decreases only by 2% during 14 days. On the other hand, 0.1 N dichloramine B in glacial AcOH containing 10% v/v Ac_2O must be standardized daily by iodometric titration in aqueous solution.[197] The initial substances can be prepared by introducing chlorine into aqueous solutions of chloramine B and T, filtering off, recrystallizing, and drying the precipitate formed.

A solution of 0.1 *N* *tert*-butylhypochlorite was prepared by dilution of a weighed amount of the substance prepared according to Teter and Bell[209] with glacial AcOH.[12] Its titer can be determined iodometrically (see Equation 50) or using sodium oxalate (see Equation 51). In the latter case, the reagent is reduced by excess oxalate whose unreacted portion is back-titrated cerimetrically using ferroin indicator. In the absence of light, the titer of the solution in glacial AcOH decreased by 3% during 28 days and that of the solution in 90% AcOH by 6% during the same time.

$$(CH_3)_3COCl + 2\,HI \longrightarrow (CH_3)_3COH + HCl + I_2 \qquad (50)$$

$$(CH_3)_3COCl + Na_2C_2O_4 + CH_3COOH \longrightarrow$$
$$(CH_3)_3COH + 2\,CO_2 + NaCl + CH_3COONa \qquad (51)$$

A 0.01 M solution of ClO_2 can be prepared by its dissolution in glacial AcOH in which it does not hydrolyze.[198] It can be standardized iodometrically in aqueous solution,[198] or by titration with hydroquinone in AcOH.[199] The solution must be stored in a brown bottle with a ground-glass stopper.

2. *Coulometric Generation of Elemental Chlorine*

A 100% current efficiency can be attained in the coulometric generation of elemental chlorine at a platinum electrode in 80 to 90% AcOH and 0.2 to 2 *N* HCl.[200-203]

3. *Determination of Inorganic Substances*

It follows from the conductometric titration of As(III), Sb(III), and P(III) with a solution of chlorine in Ac_2O that these reactions obey Equations 52 to 55,[192] where X is a halogen and Ph is phenyl. However, analytical usefulness of these reactions has not yet been evaluated.

$$PX_3 + Cl_2 + (CH_3CO)_2O \longrightarrow PX_3Cl^+ + CH_3COO^- + CH_3COCl \qquad (52)$$

$$Ph_3P + Cl_2 + (CH_3CO)_2O \longrightarrow Ph_3PCl^+ + CH_3COO^- + CH_3COCl \qquad (53)$$

$$Ph_3As + Cl_2 + (CH_3CO)_2O \longrightarrow Ph_3AsCl^+ + CH_3COO^- + CH_3COCl \qquad (54)$$

$$Ph_3Sb + Cl_2 + (CH_3CO)_2O \longrightarrow Ph_3SbCl^+ + CH_3COO^- + CH_3COCl \qquad (55)$$

Chloramine T or dichloramine T can be used for the titration of CN^- in AcOH,[412] dichloramine B in glacial AcOH was employed for potentiometric titration of aqueous solutions of Tl(I), Sb(III), and $[Fe(CN)_6]^{4-}$,[197] and dichloramine T for titration of Fe(II), As(III), and I^- in glacial AcOH.[194]

ClO_2 in glacial AcOH reacts with I^- according to Equation 56, which was used for the titration of I^- in the presence of Cl^- and Br^-.[199] In the presence of CH_3COONH_4, the titrant consumption is about three times as large, so that it can be assumed that the reaction obeys Equation 57. However, a large error of up to several percent precludes analytical use of the reaction.

$$2\ ClO_2 + 10\ I^- + 8\ H^+ \longrightarrow 5\ I_2 + 2\ Cl^- + 4\ H_2O \qquad (56)$$

$$6\ ClO_2 + 10\ I^- \longrightarrow 4\ IO_3^- + 3\ I_2 + 6\ Cl^- \qquad (57)$$

4. *Determination of Organic Substances*

A standard solution of chloramine T in MeOH was used for potentiometric titration of mercaptans, dithiocarbamates, and xanthates.[41] Aqueous solutions of chloramine B[193] and T[211] were used for titration of unsaturated alcohols in AcOH and for a spectrophotometric determination of phenothiazines in EtOH.[71] A standard solution of dichloramine B in glacial AcOH was employed for potentiometric titration of aqueous solutions of hydrazine, ascorbic acid, and oxime and for indirect titration of crotyl- and cinnamylalcohol.[197] Indigocarmine can be titrated with a chloramine B standard solution in glacial AcOH[396] and ascorbic acid with a dichloramine T solution in the same solvent.[194] The reaction is described by Equation 58.

$$2\ C_6H_8O_6 + CH_3C_6H_4SO_2NCl_2 \longrightarrow 2\ C_6H_6O_6 + CH_3C_6H_4SO_2NH_2 + 2\ HCl \qquad (58)$$

Potentiometric titration of thioglycolic acid[195] and biamperometric titration of sulphonamide[196] with this reagent also yielded good results.

To determine the titer of a ClO_2 standard solution in glacial AcOH, the reaction with hydroquinone, described by Equation 59, can be employed.[199]

$$2\ ClO_2 + C_6H_6O_2 \longrightarrow C_6H_4O_2 + HClO_2 \qquad (59)$$

A standard solution of *tert*-butylhypochlorite in glacial AcOH was used for determination of unsaturated substances on the basis of chlorine addition.[12] For potentiometric or biamperometric indication, lithium chloride must be added to enable formation of the chlorine-chloride system.

Chlorine generated coulometrically in a mixture of AcOH and HCl was used for analyses of mixtures of styrene and methyl oleate, with amperometric end-point indication[200] and for the determination of higher unsaturated acids with biamperometric indication.[201] Coulometric biamperometric titration of hydrazine and its derivatives with chlorine in 80% AcOH has also been described.[202] The reaction is rather slow and the authors assume that the current efficiency also does not attain 100%. Organosilicon compounds can be determined by coulometric titration with chlorine in 90% AcOH containing 0.2 *N* HCl.[203]

J. Bromine and its Compounds

Most titrations with bromine and its compounds in nonaqueous media are based on addition and substitution reactions. The exceptional importance of these reactions is responsible for the fact that standard solutions of bromine and its compounds belong among the reagents that have been most deeply studied in nonaqueous media. The same holds for coulometric generation of bromine, especially in glacial AcOH.

1. Standard Solutions

Standard solutions of Br_2 in glacial AcOH,[15] DMF,[47] $CHCl_3$,[217] in MeOH saturated with NaBr,[215,216] in liquid hydrogen chloride[204,205] and in HSO_3F[206] can be prepared by dissolving the weighed substance in the solvents. The solution in glacial AcOH is most stable and can be standardized iodometrically or using AsO_3^-.[15] The DMF solution must be handled at low temperature because of an exceptionally high Br_2 vapor pressure in this solvent.[22]

Standard solutions of *N*-bromosuccinimide in MeCN[218] or glacial AcOH,[219,220] dibromoamine B[398] or T[214] in glacial AcOH, BrCN in glacial AcOH, in its mixture with Ac_2O and in MeCN, MeOH or EtOH,[223] BrCl in glacial AcOH,[224] and $KBrO_3$ in fused $CH_2ClCOOH$[75] can be prepared by dissolving weighed amounts of the substances in the solvents. The titer decreases by 0.5% during 5 days and by 1.4% during 15 days with dibromoamine B,[398] by 2% during 5 days and by 4% during 15 days with dibromoamine T,[214] and by less than 1% in 2 months with BrCN.[223]

2. Coulometric Generation of Elemental Bromine

Many works have been devoted to coulometric titrations with Br_2 in glacial AcOH,[225,226,308] or in its mixture with H_2O.[200,203,227-235] As the anolyte, 0.3 to 1.3 *M* CH_3COOK or 0.2 *M* $NaClO_4$ in glacial AcOH saturated with KBr,[308] 0.1 *M* KBr in 90%[203] or 50%[227] AcOH have been used, as well as a mixture of AcOH, Py, and H_2O.[236] In a mixture of AcOH and MeOH (3:1), 0.15 *M* KBr was used as the anolyte.[202,237-239]

MeOH alone,[240,241] in mixture with H_2O,[242] and EtOH-benzene[243] and EtOH-benzene-H_2O[244] mixtures have also been used. A coulometric titration with Br_2 generated and detected on a rotating ring-disk electrode in a water-alcoholic medium has also been described.[246] In $CHCl_3$, 0.5 *M* $(C_2H_5)_4NBr$ anolyte gave good results.[245]

3. Determination of Inorganic Substances

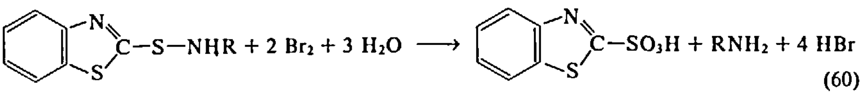
A solution of Br_2 in glacial AcOH was used for potentiometric titration of Tl(I), Fe(II), Sb(III), and Se(IV), with an addition of CH_3COONa. The titration of Ti(III) can best be carried out if the solution titrated is saturated with gaseous hydrogen chloride, and the titration of Hg(I) and As(III) must be performed at 50 to 60°C.[15] Biamperometric titration of Hg(I), Fe(II), As(III), Sb(III), SO_3^{2-} and SCN^- with this reagent requires analogous conditions.[247] A coulometric titration of As(III) and Sb(III) with Br_2 in glacial AcOH has also been described.[225] A Br_2 solution in $CHCl_3$ was used for potentiometric titration of $(CH_3)_4NBr$ and ferrocene.[217] This work is interesting from the point of view of the theory, because the redox reactions in this inert solvent must be written in a nonionic form. Therefore, the description of the strength of the redox system in this medium is also more complicated. Only a relative strength can be expressed on the basis of the values of the appropriate equilibrium constants which can be calculated from the potentiometric titration curves. For example, for the reaction, $2\,Fc + Fc^+Br_3^- \rightleftharpoons 3\,Fc^+Br^-$, it has been found that log K = 6.7 to 7.1 and for the reaction, $(CH_3)_4N^+Br^- + Br_2 \rightleftharpoons (CH_3)_4N^+Br_3^-$, log K = 8.3. (Fc is ferrocene, Fc^+ is the ferricenium cation, and $(CH_3)_4N^+$ is the tetramethylammonium cation; due to ion-pairing, these cations keep all the reactants in solution).

A conductometric or visual titration of iron pentacarbonyl with a Br_2 solution in liquid hydrogen chloride,[204] a conductometric titration of terpenes with Br_2 in DMF,[411] potentiometric titration of aqueous solutions of Tl(I), Fe(II), As(III), Sb(III), I^-, and $[Fe(CN)_6]^{4-}$ with a standard solution of dibromoamine T in glacial AcOH,[214] and a titration of Sn(II), As(III), Sb(III), S^{2-}, and SO_3^{2-} with a standard solution of BrCN in AcOH or in a mixture of AcOH with Ac_2O[223] have been described.

4. Determination of Organic Substances

A solution of Br_2 in glacial AcOH was employed for titration of pyrocatechol, resorcinol, hydroquinone, *p*-amino-phenol, metol, and diphenylamine.[15] However, these substances are not oxidized but brominated. The same holds for the determination of various sulfamides,[248] *N*-methyl- and *N*-ethylaniline,[249] a number of pharmaceuticals,[250] anesthetics,[251] sulphanilamide[252] and pyrrazole[253] derivatives, and other organic compounds[154,254-258] in glacial AcOH or in a mixture of AcOH with H_2O.[259] Good results have been obtained with potentiometric[15] and bipotentiometric[257] end-point detection, or using amperometry with a rotating platinum[215] or dropping mercury[256] electrode.

Substances containing the –SH functional group were potentiometrically titrated with a Br_2 solution in DMF; the substances are oxidized to the corresponding sulfides by the reagent.[47] Amperometric titration of sulfenamides with a Br_2 solution in MeOH is based on the oxidation of the substances according to Equation 60.[215]



(60)

(R is the benzene, cyclohexane, oxydiethylene, and benzothiazole radical). Potentiometric and amperometric titration of α,β-unsaturated aldehydes in the presence of saturated aldehydes with a Br_2 solution in MeOH saturated with NaBr has also been described.[216]

N-bromosuccinimide in MeCN was used for potentiometric and visual titrations of ethylxanthate, iso-propylxanthate, *n*-butylxanthate, *n*-amylxanthate, and of methyl-, ethyl-, *n*-propyl-, iso-propyl-, dimethyl-, and diethyldithiocarbamate.[218] Alkylisothiocyanates, isocyanates, carbon disulfide and urea do not interfere up to a five-fold molar excess. A titration of organotrithiocarbamates with this reagent has also been described.[413] Phenol in MeOH,[219] hydroquinone and resorcinol in MeOH,[220] pyrocatechol in anhydrous formamide,[220] and olephins in AcOH[302] can be titrated with a solution of this reagent in AcOH. Acridine dyes were titrated in 40% AcOH with an aqueous solution of *N*-bromosuccinimide.[260]

Attention has also been paid to the titration of aqueous solutions of hydroquinone, ascorbic acid, hydrazine, aniline, phenol, oxime and oximates of various metals, thiourea and its complexes with metals with a standard solution of dibromoamine T[214] or B[398] in AcOH. Indigocarmine was determined with bromoamine T and dibromoamine T in glacial AcOH.[396]

An aqueous solution of BrCl was used for determination of ascorbic acid,[222] amines and phenols,[261] pyrrole derivatives,[262] unsaturated compounds,[263] histamine and some pharmaceuticals,[264] and hydrazine derivatives[265] in glacial AcOH. Potentiometric titration of hydrazine and its derivatives with BrCN in glacial AcOH is based on the oxidation of the substances according to Equations 61 and 62.[223]

$$2\,N_2H_4 + 2\,Br^+ \longrightarrow NH_3 + N_3H + 4\,H^+ + 2\,Br^- \qquad (61)$$

$$2\,R_1R_2NNH_2 + 2\,Br^+ \longrightarrow R_1R_2NN{=}NNR_1R_2 + 4\,H^+ + 2\,Br^- \qquad (62)$$

On the other hand, in a mixture of AcOH with Ac_2O, hydrazine and its derivatives are acetylated, and the products formed are oxidized according to Equations 63 and 64.

$$2\,CH_3CONHNH_2 + 2\,Br^+ \longrightarrow CH_3CONHNHCOCH_3 + N_2 + 4\,H^+ + 2\,Br^- \qquad (63)$$

$$2\,R_1R_2N{-}NHCOCH_3 + Br^+ \longrightarrow R_1R_2N{-}N(COCH_3){-}N(COCH_3){-}NR_1R_2 + 2\,H^+ + Br^- \qquad (64)$$

Thiourea and its derivatives cannot be titrated with BrCN in AcOH, but good results can be obtained in their potentiometric titration with this reagent in EtOH, where the reaction in Equation 65 takes place. In this way, not only thiourea, ethylthiourea, and isopylthiourea can be determined, but also α-phenylthiourea, benzylthiourea, and *o*-tolylthiourea, which, in contrast to the previous compounds, cannot be titrated in aqueous solution.[223]

$$2\,R_1HN{-}C({=}NH){-}SH + Br^+ \longrightarrow R_1HN{-}C({=}NH){-}SS{-}C({=}NH)NHR_1 + 2\,H^+ + Br^- \qquad (65)$$

A determination of thiourea and its derivatives using excess BrCl in glacial AcOH and its iodometric back-titration in aqueous solution is based on the same principle.[224] Methyl-, ethyl-, diethyl-, and isopropyldithiocarbamates can be potentiometrically titrated with BrCN in MeOH or MeCN; the reaction is described by Equation 66.[223]

$$2\ R_1R_2NCSS^- + Br^+ \longrightarrow$$
$$R_1R_2N{-}C({=}S){-}SS{-}C({=}S){-}NR_1R_2 + Br^- \qquad (66)$$

The titration of phenols, cresols, pyrocatechol, resorcinol, hydroquinone, floroglucine, and β-naphthol with BrCN in glacial AcOH or in an AcOH-Ac_2O mixture is based on electrophilic substitution of the substances by Br^+.[266]

N-bromoacetamide was used for an indirect microdetermination of indoles in AcOH. The excess reagent was determined iodometrically.[267] Thiourea and hydrazine derivatives and ascorbic acid can be potentiometrically titrated with $KBrO_3$ in fused $CH_2ClCOOH$.[75] An aqueous solution of this reagent was used for spectrophotometric titration of unsaturated hydrocarbons in a CCl_4-MeOH-AcOH mixture[268] and for potentiometric titration of benzothiazole-2-sulfonamide in an AcOH-H_2O mixture.[221]

5. *Coulometric Titrations of Organic Substances*

The fact that the products of the one-electron oxidation of *p*-phenylenediamine derivatives, which are unstable in water, are sufficiently stable in $CHCl_3$ was used for their coulometric potentiometric titration with Br_2 in this medium.[245] The reactions can be described by Equations 67 and 68, where A are the phenylenediamine derivatives (diphenyl-*p*-phenylenediamine, tetramethyl-*p*-phenylenediamine, *p*-hydroxydiphenylamine and dimethyldiphenyl-*p*-phenylenediamine), and $A^{\dot{+}}$ are the intensely colored radical cations formed by their one-electron oxidation.

$$Br^- \longrightarrow 1/2\ Br_2 + e^- \qquad (67)$$

$$A + 1/2\ Br_2 \longrightarrow A^+ + Br^- \qquad (68)$$

Coulometric titration of hydrazine and its derivatives with Br_2 in a mixture of AcOH with MeOH and using biamperometric indication was studied in detail.[202] It has been found that hydrazine alone and its monosubstituted derivatives are oxidized according to Equation 69, provided that the substituent is not a deactivated aryl.

$$RNHNH_2 + 2\ Br_2 + H_2O \longrightarrow ROH + N_2 + 4\ HBr \qquad (69)$$

R was H, CH_3, C_6H_5, CH_3CO, and $CH_3CONHC_6H_4SO_2$. $(CONHNH_2)_2$ reacts analogously. Nonsymmetrically substituted hydrazine derivatives [$(CH_3)_2NNH_2$ and $(C_6H_5)_2NNH_2$] react more slowly with a consumption of six equivalents of bromine and with the formation of the corresponding tertrasubstituted derivatives of hydrazine. Symmetrically substituted hydrazines ($CN_3NHNHCH_3$) do not yield reproducible results and the mechanism of their oxidation has not been clarified. α-Methylphenetylhydrazine and *o*-methoxy-α-methylphenetylhydrazine consume 3 mol of Br_2, which is explained by spontaneous dehydration of the primary product and subsequent addition of Br_2 to the double bond, according to Equations 70 to 72.

$$CH_3O{-}C_6H_4CH_2{-}CH(CH_3){-}NHNH_2 + H_2O + 2\ Br_2 \longrightarrow$$
$$CH_3O{-}C_6H_4{-}CH_2{-}CH(CH_3)OH + N_2 + 4\ HBr \qquad (70)$$

$$CH_3O{-}C_6H_4{-}CH_2{-}CH(CH_3)OH \xrightarrow{H^+}$$
$$CH_3O{-}C_6H_4{-}CH{=}CHCH_3 + H_2O \qquad (71)$$

$$CH_3O{-}C_6H_4{-}CH{=}CHCH_3 + Br_2 \longrightarrow$$
$$CH_3O{-}C_6H_4{-}CHBr{-}CHBrCH_3 \qquad (72)$$

2,4-Dinitrophenylhydrazine reacts very slowly according to Equation 73.

$$2\,(O_2N)_2C_6H_3{-}NHNH_2 + 2\,Br_2 \longrightarrow$$
$$(O_2N)_2C_6H_3{-}NH{-}N{=}N{-}NH{-}C_6H_3(NO_2)_2 + 4\,HBr \qquad (73)$$

In the determination of stearic acid hydrazide, which is insoluble in water, 0.1 *M* KBr and 0.3 *M* HCl in 85% aqueous MeOH was used as the anolyte.[239] In a MeOH-AcOH mixture the Br_2 consumption was lower, which is explained by a reaction of the substance to be determined with AcOH with formation of secondary hydrazide reacting with Br_2 only very slowly. On the other hand, conditions have been found for the coulometric titration of hydrazine and its derivatives with Br_2 in AcOH alone.[226]

A coulometric determination of organosilicon compounds in 90% AcOH is based on the following reaction.[203]

$$-\overset{|}{\underset{|}{Si}}-H + Br_2 \longrightarrow -\overset{|}{\underset{|}{Si}}-Br + HBr \qquad (74)$$

The determination of organotin compounds $[(C_2H_5)_6Sn_2$, $(C_3H_7)_6Sn_2$, $(C_4H_9)_6Sn_2$, and $(CH_3)_3Sn\text{-}Sn(C_6H_5)_3]$[241] and compounds of the type $R_3M\text{-}MR_3$, where R is methyl or ethyl and M is lead or tin,[240] is analogous and is based on the reaction with Br_2 described by Equation 75.

$$R_3M{-}MR_3 + Br_2 \longrightarrow 2\,R_3MBr \qquad (75)$$

Both determinations are carried out in MeOH with amperometric indication, whereas an analogous determination of lead(IV) organic compounds is performed in a MeOH-H_2O mixture.[242]

A coulometric titration of hydroquinone with Br_2 can be performed in glacial AcOH,[308] sulfamides can be titrated in an EtOH-benzene mixture[243] and thiodiglycol in 50% AcOH.[227] Attention has also been paid to coulometric titration of olephins in a MeOH-AcOH mixture with spectrophotometric[237] and biamperometric[238] indication, other unsaturated hydrocarbons in an EtOH-benzene-H_2O mixture with biamperometric indication[244] and to titration of amines,[228] and indanedione and its derivatives[229-231] in an AcOH-H_2O mixture. A coulometric determination of many alkylphenols in an AcOH-H_2O-Py mixture[236] and of chloro-, bromo-, nitro-, and carboxy- derivatives of phenol in an AcOH-H_2O mixture[232] has also been described. Coulometric titrations of various alkylanilines[233,234] and imines and enolethers of 2-arylindane-1,3-diones[235] can be carried out in the same medium. Different rates of the addition of generated Cl_2 and Br_2 to styrene and methyloleate have been utilized in the analysis of mixtures of these substances.[200]

K. Iodine and its Compounds

In titrations with iodine and its compounds in nonaqueous media, addition and substitution reactions sometimes occur, but most of the methods are based on the oxidation of the substances to be determined. The determination of water by the K.Fischer reagent is not discussed here, because the determinand does not undergo a common redox reaction here. A number of references concerning this method can be found in the reviews.[5,7,26,27]

1. Standard Solutions

Standard solutions of I_2 in anhydrous MeOH or EtOH,[269-271] $CHCl_3$,[217,272] CCl_4,[273] MeCN,[274] DMF,[47] formamide,[153] Ac_2O,[192] HSO_3F,[206,275] fused $CH_2ClCOOH$,[179] and hexamethylphosphotriamide[276] can be prepared by dissolving weighed amounts of the p.a. substances in the solvents. The titer must generally be determined every day; with a MeCN solution it decreases by 7.7% during 30 days.[274]

Solutions of ICl in anhydrous AcOH,[277] MeCN,[274] or Ac_2O[192] can be prepared by dissolving the recrystallized substance in the solvent and standardized iodometrically in aqueous solution or, with AcOH, by titration of hydroquinone in a nonaqueous medium.[154] In the absence of light and atmospheric moisture, the titer of the MeCN solution did not change during 5 days and decreased by 4% during subsequent 25 days.[274] Standard solutions of this reagent have also been prepared in liquid hydrogen chloride,[205] HSO_3F,[206] and fused $CH_2ClCOOH$.[75] A solution of IBr in MeCN can be prepared[274,278-279] by dissolving a weighed amount of the substance, prepared according to Popov and Skelly.[307] In the absence of light and atmospheric moisture, the titer of the solution did not change during 10 days and decreased by only 2% during the next 20 days. Standard solutions of IBr in DMF[280] and ICN inMECN,[41] EtOH, Me_2CO and an EtOH-$CHCl_3$ mixture[281] have also been prepared. An analytical use of IBr solutions in glacial AcOH is prevented by a low reactivity of the substance in this medium.[154]

A standard solution of ICl_3 in glacial AcOH[282] and MeCN[274] was prepared by dissolving the purified substance in the solvent and standardized daily iodometrically in an aqueous medium.

A standard solution of iodosobenzenedichloride in glacial AcOH can be prepared[283,284] by dissolving the solid substance prepared according to Vogel[285] in the solvent. The solution must be protected against light and atmospheric moisture and be standardized daily. A standard solution of this reagent in MeCN was also prepared.[41] A standard solution of iodosobenzenediacetate in glacial AcOH can be obtained[286] by dissolving the substance prepared according to Pausacker[287] or Sharefkin and Saltzman,[288] the former procedure being simpler and more advantageous. The solution is standardized iodometrically in aqueous solution and the titer remains constant for 30 days in darkness and for 7 days in the light.

A standard solution of *N*-iodosuccinimide in MeCN[289] was prepared by dissolving the weighed substance prepared according to Djerassi and Lenk,[290] standardized iodometrically in aqueous solution, and stored in the dark. Standard solutions of KIO_3 in fused $CH_2ClCOOH$[75] and KIO_4 in an AcOH-trimethylamine mixture[181] have also been prepared.

2. Coulometric Generation of Elemental Iodine

For generation of I_2 in MeOH, 0.03 *M* KI and 0.5 *M* HCl or 0.1 *M* KI and 3.5 *M* CH_3COONa in MeOH were used as the anolytes.[291] A 0.05 *M* or 0.1 *M* KI anolyte was used in a MeOH-H_2O mixture (1:1).[292,293] A platinum generation electrode was always used.

3. Determination of Inorganic Substances

The reactions of decaborane and tetraborane with I_2 in MeOH, described by Equations 76 and 77, have been used for the determination of the substances, back-titrating excess I_2 with thiosulfate or measuring the volume of the hydrogen formed.[294]

$$B_{10}H_{14} + 20\ I_2 + 30\ CH_3OH \longrightarrow 10\ B(OCH_3)_3 + 40\ HI + 2\ H_2 \quad (76)$$

$$B_4H_{10} + 9\ I_2 + 12\ CH_3OH \longrightarrow 4\ B(OCH_3)_3 + 18\ HI + 2\ H_2 \quad (77)$$

Triphenylantimony can be determined in MeOH, EtOH, or their mixtures with AcOH by titration with I_2 in the same solvent. The end point can be detected conductometrically, potentiometrically (Pt-SCE), or visually on the basis of the yellow coloration caused by excess I_2.[269]

I_2 in DMF can be potentiometrically titrated with Tl(III) or Cr(II),[22] which is useful for back-titrations in indirect determinations. It can be expected that the reverse titration would also be possible. The reactions of I_2 with Sn(II) and V(III) in DMF[47] and with Sn(II), As(III), Sb(III), and $Na_2S_2O_3$ in formamide[153] were studied. A potentiometric[403] and amperometric or biamperometric[404] titration of Sn(II), As(III), and Sb(III) with I_2 in MeCN, MeOH, EtOH, and iso-PrOH was described. An I_2 standard solution in fused $CH_2ClCOOH$ was used for potentiometric or visual titration of $SnCl_2$, $FeCl_2$, $AsCl_3$, $SbCl_3$, PCl_3, and $Na_2S_2O_3$,[179] and a solution in HSO_3F for visual or conductometric titration of As(III) and P(III)[206]

Great attention has been paid to the behavior of the I_2/I^- system in $CHCl_3$.[217] The formation of complex anion I_3^- and ion pairing with quarternary ammonium and ferricenium cations have been confirmed. Good curves were obtained in potentiometric titration of $(C_4H_9)_4NI$ with iodine and in the reverse titration, as well as in titration of ferrocene and cobaltocene with iodine. Two breaks were obtained with cobaltocene, corresponding to reactions in Equations 78 and 79, where Cc is cobaltocene and Cc^+ the cobaltocenium cation. The equilibrium constants have been calculated from all the potentiometric curves.

$$2\,Cc + I_2 \rightleftharpoons 2\,Cc^+I^- \qquad (78)$$

$$2\,Cc^+I^- + 2\,I_2 \rightleftharpoons 2\,Cc^+I_3^- \qquad (79)$$

The reaction of I_2 with Sn(II) in MeCN[73] and the visual or conductometric titration of AsX_3, SbX_3, and PX_3 (where X is a halogen), triphenylphosphine and triphenylstibine with I_2 in Ac_2O[192] were studied. Sn(II), As(III), and Sb(III) can be coulometrically biamperometrically titrated with I_2 in MeOH.[291]

An ICl standard solution in Ac_2O was employed for visual and conductometric titration of halides and organic compounds of As(III), Sb(III), and P(III),[192] and a solution in glacial AcOH for potentiometric and amperometric titration of various inorganic systems.[277] Three breaks were observed in the titration of SO_3^{2-} in the presence of CH_3COONa, the first corresponding to the oxidation of SO_3^{2-} to SO_4^{2-}, the second to the oxidation of the I^- formed to I_3^- and the third to the oxidation of I_3^- to I_2. The titration of Hg(I) can be performed even in the absence of CH_3COONa, whereas the titrations of Fe(II), As(III), and Sb(III) require the presence of this base.

Many inorganic systems can be potentiometrically or amperometrically titrated with ICl_3 in glacial AcOH.[282] The oxidation of SO_3^{2-} is slow, but can be hastened by adding CH_3COONa. The solution turns yellow at the equivalence point, due to the presence of I_3^- formed by the reaction in Equation 80, which is further oxidized in reactions in Equations 81 and 82, and only then does excess ICl_3 appear in the solution titrated. Hence the titration curve contains four breaks corresponding to the oxidation of SO_3^{2-} to SO_4^{2-} and to the three steps of the oxidation of I^- formed. The titrations of As(III) and Sb(III) are analogous, and reliable results are only obtained in the presence of CH_3COONa. Hg(I) can be titrated in the absence of acetate, but an addition of a small amount of acetate. (0.01 *M*) helps in the determination, because the redox potential of the Hg(II)/Hg(I) system is decreased.

$$5\,I^- + ICl_3 \longrightarrow 2\,I_3^- + 3\,Cl^- \qquad (80)$$

$$3\,I_3^- + ICl_3 \longrightarrow 5\,I_2 + 3\,Cl^- \qquad (81)$$

$$I_2 + ICl_3 + 3\,Cl^- \longrightarrow 3\,ICl_2^- \qquad (82)$$

Standard solutions of iodosobenzenedichloride[283,284] and iodosobenzenediacetate[286] in anhydrous AcOH were used for potentiometric titration of Fe(II), Sn(II), As(III), and I^-. Direct titration of $[Fe(CN)_6]^{4-}$ does not yield reliable results and the determination must be carried out in the presence of Br^-, when Br_2 is generated *in situ*. The reaction in titration of Tl(I) must be catalyzed by HCl and that of Sb(III) by osmic acid. The coloration produced by the first excessive drop of the reagent can sometimes be used for end-point detection. A titration of decaborane with KIO_3 in AcOH was also described.[295]

4. Determination of Organic Substances

Organic compounds of arsenic can be potentiometrically or conductometrically titrated with I_2 in anhydrous MeOH.[297] A standard solution of I_2 in EtOH was used for the determination of −SH substances.[271] In the determination of thiophenol, a solution of the substance in ether, benzene, *tert*-butylalcohol, or chlorobenzene is titrated with I_2 in EtOH, with catalysis by pyridine. Phenylthioacetate is first hydrolyzed to thiophenol and diphenylsulfide is reduced to thiophenol. A solution of I_2 in EtOH was also used for the determination of dithiocarbamates. For the end-point indication, the coloration produced by the reagent excess or the reaction with starch on a drop board was used.[270]

The determination of xanthates and dithiocarbamates with I_2 in MeCN[274] is based on their oxidation according to Equations 83 and 84. A reagent excess produces a yellow color of the solution titrated, but the end pint can also be indicated potentiometrically. The determination of dithiocarbamates with iodine and iodine halides in MeCN is also described.[300]

$$2\,RO{-}CSS^- + I_2 \longrightarrow RO{-}CSSSCS{-}OR + I^- \qquad (83)$$

$$2\,R_1R_2N{-}CSS^- + I_2 \longrightarrow R_1R_2N{-}CSSSCS{-}NR_1R_2 + 2I^- \qquad (84)$$

Water-insoluble diethyldithiocarbamates of Hg, Pb, Cd, and Zn were spectrophotometrically titrated with I_2 in $CHCl_3$.[272] In the titration, 1 mol I_2 reacts with 1 mol of the substance titrated, which corresponds to the expected formation of tetraethylthiuramdisulfide. −SH substances were potentiometrically titrated with I_2 in DMF, with the oxidation to the corresponding disulfides.[47]

A solution of potassium triiodide (KI_3) in hexamethylphosphotriamide was used for an indirect determination of ethylmagnesiumbromide and diethylmagnesium, with a back-titration of its excess by $Na_2S_2O_3$.[276] Iodometric determinations of analgine in 95% EtOH,[298] a determination of aqueous oxalic acid with I_2 in CCl_4,[273] and a determination of ascorbic acid, hydroquinone, and metol in MeOH based on the oxidation of the substances with excess I_2 and potentiometric back-titration of the I^- with $AgNO_3$ using an iodide ion-selective electrode[299] have been described.

With coulometrically generated I_2 in MeOH, a number of organotin compounds [241] and of compounds of the type $R_3M{-}MR_3$, where R is methyl or ethyl and M is Pb or Sn,[240] can be amperometrically titrated. Coulometric titration with I_2 in EtOH was used for the determination of aldehydes[301] and in an $EtOH{-}H_2O$ mixture for the determination of 2,3-dimercaptopropanol[292] and thionalide,[293] which is oxidized according to Equation 85.

$$2\,C_{10}H_7{-}NHCOCH_2SH + I_2 \longrightarrow$$
$$C_{10}H_7{-}NHCOCH_2SSCH_2CONH{-}C_{10}H_7 + 2\,HI \qquad (85)$$

It has been found in titrations of mercaptans, dithiocarbamates, and xanthates with ICl, ICN, ICl_3, and iodosobenzenedichloride in a MeCN-MeOH mixture[41] that the reactions in MeCN alone are substantially slower than in the presence of MeOH. This phenomenon has been explained by the formation of the $RSHI_2$ complex in MeCN alone. In the presence of MeOH, reactions in Equations 86 to 89 take place, i.e., the dissociation of the complex, and thus the whole reaction is accelerated by the effect of MeOH as a base.

$$RSHI_2 + CH_3OH \longrightarrow RSI_2^- + CH_3OH_2^+ \tag{86}$$

$$RSI_2^- \longrightarrow RSI + I^- \tag{87}$$

$$RSI + RSH \longrightarrow RSSR + HI \tag{88}$$

$$I^- + CH_3OH_2^+ \longrightarrow HI + CH_3OH \tag{89}$$

A standard solution of ICl in MeCN was used for potentiometric titration of xanthates and dithiocarbamates[274] and a solution in glacial AcOH for potentiometric titration of hydroquinone and for the determination of oleic acid, resorcinol, antipyrine, amidopyrine,[154] and olephins[302] on the basis of addition or substitution reactions. IBr in MeCN oxidizes xanthates and dithiocarbamates to the corresponding dixanthogenates and thiuramdisulfides according to Equations 90 and 91. Thiourea does not react with this reagent in MeCN alone, but it is readily oxidized in an aqueous medium according to Equation 92. This fact has been utilized in analyses of mixtures of thiourea with xanthates or dithiocarbamates.[278]

$$2\ ROCSS^- + IBr \longrightarrow ROCSSSCSOR + I^- + Br^- \tag{90}$$

$$2\ R_1R_2NCSS^- + IBr \longrightarrow R_1R_2NCSSSCSNR_1R_2 + I^- + Br^- \tag{91}$$

$$\begin{aligned} &2\ RHN{-}C({=}NH){-}SH + IBr \longrightarrow \\ &\qquad RHN{-}C({=}NH){-}SS{-}C({=}NH)NHR + HI + HBr \end{aligned} \tag{92}$$

The same reagent was used for the determination of primary and secondary amines after their conversion into dithiocarbamates by reaction with carbon disulfide,[279] of isocyanates and isothiocyanates after their conversion into urea and thiourea derivatives by reaction with *N*-butylamine in DMF,[303] and for the determination of other xanthates and dithiocarbamates in MeCN.[274] A standard solution of IBr in DMF was employed for potentiometric titration of ethylxanthates and dithiocarbamates of Cd, Zn, Pb, and Hg,[280] Ni xanthates,[400] and for analyses of mixtures of amines and dithiocarbamates after their reaction with thiourea in DMF.[401]

Dithiocarbamates can be potentiometrically titrated with ICN in EtOH, Me_2CO or an EtOH-$CHCl_3$ mixture[281] and phenols in AcOH, or an AcOH-Ac_2O mixture can be titrated with an aqueous solution of the reagent.[266]

Potentiometric titration of xanthates and dithiocarbamates with ICl_3 in MeCN[274] and an indirect determination of thiosemicarbazide and thiourea and of their derivatives with this reagent in an AcOH-MeOH-H_2O mixture have also been studied.[304] Various organic substances can be determined by using a suitable reaction in which I_2 is produced, which is extracted into CCl_4 and titrated with aqueous ICl_3 in this phase to its discoloration.[305]

In the determination of thiols, xanthates, and dithiocarbamates with an *N*-iodosuccinimide standard solution in MeCN, excess KI is added to the sample solution in MeOH and is titrated potentiometrically or visually to the appearance of the yellow color of excess I_2. The sample volume must be chosen so that MeOH amounts to at least 80% of the solvent volume at the end of the titration.[289] In MeCN or AcOH alone the reactions are too slow. The effect of MeOH is apparently based on deprotonation of an intermediary complex. Therefore, the whole determination can be described by Equations 93 to 97.

$$\mathrm{RSH + (C_4H_4O_2)NI \rightleftharpoons (C_4H_4O_2)NISHR} \qquad (93)$$

$$\mathrm{(C_4H_4O_2)NISHR + CH_3OH \rightleftharpoons (C_4H_4O_2)NISR^- + CH_3OH_2^+} \qquad (94)$$

$$\mathrm{(C_4H_4O_2)NISR^- \xrightarrow{fast} RSI + (C_4H_4O_2)N^-} \qquad (95)$$

$$\mathrm{(C_4H_4O_2)N^- + CH_3OH_2^+ \rightleftharpoons (C_4H_4O_2)NH + CH_3OH} \qquad (96)$$

$$\mathrm{RSI + RSH \rightleftharpoons RSSR + HI} \qquad (97)$$

With a standard solution of iodosobenzenedichloride in glacial AcOH, ascorbic acid can be determined, which is oxidized to dehydroascorbic acid,[283,284] and with a solution of iodosobenzenediacetate in this solvent, ascorbic acid can be determined, as well as hydroquinone, which is oxidized to quinone.[286] In the titration of hydrazine with this reagent, an addition of KBr is recommended, so that this is actually the oxidation with generated Br_2. The same holds for the determination of phenol, aniline, and oxime with this reagent, based on bromination of the compounds to be determined.[286] The reaction of KIO_3 with organic sulfides in an AcOH-HCl-benzene mixture[306] and the reaction of KIO_4 with hydrazine in an AcOH-trimethanolamine mixture[181] have also been studied.

L. Some Other Oxidizing Agents

1. *Divalent Mercury*

A 0.1 *M* Hg(II) solution in DMF was prepared by dissolving an accurately weighed amount of $Hg(CH_3COO)_2$ with an addition of several drops of concentrated HCl or by direct dissolution of $HgCl_2$ in this solvent.[45,46]

Ascorbic acid and Co(II) can be titrated with this reagent in DMF, the reverse titrations also yielding good results. On the other hand, the titrations of Ti(III) and of thiolactic acid are poorly reproducible, and no potential break is obtained in the titration of cysteine.[46] Among visual indicators, methylene blue gave good results for the titration of ascorbic acid and alizarine red in the titration of thiolactic acid.[53] The titration of Co(II) can be indicated spectrophotometrically.[45]

2. *Compounds of Vanadium*

During electrochemical dissolution of vanadium in glacial AcOH, V(IV) and V(V) are formed, in dependence on the current density and the base electrolyte used. In 0.5 *M* $HClO_4$ in glacial AcOH, V(V) can be used for coulometric titration of Fe(II), Sn(II), ascorbic acid, thiourea and its derivatives, and many aromatic disulfides, with potentiometric or biamperometic indication.[309]

The possibility of generating V(III), V(IV), and V(V) on a vanadium electrode in MeCN, DMF, and Py in the presence of $HClO_4$ or H_3PO_4 was studied and conditions were found for coulometric titration of hydroquinone, metol, thiosulfate, and thiourea with V(V) in these solvents.[310]

3. *Diverse Oxidants*

A solution of nitrosyl chloride was used for conductometric titration of As(III), Sb(III) and P(III) in Ac_2O,[192] As(III) and P(III) in HSO_3F,[206] and of iron pentacarbonyl in liquid hydrogen chloride.[204]

The oxidizing effects of AsF_5 and SbF_5 in liquid hydrogen fluoride[311] and of $Sn(CH_3COO)_4$ in fused $CH_2ClCOOH$[179] are interesting from the point of view of general rather than analytical chemistry.

A 0.01 *N* solution of 4,7-dichloroquinoline-bromide-perbromide in a $CHCl_3$-AcOH mixture (95:5) was used for biamperometric titration of tetraphenylborate in a mixture of MeOH and AcOH (95:5).[312]

V. REDUCING AGENTS

A. Compounds of Divalent Chromium

Solutions of Cr(II) in DMF,[22] THF,[314] and dioxan[315-317] have so far been used for titrations in nonaqueous media. Coulometric generation of Cr(II) in a MeCN-H_2O mixture was also studied.[318] Both the solution preparation and the determinations themselves are carried out under an inert atmosphere. The end point is detected potentiometrically or bipotentiometrically. The Cr(III)/Cr(II) system has a redox potential of −0.510 V (SCE) in DMF containing 0.05 *M* HCl.[21]

1. Standard Solutions

The maximum concentration of $CrCl_2$ standard solutions in DMF is 0.1 *M*, because of limited solubility of the substance.[22] These solutions are not completely stable even in the presence of solid $CrCl_2$ and the stability is further decreased by the effect of light. The titer decreases by about 0.2% during 24 hr even in the dark. A $CrCl_2$ standard solution in THF can be prepared by the reaction of dry hydrogen chloride with chromium under purified THF.[314]

Approximately 0.03 *M* solutions of $Cr(CH_3COO)_2$ in dioxan can be obtained by adding an aqueous solution of $CrCl_2$ to a saturated CH_3COONa solution, filtering off the red crystalline precipitate formed, washing it with water, and dissolving in dioxan.[315-317] The operations are carried out in a special apparatus under a nitrogen atmosphere and the solution is stored under carbon dioxide.

The conditions for coulometric generation of Cr(II) in a MeCN-H_2O mixture[318] are discussed in the paragraph on determination of organic substances.

2. Determination of Inorganic Substances

A standard solution of $CrCl_2$ in DMF was used for titration of I_2, Br_2, ICl, Cu(II), Fe(III), Ti(IV), and Sb IV).[22] In potentiometric titration of these substances it was recommended that more than 90% of the expected consumption be added in one portion and then the titration be slowly completed. Low results were obtained in the titration of Br_2 at laboratory temperature; more accurate results were obtained when titrating at a decreased temperature (around 0°C).

A standard solution of $Cr(CH_3COO)_2$ in dioxan was used for titration of Cu(II), V(V), U(VI), and Mo(VI). The potentiometric titrations (Pt-SCE or bimetallic systems) were carried out in an inert atmosphere.[317] This reagent was employed for titrations of 8-oxyquinoline complexes of the metals after their extraction into $CHCl_3$, carried out directly in the extractant medium. In the titration of Cu(II), the metal is reduced to Cu(I), and excess reagent causes slow reduction to Cu(0). In titrations of V(V) and Mo(VI) two pronounced breaks appear, corresponding to the reduction, V(V) ⟶ V(IV) and V(IV) ⟶ V(III), or Mo(VI) ⟶ Mo(V) and Mo(V) ⟶ Mo(III). In the titration of U(VI), the potential break corresponds to the reduction, U(VI) ⟶ U(IV). It has been confirmed that Cu(II) and V(V), or V(V) and U(VI) can be subsequently determined in this way. If the chloroform extract is not acidified, then Cu(II) complex is not reduced and V(V) is only reduced to V(IV).

In the determination of uranyl nitrate, its solution in EtOH, tributylphosphate or ethyl acetate is acidified with H_2SO_4 and is potentiometrically titrated with 0.02 *M* $Cr(CH_3COO)_2$ in dioxan.[316,317]

3. *Determination of Organic Substances*

In direct coulometric titration of water-insoluble nitrocompounds with Cr(II) ions in a $MeCN\text{-}H_2O$ mixture, 0.1 *M* $CrBr(H_2O)_5^{2+}$ in 1.5 *M* HCl was used as the base electrolyte. A mercury pool generation cathode and a cadmium anode separated by a frit was used, with a generation current of 20 mA. A solution of the test substance in MeCN was added to this solution and the end point was detected bipotentiometrically. In this way, *p*-nitrobenzoic acid, *o*-nitrotoluene, *m*-nitrotoluene, *o*-nitroanisol, 4-nitrophthalic acid, 2,4-dinitroanisol, and 1-nitronaphthalene were determined. Except for the last two compounds, an exchange of four electrons was observed, corresponding to the reduction of the $-NO_2$ group to the $-NHOH$ group. Six electrons were exchanged in the reduction of 1-nitronaphthalene, corresponding to the reduction to the $-NH_2$ group. An unusual exchange of five electrons was observed with *p*-nitrotoluene, *o*-nitrophenol, and 5-nitro-1-naphthylamine and ten electrons with 2,4-dinitroanisol.[318]

B. Compounds of Divalent Tin

Solutions of Sn(II) in aqueous media are very unstable.[2,36] In glycerol their stability substantially increases.[320] This effect is explained by the function of glycerol as a negative catalyst of the Sn(II) oxidation with atmospheric oxygen.[322,323] The problems caused by a great viscosity of this solution can be eliminated by adding EtOH.[320,321] The use of this reagent in inorganic analysis is limited to alkaline media, because glycerol is oxidized by most oxidants in acidic solution. Newer studies[324,325] have also found that the reducing ability of Sn(II) is somewhat lower in glycerol, and thus the reagent was used mainly for determinations of some organic substances.[324,325,329] Standard solutions of Sn(II) is monoethanolamine,[319] AcOH,[326] Py,[47] and other organic solvents[14,327] have so far found only limited use.

1. *Standard Solutions*

A 0.1 *N* $SnCl_2$ solution in glycerol can be prepared by dissolving 11.2825 g $SnCl_2.2\,H_2O$ in 750 mℓ of glycerol (the dissolution takes about 1 hr) and diluting with EtOH to 1ℓ.[320] Its titer can be determined by potentiometric titration of $[Fe(CN)_6]^{3-}$ or $Cr_2O_7^{2-}$ in aqueous solution, using an ammoniacal solution of $AgNO_3$ or the Fe(II) complex with glyoxime as the indicator, respectively. The titer is constant for several months when the solution is stored in a well-stoppered flask.[320] However, it follows from newer references[324,325] that the titer of a 0.1 *N* solution stored under an inert atmosphere decreases by 1.6%/month and by 5% in the presence of atmospheric oxygen. This decrease is even more pronounced with a 0.01 *N* solution and amounts to up to 10%/month in the presence of the air.

A 0.1 *N* $SnCl_2$ solution in monoethenolamine was prepared by dissolving 2.82038 g $SnCl_2.\,H_2O$ p.a. in 187.5 mℓ monoethanolamine and diluting with EtOH to 250 mℓ. The two solvents were first freed of oxygen, and the standard solution was stored under an inert atmosphere. The solution titer, which decreases by 3 to 5%/day and thus limits the practical usefulness of the reagent, can be determined using $Cr_2O_7^{2-}$.[319] $SnCl_2$ is a very strong reductant in glacial AcOH, but its practical use is prevented by its high instability.[326]

Solutions of 0.1 to 0.01 N $SnCl_2$ in Py were prepared by dissolving weighed amounts of the solid substance in the solvent.[47] Mergens and Ewing[14] also prepared 0.02 N $SnCl_2$ in Py, MeCN, Me_2CO, acetylacetone, and glacial AcOH by dissolving weighed amounts of the solid substance in the solvents. They determined the titer of these solutions by their titration with aqueous $FeCl_3$ or $KMnO_4$. The preparation and all the operations with the solutions were carried out in a box with an inert atmosphere. The authors claim that the stability of these solutions suffices for analytical use, but concrete data have not been published. The same holds for Sn(II) solutions in MeCN,[73] DMF, and DMSO.[327]

2. Determination of Inorganic Substances

A standard solution of Sn(II) in a glycerol-EtOH mixture was used for titration of aqueous solutions of Hg(II), Hg(I), Os(VIII), $[Fe(CN)_6]^{3-}$, $Cr_2O_7^{2-}$ and $PtCl_6^{4-}$.[321] $Cr_2O_7^{2-}$ and $[Fe(CN)_6]^{3-}$ can be determined in alkaline media even in the presence of reductants (e.g., SO_3^{2-}, SCN^-, and I^-).[320] The reagent was further used for the determination of Cr(VI), Fe(III), Ag(I), H_2O_2, I_2, and ClO^- [324,325] and for the determination of V(V).[328] These titrations were indicated either potentiometrically (Pt-SCE), or visually using resazurine.[321] Barium diphenylaminosulfonate was used in the titration of V(V) with this reagent.[328] On the basis of a voltammetric and polarographic study of the Sn(IV)/Sn(II) system in glycerol, bipotentiometry and biamperometry was used for the end-point detection, in addition to equilibrium potentiometry.[324,325]

Mergens and Ewing studied[14] the reaction of Sn(II) with various oxidants in many nonaqueous media using potentiometric indication (Pt-SCE separated by a bridge filled with the solvent). Well-developed titration curves were obtained in the titration of Sn(II) with a Fe(III) solution in Py; the titration cannot be carried out in AcOH, MeCN, Me_2CO, and acetylacetone. On the other hand, good results were obtained in the titration of Sn(II) with a $KMnO_4$ solution in AcOH, Py, and Me_2CO, or with a Cu(II) solution in MeCN. The potentiometric titration of Sn(II) with a Cu(II) solution in Me_2CO, Py, and AcOH cannot be performed, because the sparingly soluble $CuCl_2$ precipitates. Sn(II) can be titrated with I_2 in all the above solvents.

A standard solution of Sn(II) in MeCN was used for potentiometric titration of I_2.[73] Potentiometric indication (Pt-SCE) was also used in titrations of oxidants with $SnCl_2$ in Py.[47] Conductometric and potentiometric titration of Sn(II) with I_2 in DMF and DMSO[327] and potentiometric titration of Sn(II) with Co(III) in glacial AcOH were also described.[87]

3. Determination of Organic Substances

An Sn(II) standard solution in a glycerol-EtOH mixture was used for potentiometric and bipotentiometric titration of aqueous solutions of chloramine T, *N*-bromosuccinimide, and pyridineazoresorcinol.[324,325] The same standard solution was employed for selective determinations of aromatic nitro compounds dissolved in absolute EtOH saturated with dry hydrogen chloride. Because of a rather slow potential stabilization, the authors recommend amperometric titration or visual indication using gallocyanine, 4-methyl-7-amino-3-phenoxazone, or 2-amino-3-phenoxazone. Under these conditions, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, 2-nitroso-1-naphthol-4-sulfonic acid, 1-nitroso-2-naphthol-3-carboxylic acid, 4-nitrosophenol, 4-nitrosoresorcinol, and 2,4-dinitrosoresorcinol are reduced according to Equation 98 and 4-nitroso-*N,N*-dimethylaniline, 3-methyl-4-nitrosophenol, and nitrosouracil according to Equation 99. These reactions can be utilized for rapid and selective titration of the above substances.[329] However, the dissolution of 3-methyl-4-nitrosophenol takes 2 days, and the titration of 2-nitroso-1-naphthol-4-sulfonic and 2-nitroso-1-naphthol-3-carboxylic acids must be carried out at 50 to 60°C. The method can be utilized for the determination of the $-\overset{|}{\underset{|}{C}}-N{=}O$ group, whereas the reduction of the $-O-N{=}O$ and $\rangle C{=}N-OH$ groups is nonstoichiometric. The presence of aldehydes, ketones, and nitro compounds at a ratio of 1:1 does not interfere, and in the presence of a 100-fold excess of nitrocompounds the results are only negligibly higher.

$$R{-}NO + Sn^{2+} + 2\,H^{+} \longrightarrow R{-}NHOH + Sn^{4+} \qquad (98)$$

$$R{-}NO + 2\,Sn^{2+} + 4\,H^{+} \longrightarrow R{-}NH_2 + 2\,Sn^{4+} + H_2O \qquad (99)$$

An $SnCl_2$ aqueous solution was used for the determination of ascaridol in AcOH.[330]

C. Compounds of Divalent Iron

Compounds of Fe(II) have been used in nonaqueous solvents because of an increase in their reducing ability (e.g., in concentrated H_3PO_4[139,296,331] or in the presence of triethanolamine[2]) and because of limited solubility of the titrant (e.g., ferrocene[332]) or of the titrand in water.

The Fe(III)/Fe(II)[19,21,39,333] and the ferricenium ion/ferrocene[333-338] systems have been studied in detail in nonaqueous and mixed media from the point of view of their electrochemical behavior. The formal redox potential of the Fe(III)/Fe(II) system is 0.405 V in DMF containing 0.05 *M* HCl and 0.695 V in Py containing 0.05 *M* HCl (vs. SCE).[21] In MeCN, Fe(III) is irreversibly reduced to Fe(II) at +1.1 V at a rotating platinum electrode, whereas the oxidation of Fe(II) to Fe(III) occurs at +1.6 V (SCE). At a dropping mercury electrode, Fe(III) is reduced at a potential of mercury dissolution in this medium.[39] The formal redox potential of the Fe(III)/Fe(II) system in MeCN is +1.55 V vs. Ag/0.01 *M* $AgNO_3$ in MeCN reference electrode.[19] Using the Rb^+/Rb reference system to compare the potentials in MeCN and H_2O it has been estimated[339] that the redox potential of the Fe(III)/Fe(II) system in MeCN is about 1.3 V higher than that in H_2O. This fact can be attributed to complexing effects of MeCN leading to stabilization of Fe(II) and to the lower dielectric constant of this solvent, which may cause destabilization of Fe(III).[19]

In mixtures of mineral acids with organic solvents the redox potential of the (Fe(III)/Fe(II) system strongly depends on the quality and concentration of both the acid and the solvent and may vary from +0.2 to +1.0 V vs. NHE.[333] Apparently effects connected with different solvation abilities of the solvents and with different complexing abilities of the acids play a role here. These effects can often be directed oppositely; e.g., the redox potential of the Fe(III)/Fe(II) system increases with increasing MeCN content in the presence of H_2SO_4, whereas in the presence of HCl the effect is opposite. In a H_3PO_4-H_2O mixture, the formal redox potential of this system decreases from 0.626V (NHE) in 0.177 *M* H_3PO_4 to 0.400 V in 11.58 *M* H_3PO_4,[340] which was employed for titration of many systems in concentrated H_3PO_4.[139,296]

It was originally assumed that the ferricenium ion/ferrocene system is reversible, and the value of its redox potential is independent of the nature and composition of the solvent, due to weak and virtually identical solvation of the oxidized and reduced forms.[336] However, later studies[334,335,337] have shown that the system is quasireversible, due to instability of the ferricenium ion. A detailed study of the electrochemical behavior of this system in H_2O, MeCN, EtOH, DMF, and DMSO has revealed that the electron transfer is always followed by a slow chemical reaction of the ferricenium cation formed.[337] The electrochemical oxidation of ferrocene at a graphite electrode in an EtOH-H_2O mixture is preceded by its fast protonation.[335] The formal redox potential of this system in mixtures of water and organic solvents can be varied from +0.1 to +0.7 V by varying the mineral acid (H_2SO_4, HCl, $HClO_4$, HBF_4) and its concentration and by varying the solvent (AcOH, MeCN, Me_2CO, EtOH, DMF, and DMSO).[333] These changes are again caused by different solvation abilities of the solvents, by formation of a ferricenium cation complex with the acid anion, and by the formation of the protonated ferrocene form, the extent of which depends on the donor-acceptor properties of the solvent.[342] Increasing content of an organic solvent leads sometimes to a decrease (AcOH) and sometimes to an increase (MeCN, EtOH, DMF, DMSO) in the redox potential. A mathematical relationship has been formulated[341] for the calculation of the redox potential of this system in an aqueous-organic medium from the known concentrations of the medium components. The quality and concentration of the solvent also affect the rate of the redox reactions taking place.[333] The formal redox potentials of substituted ferrocenes of the type $C_5H_5FeC_5H_4R$, where R is $CHOHCH_3$, CH_2OCH_3, CH_2OH, H, C_4H_9, $COOCH_3$, I, $Si(CH_3)_3$, CH_3, $Si_2O(OCH_3)_4$, and $C_6H_4(NO_2)_2$, were studied in water-organic solvent mixtures.[338] Methyl and butylferrocene were pointed out as promising reductants. The stability of ferrocene solutions is higher in neutral and alkaline solutions (Me_2CO, MeOH, EtOH, isoPrOH, MeCN, DMF) than in acidic solvents (AcOH, HCOOH).[335]

1. Standard Solutions

A 0.1 to 0.01 *N* solution of $Fe(ClO_4)_2$ in glacial AcOH was prepared by dissolving a weighed amount of $Fe(ClO_4)_2.6H_2O$ in the solvent which was deaerated with nitrogen and to which an amount of Ac_2O, required for removal of water, was added.[343] The titer of a 0.025 N solution does not change for 3 days in an inert atmosphere, whereas it decreases by as much as 4% per day in the presence of the air. Absolutely anhydrous solutions of Fe(II) in MeCN can be prepared by dissolving $Fe(ClO_4)_2.6MeCN$, prepared by azeotropic distillation of a $Fe(ClO_4)_2.6H_2O$ solution in MeCN at a decreased pressure in the presence of a molecular sieve.[19] Dissolution of $FeCl_2$ in glacial AcOH yields solutions with a concentration not greater than 0.01 *N*.[15] The preparation of this reagent in DMF and Py has also been described.[21] A 0.1 *N* $(NH_4)_2Fe(SO_4)_2$ solution in glycerol was prepared by dissolving a weighed amount of the p.a. substance in a minimal amount of water and diluting with glycerol to 1ℓ.[344] The solution titer can be determined using $[Fe(CN)_6]^{4-}$ in aqueous solution and is reported to be constant for several days even in the presence of the air. In titrations with this reagent, triethanolamine is added to the determinand solution in DMF, which forms a strong complex with Fe(III) and thus decreases the formal redox potential of the Fe(III)/Fe(II) system.[2] In spite of this, these titrations can be carried out in the presence of the air.

A 0.01 *M* ferrocene solution in MeCN or EtOH was prepared by dissolving a weighed amount of the substance in the solvent and standardized by amperometric titration of Re(VII) or by potentiometric or photometric titration of Cu(II).[332,346] Solutions with concentrations of 0.005 and 0.001 *M* can be prepared by diluting the 0.01 *M* solution and their titer remains constant for at least 5 days.[347]

2. Determination of Inorganic Substances

Biamperometry is used in the titration of Cr(VI) and Mn(VII) with 0.1 to 0.01 *N* $Fe(ClO_4)_2$ in glacial AcOH because of slow potential stabilization in equilibrium potentiometry.[343] The reaction of Fe(II) with Ce(IV) in 6 to 12 *M* H_3PO_4 was used for analyses of binary mixtures of Fe(II) with Sn(II), Ti(III), U(IV), Mo(V), and Fe(III) and mixtures of Ce(IV) with Cu(II), V(V), Mo(VI) and U(VI).[139] Small amounts of Sn(IV) can be determined by photometric titration with Fe(II) in 80% H_3PO_4.[331] An aqueous solution of $FeSO_4$ was used for potentiometric titration of Pd(II), Pt(IV), and Ir(IV) in alkaline triethanolamine in an inert atmosphere[348] and for titration of NO_2^-, NO_3^-, $S_2O_8^{2-}$ and BO_3^- in concentrated H_3PO_4.[296]

A ferrocene standard solution in MeCN or EtOH was used for amperometric titration of Hg(I) and Hg(II) in 50% AcOH,[349] potentiometric or spectrophotometric titration of Cu(II) in a Me_2CO-HCl mixture,[346] and amperometric titration of Re(VII) in an AcOH-HCl mixture,[332,350,370] or Ag(I) in a mixture of H_2SO_4 with AcOH, Me_2CO or EtOH.[351] An amperometric titration of Sb(V) in a mixture of HCl with EtOH, isoPrOH, MeCN, AcOH, HCOOH or Me_2CO[352] and a potentiometric[353] or amperometric[354] titration of

Mo(VI) in this medium have been described. An amperometric titration of molybdophosphate in a Me_2CO-HCl-isoBuOH mixture was employed for the determination of phosphorus in steels after its conversion into molybdophosphate and extraction into isoBuOH.[355] A selective determination of Mo(VI) is based on its precipitation with 8-hydroxyquinoline, dissolution of the precipitate in an AcOH-HCl mixture, and its titration with a ferrocene solution in EtOH with a potentiometric end-point indication.[356] The oximates of Cr(III), Fe(III), Al(III), and W(VI) are not reduced under these conditions. An amperometric titration of V(V) and V(IV) can be carried out in an AcOH-H_2SO_4-H_3PO_4 mixture,[347,357] that of V(IV) in an EtOH-H_3PO_4-HCl mixture,[358] that of Fe(III) in a Me_2CO-H_2SO_4,[360] AcOH-H_2SO_4,[357] and other mixtures.[361] Conditions have been found for the determination of V(V) and Mo(VI)[359] and Fe(III) and Tl(III)[362] in the presence of one another. Tl(III) alone can be titrated in an AcOH-H_2SO_4 mixture[362] and Se(IV) in an AcOH-HCl mixture.[363] A spectrophotometric determination of Se(IV)[364] and Te(IV)[365] is based on the measurement of the absorbance of the ferricenium ion formed. The optimal conditions for most of these determinations have been proposed on the basis of a kinetic study of the appropriate reactions and the redox potentials of the reacting systems determined, in dependence on the composition of the reaction medium. The same approach was also taken in determining the optimal conditions for amperometric titrations of Pb(IV),[366] Ce(IV),[367] Mo(VI), and Re(VII).[368] Detailed information on the above methods can be found in the monograph.[371]

3. *Determination of Organic Substances*

A 0.1 *N* $(NH_4)_2Fe(SO_4)_2$ solution in glycerol was used for potentiometric titration of 4,4′-bis(1-oxy-4-sulphonaphthalene-2-azo)benzophenone, 4,4′-bis(7-amino-1-oxy-3-sulphonaphthalene-2-azo)benzophenone, 4,4′-bis(8-amino-1-oxy-3,6-disulphonaphthalene-2-azo)benzophenone, 4-(1-oxy-4-sulphonaphthalene-2-azo)benzophenone, 4-(8-amino-1-oxy-3,6-disulphonaphthalene-2-azo)benzophenone, and 4-(7-amino-1-oxy-3-sulphonaphthalene-2-azo)benzophenone in a DMF-triethanolamine-glycerol mixture.[344] The substances in this titration and other azo dyes[369] are reduced to the corresponding amino compounds.

An aqueous solution of $FeSO_4$ was used for titration of methylene blue, thionine, a nitroso-R-salt, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol in 12 *M* H_3PO_4,[345] and for back-titration of unreacted $Ce(SO_4)_2$ in an indirect determination of rhodamine in acidified MeOH.[140]

D. Compounds of Trivalent Titanium

So far, solutions of Ti(III) in DMF,[21,22,46] Py,[21] AcOH,[15] glycerol,[374,375] and a solution of a formate complex of Ti(III) in a DMF-glycerol mixture[373,376-381] have been used. The formal redox potential of the Ti(IV)/Ti(III) system in DMF containing 0.05 *M* HCl is 0.00 V and in Py containing 0.2 *M* HCl it is −0.190 V vs. SCE with a bridge containing a saturated solution of KCl in MeOH.[21] This value is −0.374 V vs. SCE in a DMF-glycerol mixture containing formate.[373]

1. *Standard Solutions*

A Ti(III) standard solution in DMF was prepared by dissolving $TiCl_3$ in the solvent freed of traces of water by using a molecular sieve and standardized using I_2 or Cu(II).[22,46] Solutions of Ti(III) in AcOH can be prepared by dissolving 15% aqueous $TiCl_3$, adding the required amount of Ac_2O.[15] Solutions containing 1 to 2% H_2O are relatively stable in an inert atmosphere, in contrast to absolutely anhydrous solutions or those containing a small excess of Ac_2O. Operations with all these solutions must be carried out in an inert atmosphere. On the other hand, the titer of the formate complex of

Ti(III) in a DMF-glycerol mixture does not change during 4 days, even in the presence of oxygen.[376] This solution can be prepared by dissolving 30 mℓ 15% $TiCl_3$ and 0.6 g HCOOH in 170 mℓ of glycerol and diluting with DMF to 250 mℓ.

2. Determination of Inorganic Substances

A Ti(III) standard solution in DMF was used for titration of I_2, Br_2, Cu(II), Fe(III), and Sb(V).[22] In addition to potentiometry, the change in the coloration from light yelow to light blue can be employed for the end-point detection. Volatilization of I_2 can be suppressed by using more dilute solutions and that of Br_2 by cooling of the solution titrated. The small potential change in the titration of Fe(III) can be increased by adding SCN^-. As the reference electrode, a platinum wire sealed in the burette stop-cock was used, which has a rapidly stabilizing and constant potential given by the titrant composition.[372] The electric contact is provided by immersing the burette tip in the solution titrated. In titration of Cu(II) with this reagent, many metal electrodes[56] or visual indication with methylene blue or Janus green[53] have been employed. In the titration of Fe(III), SCN^- indicator was used[53] or, in work on a semimicroscale, a Pt indicator and an Ag/0.01 *M* $AgNO_3$ in DMF reference electrode.[46]

To increase the potential break at the end point of the potentiometric titration of Br_2, $Cr_2O_7^{2-}$, and MnO_4^- with a Ti(III) standard solution in AcOH, the solution titrated should be saturated with gaseous hydrogen chloride. The redox potential of the reacting systems cannot be influenced by a change in the acidity, because an addition of CH_3COONa or H_2SO_4 leads to precipitation of insoluble Ti(III) compounds. Too large an error of the titrations of Cu(II), Hg(I), and Hg(II) prevents their practical use.[15]

A standard solution of the formate complex of Ti(III) in a DMF-glycerol mixture was used for titration of aqueous solutions of $Cr_2O_7^{2-}$ and $[Fe(CN)_6]^{4-}$,[376] Ce(IV),[379] BrO_3^-, IO_3^-, and IO_4^-.[380]

3. Determination of Organic Substances

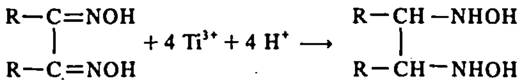
A standard solution of the formate complex of Ti(III) in a DMF-glycerol mixture was used for the determination of azo dyes,[373] quinones,[377] aromatic nitro and nitroso compounds,[378] and hydroxylamine and oximes.[381] Methyl orange, tropaeolin O, methyl red, *p*-aminoazobenzene, *p*-dimethylaminoazobenzene, chrysoidine, 1-(2-pyridylazo)-2-naphthol and 1-(2-thiazolylazo)-resorcinol are in direct titration rapidly and quantitatively reduced according to Equation 100, whereas the reduction of azobenzene, 1-(2-thiazolylazo)-4-methylphenol and 1-(2-thiazolylazo)-4-methoxyphenol is not quantitative, and the results are subject to an error as large as 30%.[373]

$$R_1{-}N{=}N{-}R_2 + 4\,Ti^{3+} + 4\,H^+ \longrightarrow R_1{-}NH_2 + R_2{-}NH_2 + 4\,Ti^{4+} \qquad (100)$$

1,4-benzoquinone, 2,6-dibromoquinone-4-chloroimine, 2,6-dichloroquinone-4-chloroimine, chloranil, 2,5-dihydroxy-1,4-benzoquinone, 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone-6-sulphonic acid, 4-anilido-1,2-naphthoquinone, 1-hydroxy-9,10-anthraquinone, 1,2-dihydroxy-9,10-anthraquinone, phenanthraquinone, benzanthrone, and 9,10-anthraquinone-1-sulphonic acid were directly titrated with potentiometric (Pt-SCE) or visual (gallocyanine, resazurine or 7-aminophenoxazone) end-point detection.[377] Hydroxylamine is reduced with this reagent according to Equation 101, oximes according to Equation 102 and dioximes according to Equation 103. Hydroxylamine can be determined directly, while acetoxime, cyclohexanoneoxime, α-furilmonoxime, salicylaldehydeoxime, β-isatineoxime, benzoylhydroxamic acid, *p*-dimethylaminobenzaldehydeoxime, *p*-chlorobenzaldehydeoxime, *o*-benzocyclohexanoneoxime, α-benzildioxime, and dimethylglyoxime must be reduced at 50 to 60°C and back-titrated with a Cu(II) solution in DMF potentiometricylly or using the above indicators.[381]

$$NH_2OH + 2\,Ti^{3+} + 2\,H^+ \longrightarrow NH_3 + 2\,Ti^{4+} + H_2O \qquad (101)$$

$$(CH_3)_2C{=}NOH + 4\,Ti^{3+} + 4\,H^+ \longrightarrow (CH_3)_2CH-NH_2 + 4\,Ti^{4+} + H_2O \qquad (102)$$



$$\begin{array}{l} R-C{=}NOH \\ \quad | \\ R-C{=}NOH \end{array} + 4\,Ti^{3+} + 4\,H^+ \longrightarrow \begin{array}{l} R-CH-NHOH \\ \quad | \\ R-CH-NHOH \end{array} + 4\,Ti^{4+} \qquad (103)$$

In direct potentiometric titration (Au-SCE) of 2-nitroso-1-naphthol-4-sulphonic acid, 2-nitroso-1-naphthol, 4-nitroso-*N,N*-dimethylaniline and 1-nitrosonaphthalenesulphonic acid, the substances are reduced to the corresponding amino compounds.[378] The titration is carried out in a MeOH-DMF mixture containing $CoCl_2$ or NH_4Cl to increase the conductivity. Because of a rather slow potential stabilization, an indirect determination has been developed, based on back-titration of Ti(III) with a Cu(II) solution in DMF. In this way, 4-nitrosophenol, 1-nitroso-2-naphthol, and 1-nitrosonaphthoresorcinol can also be determined. The reduction of 3-nitrophenol, 1-nitro-2-naphthol, 4-nitrophenol, 3-nitronaphthalenesulphonic acid, 1-nitro-2-acetaminonaphthalene, and 1,2-dimethyl-3-nitro-4-aminobenzene with this reagent obeys Equation 104, while 2-nitrophenol, 1-nitro-2-acetaminonaphthalene, and 1-methyl-2-nitro-3,5-dihydroxybenzene are quantitatively reduced according to Equation 105 by prolonged treatment with excess reagent at an elevated temperature. These reactions have been used for indirect determinations of the above nitro compounds, determining excess Ti(III) by the above method.[378]

$$R-NO_2 + 4\,Ti^{3+} + 4\,H^+ \longrightarrow R-NHOH + 4\,Ti^{4+} + H_2O \qquad (104)$$

$$R-NO_2 + 6\,Ti^{3+} + 6\,H^+ \longrightarrow R-NH_2 + 6\,Ti^{4+} + 2\,H_2O \qquad (105)$$

Coulometrically generated Ti(III) was used for the determination of phenoxazones in a H_2O-EtOH mixture.[409]

E. Some Other Reducing Agents

1. Ascorbic Acid

Althought the reducing ability of ascorbic acid is lower in nonaqueous media than in water,[212,213] its solutions in AcOH[383] and in its mixtures with MeCN,[63,127] in DMF[46] and in H_3PO_4[382] have been used.

As the substance is soluble in glacial AcOH, 0.05 *N* solutions in this solvent can readily be prepared. A 0.01 *N* solution can only be prepared with an addition of CH_3COONa which, however, decreases its stability.[383] A preparation of this reagent in an AcOH-MeCN mixture and its use for titration of Cu(II)[63] and Ce(IV)[127] have also been described. Due to the formation of an acetate complex of Fe(III), the redox potential of the Fe(III)/Fe(II) system decreases in glacial AcOH; therefore, Fe(III) does not oxidize ascorbic acid and thus does not interfere in ascorbinometric titrations.[384] The redox potential of the I_2/I^- system is also so decreased in glacial AcOH that the reaction of I_2 with ascorbic acid is not quantitative. On the other hand, Br_2 can be potentiometrically or visually titrated. Because of a low partial pressure of Br_2 over its solutions in glacial AcOH, the titer of the solutions is exceptionally stable, and they can be used for the determination of the titer of ascorbic acid standard solutions in this solvent. The titration of Au(III) proceeds in two steps (see Equations 106 and 107) and the end point can be detected potentiometrically. The end point potential break is increased by an addition of CH_3COONa. In practical determinations, the use of the second, sharper break is more suitable.

$$Au^{3+} + C_6H_8O_6 \longrightarrow Au^+ + C_6H_6O_6 + 2H^+ \quad (106)$$

$$2\,Au^+ + C_6H_8O_6 \longrightarrow 2\,Au + C_6H_6O_6 + 2\,H^+ \quad (107)$$

In potentiometric titration of Hg(I) and Hg(II), the substances are reduced to Hg(O) according to Equations 108 and 109. The potential break is very sharp. In the titration of Hg(II), an inflection point can be observed on the titration curve, corresponding to the reduction to Hg(I); however, this point is not sufficiently pronounced for its use for the end-point detection.

$$Hg^{2+} + C_6H_8O_6 \longrightarrow Hg + C_6H_6O_6 + 2\,H^+ \quad (108)$$

$$Hg_2^{2+} + C_6H_8O_6 \longrightarrow 2\,Hg + C_6H_6O_6 + 2\,H^+ \quad (109)$$

Well-developed and reproducible titration curves were obtained in the potentiometric titration of MnO_4^-, ICl, Pb(IV), Cr(VI), and V(V), but the unusual stoichiometry found has not yet been explained.[384]

A 0.1 *M* solution of ascorbic acid in DMF can be prepared by dissolving a weighed amount of the substance in the solvent and standardized iodometrically.[46] Cu(II) and Hg(II) can be potentiometrically titrated with this reagent,[46] and Cr(VI) can be titrated visually using methylene blue indicator.[53] An aqueous solution of ascorbic acid was used for titration of NO_2^- and NO_3^- in 12 *M* H_3PO_4.[382]

2. *Organic Radicals*

A standard solution of the fluorene radical in a mixture of THF and 1,2-dimethoxyethane was prepared by the reaction of sodium metal with fluorene in 1,2-methoxyethane and dilution with THF. All the operations were carried out in an inert atmosphere, and both solvents were previously distilled first with $LiAlH_4$ and then with sodium metal. This exceptionally strong reductant was standardized using freshly distilled 2,4-pentadione and used for biamperometric titrations of many carbonyl compounds in THF.[385]

A standard solution of the anthracene radical in THF was prepared by the reaction of anthracene with sodium metal in the solvent. This solution must be protected against atmospheric oxygen and moisture and was used for titration of I_2 in hexane and for the determination of various alcohols, monobasic carboxylic acids, anhydrides, and ketones in THF.[386,387]

A standard solution of the biphenyl radical can be prepared by the reaction of sodium metal with biphenyl in THF or 1,2-dimethoxyethane. This considerably unstable reagent was used for tedious and time-consuming titrations of various aromatic hydrocarbons.[388,389]

Coulometrically generated biphenylradical monoanion in DMF was used for potentiometric titration of anthracene, nitrobenzene, nitromethane, benzophenone, and azobenzene. Organic halides, pyrene, perylene, and benzanil do not yield accurate results. It can be assumed that this reagent will rapidly react with most organic reducible substances in organic solvents (e.g., DMF, THF, 1,2-dimethoxyethane) ensuring a sufficient solubility of the substances to be determined. Its intense color can be used for visual indication, and its reversible behavior enables the use of electrometric indication methods.[390] Coulometrically generated naphthalene radical in THF was used for the determination of −OH groups and water bound on the surface of heterogeneous catalysts.[410]

Coulometric generation of 1,4-benzosemiquinone from quinone in MeCN or DMSO was also described. The reagent reacts rapidly and quantitatively with, e.g., generated I_2, but is decomposed by H^+ ions.[313]

3. *Pyrocatechol*

A 0.1 *N* pyrocatechol solution was prepared by dissolving 0.5506 g of the p.a. substance in glacial AcOH and diluting to 100 mℓ. Its titer was determined by potentiometric titration of Pb(IV). Titrations of Br_2 and ICl, with an addition of CH_3COONa, were further described.[326]

4. *Compounds of Divalent and Tetravalent Vanadium*

A 0.05 *N* $VO(CH_3COO)_2$ solution in glacial AcOH can be prepared by heating V_2O_5 with $(COOH)_2$ and dissolving the melt formed in the solvent. The titer can be determined using MnO_4^-. Pb(IV) can be titrated with this reagent at 20°C, Cr(VI) and BrO_3^- at 70 to 80°C. MnO_4^- can be titrated at 20°C only when the solution has been acidified with H_2SO_4. The corresponding reactions are described by Equations 110 to 112.[326]

$$Pb(CH_3COO)_4 + 2\ VO(CH_3COO)_2 + 4\ H_2O \longrightarrow Pb(CH_3COO)_2 + 2\ HVO_3 + 6\ CH_3COOH \qquad (110)$$

$$2\ CrO_3 + 6\ VO(CH_3COO)_2 + 9\ H_2O \longrightarrow Cr_2O_3 + 6\ HVO_3 + 12\ CH_3COOH \qquad (111)$$

$$2\ KMnO_4 + 10\ VO(CH_3COO)_2 + 3\ H_2SO_4 + 12\ H_2O \longrightarrow K_2SO_4 + 2\ MnSO_4 + 10\ HVO_3 + 20\ CH_3COOH \qquad (112)$$

A low stability of VSO_4 standard solutions in aqueous media[36] has led to the use of the reagent in glycerol.[391] An increase in the stability of reductants in this medium is explained by the low solubility of oxygen in glycerol.[344,374] The titer of 0.1 *N* VSO_4 in a glycerol (85%)-H_2O (15%) mixture remains constant for several days and can be determined using $NH_4Fe(SO_4)_2$. The redox potential of the V(III)/V(II) system in this medium is 10.19 V vs. silver chloride electrode. An advantage of this reagent, which has been used to titrate many azo dyes, is not a necessity of work in an inert atmosphere.[391]

The electrochemical behavior of V(III) and V(IV) in MeCN, DMF, and Py was also studied. The formal redox potential of the V(IV)/V(III) system in MeCN increases from 0.634 V in 0.5 *M* H_3PO_4 to 0.825 V in 3 *M* H_3PO_4 (vs. NHE). A 100% current efficiency was attained in coulometric generation of V(IV) by electrochemical dissolution of a vanadium electrode in DMF or MeCN containing 1 *M* $NaClO_4$, which was also verified by coulometric titration of Cr(VI).[310]

An aqueous solution of VSO_4 was used for the determination of 1-nitroso-2-naphthol and its complex with cobalt in Me_2CO and for the determination of dimethylglyoxime in EtOH.[393]

5. *Sodium Dithionite*

A 0.05 *N* $Na_2S_2O_4$ in AcOH is much more stable than the aqueous solution. However, the substance is poorly soluble in glacial AcOH, and thus solutions containing 1 to 2%

H_2O must be used. The titer can be determined iodometrically in an aqueous medium or by potentiometric titration with Br_2 in glacial AcOH. The titer decreases rapidly at the beginning and then the decrease slows down, so that it amounts to about 20% in 15 days. The solution must thus be standardized daily.[326] In potentiometric titration of Br_2, CrO_3 and MnO_4^- with this reagent, well developed titration curves with sharp breaks, corresponding to the stoichiometry given by Equations 113 to 115, have been obtained.

$$2\,Br_2 + Na_2S_2O_4 + 3\,H_2O \longrightarrow 4\,HBr + NaHSO_3 + NaHSO_4 \quad (113)$$

$$4\,CrO_3 + 3\,Na_2S_2O_4 + 3\,H_2O \longrightarrow 2\,Cr_2O_3 + 3\,NaHSO_3 + 3\,NaHSO_4 \quad (114)$$

$$4\,KMnO_4 + 5\,Na_2S_2O_4 + 6\,H_2SO_4 \longrightarrow 4\,MnSO_4 + 2\,K_2SO_4 + 5\,NaHSO_3 + 5\,NaHSO_4 + H_2O \quad (115)$$

In contrast to these determinations, in which a $Na_2S_2O_4$ molecule corresponds to four equivalents, in the titrations of BrO_3^- (see Equation 116) and chloramine T (see Equation 117) this molecule corresponds to six equivalents, i.e., is oxidized as far as to SO_4^{2-}. However, in titration of IO_3^- (see Equation 118) four electrons are again exchanged.

$$KBrO_3 + Na_2S_2O_4 + H_2O \longrightarrow KBr + 2\,NaHSO_4 \quad (116)$$

$$3\,CH_3C_6H_4SO_2NClNa + Na_2S_2O_4 + 4\,H_2O \longrightarrow 3\,CH_3C_6H_4SO_2NH_2 + 2\,NaHSO_4 + 3\,NaCl \quad (117)$$

$$4\,KIO_3 + 5\,Na_2S_2O_4 + 2\,H_2SO_4 + 3\,H_2O \longrightarrow 2\,I_2 + 2\,K_2SO_4 + 5\,NaHSO_3 + 5\,NaHSO_4 \quad (118)$$

In titration of ICl, reactions described by Equations 119 and 120 proceed in parallel, so that four molecules of ICl correspond to one molecule of $Na_2S_2O_4$, because the other two ICl molecules react with the HI formed. In contrast to Br_2, I_2 alone cannot be titrated with this reagent.

$$2\,ICl + Na_2S_2O_4 + 3\,H_2O \longrightarrow 2\,HI + 2\,HCl + NaHSO_3 + NaHSO_4 \quad (119)$$

$$HI + ICl \longrightarrow I_2 + HCl \quad (120)$$

6. Diverse Reductants

$NaBH_4$ was used for titration of carbonyl compounds. A sample solution in MeOH is treated with excess reagent, which is back-titrated with HCl.[392] Various sulphonamides were titrated with this reagent in DMF, DMSO, or in their mixture with $CHCl_3$.[407]

A 0.1 *N* $AsCl_3$ in glacial AcOH was prepared by dissolving 0.4946 g of the p.a. substance in 5 mℓ of concentrated HCl and diluting with glacial AcOH to 100 mℓ. Its titer was determined iodometrically in an aqueous solution. The reagent was used for potentiometric titrations of Br_2, ICl, and $Pb(CH_3COO)_4$.[326]

Dipicrylamine and its complex with potassium in Me_2CO were titrated with an aqueous solution of Mo(III),[393] and an aqueous solution of $NaNO_2$ was used for potentiometric titration of *o,o*-diarylthiophosphatehydrazides in benzene.[394] A solution of Cu(I) in glycerol was employed for titration of Cr(VI) and Ce(IV).[399] The titer of aqueous solutions of hydroquinone can be determined by titration of Mn(III) in concentrated H_3PO_4.[395]

VI. CONCLUSIONS

The above survey demonstrates extensive possibilities of determinations of inorganic and organic substances by means of their redox titrations in nonaqueous or mixed media. Many works have been devoted to the determination of water-soluble substances by their titration in nonaqueous solutions. The importance of these works is rather theoretical, as the use of nonaqueous media always brings experimental complications compared with aqueous solutions. A certain exception is titrations of aqueous solutions of substances to be determined with a reagent solution in a nonaqueous medium, in which the reagent is more stable. Another fact justifying the use of a nonaqueous medium even in the determination of water-soluble substances is an increased reagent reactivity leading to a shortening of the time required for carrying out an indirect determination or even permitting the carrying out of an oxidation or reduction which could not be carried out in water. Sometimes, the reason for the use of a nonaqueous solution can, on the other hand, be a lower reactivity of the reagent, leading to an increased selectivity of the determination. However, all these cases are rather exceptional. Most water-soluble substances can better be determined by simpler methods based on titration in aqueous solution, so that no practical reason leads to the use of a nonaqueous medium.

The situation is quite different in the analysis of water-insoluble substances, where a great lack of suitable analytical methods has only been removed by introducing nonaqueous media. Hence a further development in the practical use of nonaqueous redox titrations can be expected primarily in this field. On one hand, preparation, standardization, and stability of new redox reagents will be studied, as well as the problems of visual and objective end-point detection; on the other hand, these redox reagents will be applied to the determination of new types of inorganic and organic substances. A promising field is the determination of various metals after their conversion into complexes with organic reagents and extraction of the complexes into a suitable solvent by redox titration directly in the extractant medium.

From the theoretical point of view it will apparently be desirable to study the kinetics and mechanism of the processes involved, which will enable more objective selection of the experimental conditions for determinations. It seems that suitable conditions for this study have been created recently by intense study of electrochemical reactions in nonaqueous media[408] and by the study of the solvent effect on molecular and ionic reactions, carried out by synthetic and physical chemists. Furthermore, due attention should also be paid to coulometric redox titrations, because of a higher sensitivity and better accuracy of these methods and easier automation of the procedure.[210] A new trend in this field is especially generation of organic radicals, which act as exceptionally strong reductants in nonaqueous media.

An increased attention should be paid to the end-point detection techniques. So far, electrometric methods (potentiometry, amperometry, biamperometry, bipotentiometry) have been most common and have also been reviewed.[406] Because of their character, these methods are limited to reactions of ions or dissociating substances. Frequent difficulties are encountered when they are used in nonaqueous media, because of high resistance of the solutions titrated. Therefore, the possibilities of visual and spectrophotometric end-point detection should be adequately investigated.

In conclusion, it thus can be stated that introduction of nonaqueous solvents into the field of redox titrations has a considerable practical importance, which will further grow on the basis of the trends mentioned above.

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