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STUDY OF THE QUANTITATIVE OXIDATION OF FERROCENES

BY COPPER(II) PERCHLORATE IN ACETONITRILE

by

(C) PETER FREDERICK QUIRK

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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The undersigned certify that they have read, and
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ABSTRACT

A study was made of possible primary oxidation-reduction
standards for solutions of copper(II) perchlorate in acetonitrile.
Of those investigated ferrocene was found most satisfactory. Two
recrystallizations of commercial ferrocene from heptane followed
by sublimation under vacuum gave material of 100.0% purity.
Ferrocene was found to be stable and nonhygroscopic in air under
normal laboratory conditions, to be oxidized stoichiometrically
and rapidly to the ferricenium ion by hydrated copper(II)
perchlorate in purified acetonitrile, and to give a sufficiently
large potential break at the equivalence point in the copper(II)
reaction to allow precise determination of the end point.

Weight titrations of ferrocene with hydrated copper(II)
perchlorate in acetonitrile and of copper(II) with EDTA in water
gave precisions of a few parts per ten thousand. The
concentrations of copper(II) as determined by the above methods
agreed within three parts per ten thousand when purified
acetonitrile was used to prepare the copper(II) solutions but a
difference of several parts per thousand was seen when technical
grade acetonitrile was employed. This discrepancy was traced to
the presence of about $10^{-4}\underline{M}$ cyanide, a previously unreported
contaminant, in the technical grade acetonitrile used. Ammonia,

ammonium acetate, acetamide, acrylonitrile, and acetic acid,

previously reported contaminants in technical grade acetonitrile,

were shown not to interfere in the copper(II)-ferrocene reaction

at the concentrations usually found in acetonitrile.

Hydrated copper(II) perchlorate in technical grade

acetonitrile, standardized with ferrocene, was shown to be a

suitable titrant for the determination of several alkyl and

monoacyl derivatives of ferrocene. The derivatives were

generally reversibly oxidized, and differential potentiometric

titrations of several mixtures of derivatives could be performed.

Solutions of ferrocene in acetonitrile were found to

be stable at the part per thousand level in air for several

days. Therefore, ferrocene can be used as a reducing titrant

of moderate strength in this solvent.

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CHAPTER I   INTRODUCTION

The vast majority of chemical reactions in solution use water as the solvent. The availability, high dielectric constant, ease of purification and handling, stability, and solvating ability of water for a large number of substances have made it at present the most important solvent. However, several of the properties of water are undesirable for many chemical systems. For example, it levels strong acids and bases to the strength of the hydronium and hydroxide ions, causes hydrolysis of many compounds, is not stable toward many reaction intermediates such as free radicals, and cannot dissolve many substances, in particular nonpolar organic compounds. Therefore, both organic and inorganic nonaqueous solvents and melts are increasingly being employed to overcome these disadvantages and extend the range of chemical study in solution.

Analytical applications of nonaqueous solvents have been limited for the most part to acid-base reactions, solvent extractions, and chromatographic processes. These solvents have been applied recently to electron-transfer, or oxidation-reduction, reactions as well. Polarography has been used in the majority of these investigations[1-3]. Potentiometric oxidation-reduction titrations also have given information on reaction stoichiometries and have made possible the analytical

determination of oxidizing and reducing agents.

In a recent review of oxidation-reduction titrations in nonaqueous solvents[4], acetic acid was reported to be the most common solvent. Tomicek and coworkers, using anhydrous acetic acid as solvent, and detecting end points potentiometrically with platinum and calomel electrodes, examined bromine, chromic acid, sodium permanganate, iodine monochloride, and lead(IV) acetate as oxidants for a number of organic and inorganic substances[5]. They also studied the reducing agents sodium dithionate, vanadyl acetate, arsenic(III) chloride, pyrocatechol, and tin(II) chloride. The rates of electron-transfer reactions in anhydrous acetic acid, with its low dielectric constant ($\varepsilon = 6.2$), were found to be slow and the equivalence points uncertain. The addition of a strong acid or base increased the rate of reaction, apparently through catalytic action.

Reviews of polarography in nonaqueous solvents indicate that acetonitrile ($\varepsilon = 36$), dimethylformamide ($\varepsilon = 37$), and dimethylsulfoxide ($\varepsilon = 47$) are popular solvents[1,2]. Of these three, acetonitrile appears to have the most desirable properties. Some of its properties are compared with those of water and acetic acid in Table I. A moderate dielectric constant of 36 allows dissolution in acetonitrile of many nonpolar organic compounds as well as a number of salts, at

Table I. Physical Properties of Water,

Acetic Acid, and Acetonitrile

Property	Water	Acetic Acid	Acetonitrile
Boiling Point (°C)	100.0	118.2^6	81.6^7
Freezing Point (°C)	0.0	16.6^6	-45.7^7
Dielectric Constant, 25°C	78.54^8	6.2^4	36.0^8
Density (g/cm^3), 25°C	0.9970^9	1.0437^1	0.7767^{10}
Viscosity (Centipoise)	$8.937^8_{25°C}$	$1.040^{11}_{30°C}$	$0.345^{10}_{25°C}$
Dipole Moment (Debye)	1.84^8	0.83^{11}	3.37^7
Heat of Vaporization at Boiling Point (Kcal/mole)	9.72^8	5.825^{11}	7.127^7
Spectral Cut-off Wavelength in Ultraviolet (mμ)	below 189	212	189^{12}
Potential at Which Oxidized (V vs. aq. SCE)	0.569^{13}	$>2.0^{14}$	2.3^{12}
Potential at Which Reduced (V vs.aq. SCE)	-0.660^{13}	-1.8^{15}	-2.7^{12}
Autoprotolysis Constant (pK), 25°C	14	14.45^{16}	$>33^{17}$
Coefficient of Cubic Expansion (per C°), 20°C	0.000205^9	0.001071^6	0.00137^{18}
Recommended Maximum Limit of Vapor Concentration in Atmosphere (ppm)	---	10^{19}	40^{19}
Vapor Pressure (mm Hg), 25°C	23.756^8	16.4^6	89.0^7

least at low concentrations. Being a polar Lewis base[4], acetonitrile solvates cations moderately well, though not as well as water. It does not solvate most anions well, however, and this reduces the solubility of salts. Salts of large symmetrical or polarizable univalent anions, because of the low charge density on the anion, have small crystal lattice energies and are more soluble in acetonitrile. The stability of acetonitrile toward oxidation and reduction is high, so powerful oxidizing and reducing reagents may be employed in this solvent.

Several procedures for purification of acetonitrile have been proposed[12,20-22]. It has been found that the solvent is stable for several weeks after purification. Water is taken up readily by the pure solvent however, and keeping the water concentration below millimolar levels requires special precautions. The toxicity is less than that of acetic acid. These properties make it a useful solvent for oxidation-reduction studies; the hygroscopicity is the most difficult problem.

Rao and Murthy were the first to study acetonitrile as a solvent for oxidation-reduction reactions. They used ammonium hexanitrocerate as an oxidant for the determination of hydroquinone[23,24], potassium iodide[23], ascorbic acid[25], oxalic acid[26], and xanthate[23,27]. The potentials were followed by a

platinum indicating and a glass or antimony reference electrode[23,25,26]. The visible indicators ferroin, diphenylamine, methyl red, Janus Green[24], and the color of cerium(IV) itself[27] also were used with reasonable success for hydroquinone and xanthate. Most of the titrations were not done in pure acetonitrile, but in acetonitrile-acetic acid mixtures of unspecified composition. The acetic acid was added to accelerate reaction rates. Results were nearly quantitative in most cases. The formal reduction potential of the nitratocerate-cerium(III) couple in pure acetonitrile was measured by these authors and was found to be 0.755V vs. the silver-0.01M silver nitrate in acetonitrile reference electrode[28]. The formal reduction potential of this couple in acetonitrile increased with addition of acetic acid until the ratio of acid to cerium reached 1000; at this point the potential became steady at 0.873V vs. the silver reference. This increase in potential was found by spectral measurements in the ultraviolet to be caused by the formation of cerium(III)-acetate complexes.

Recently iron(III) perchlorate has been examined as an oxidizing agent in acetonitrile[29]. The formal reduction potential of the iron(III)-(II) couple in dry acetonitrile is 1.57V vs. the silver reference; therefore, iron(III) is a very strong oxidizing agent in this solvent. However, minute amounts of water greatly lower the formal reduction potential of the

couple and decrease the oxidizing efficiency of the iron(III) to less than 100%, the exact value depending on the reduction potential of the species being titrated. In addition, it has been reported that iron(III) chloride oxidizes acetonitrile[30].

Silver(II) nitrate in acetonitrile has been found to be a strong oxidizing reagent, able to oxidize quantitatively copper(I) to copper(II)[31]. However, silver(II) is unstable toward traces of water in acetonitrile, so its utility is limited to use as a coulometrically-generated reagent.

In the last few years copper(II) perchlorate has been studied as an analytical oxidant in acetonitrile[32-36]. Initial polarographic work showed that the copper(II)-(I) and copper(I)-(0) couples are sufficiently separated to give two one-electron reductions of copper(II) in acetonitrile[37], as compared to a single two-electron reduction in water. Thus copper(I) appears to be stabilized by acetonitrile. Hathaway suggests that copper(I) is coordinated to four acetonitrile molecules in solution as well as in its salts[38]. Due to this difference in solvation, the reduction potential in acetonitrile of the copper(II)-(I) couple vs. the silver-0.01$\underline{M}$ silver nitrate in acetonitrile reference is 0.801V[39], a value 1.27V higher than that of the copper(I)-(0) couple[40]. Copper(II) perchlorate has been used to oxidize quantitatively selected

thioureas[34,35] and arylamines[33], hydroquinone[32], iodide[32,36], and potassium ethyl xanthate[36]. It was found that copper(II) nitrate and copper(II) chloride were weaker oxidizing agents in acetonitrile than the perchlorate salt[38,41]. Addition of sodium perchlorate increased the copper(II)-(I) reduction potential of the nitrate and chloride salts[41]. Solutions of copper(II) perchlorate in acetonitrile are stable, and are easy to standardize, prepare, and use at the few parts per thousand level.

Standardization to better than a part per thousand has not been possible as yet, however, because primary standards for aqueous oxidation-reduction titrations have not been applicable to the copper(II)-acetonitrile system. The purpose of this work was to find a suitable primary standard for copper(II) solutions. An additional goal was to establish the precise stoichiometry of an electron-transfer reaction in acetonitrile in order to determine whether analytical results of precision and accuracy comparable to those in water could be obtained.

CHAPTER II   FERROCENE AS A PRIMARY STANDARD FOR SOLUTIONS OF

HYDRATED COPPER(II) PERCHLORATE IN ACETONITRILE

Background

Although acid-base reactions in nonaqueous solvents

have been studied to a greater extent than those of oxidation-

reduction, the disparity is probably not merited, for the use

of nonaqeous media enables the range of electron-transfer

reactions to be extended greatly. The number of nonaqueous

solvents is so great and their physical properties so varied

that the amount of work possible, both theoretical and practical,

is almost unlimited. To be useful as media for oxidation-

reduction reactions, nonaqueous solvents should (1) be stable

toward the oxidizing and reducing agents used, (2) be able to

keep ionic reactants in solution, since with few exceptions one

or more of the reactants or products will carry a charge, and

(3) either be available in stable pure form, or easily treated

to remove interfering impurities. Also, for convenience the

solvents should have a useful liquid range (liquid at room

temperature without an excessively high vapor pressure) and

low toxicity.

Anhydrous acetic acid has been the most commonly used

solvent for electron-transfer reactions[4], though acetonitrile

has considerable advantages over this solvent as a medium for oxidation-reduction reactions (Table I). As previously mentioned, copper(II) perchlorate has been used as an analytical oxidant in acetonitrile for several species[32-36]. Although copper(II) solutions in acetonitrile are prepared easily and are stable, a method for determining the redox titer to better than a part per thousand has not been established. Copper(II) perchlorate is too hygroscopic to be weighed directly. Generally an aqueous titration with EDTA has been used to standardize the copper(II) titrant[32,35,36], but it was feared that complexation by EDTA in water might be susceptible to factors other than those affecting the oxidizing ability of copper(II) in acetonitrile. Therefore, titrations using 0.09$\underline{M}$ hydrated copper(II) perchlorate in technical grade acetonitrile as titrant on an automatic recording titrator were performed to survey possible primary-standard reducing agents for copper(II) perchlorate in acetonitrile.

The common primary-standard reducing agents, used in water, sodium oxalate, potassium ferrocyanide, ferrous ethylenediammonium sulfate, and arsenic(III) oxide were not sufficiently soluble in acetonitrile to be titrated. Oxalic acid dihydrate, though soluble, immediately formed a light blue-green precipitate on addition of copper(II) in acetonitrile that did not dissolve after five hours in a solution containing

a ten per cent excess of copper(II). This behavior is similar to that of cerium(IV) with oxalic acid in acetonitrile, in which a precipitate of cerium(IV) oxalate forms. However, in the latter case, after ten minutes in a ten per cent excess of cerium(IV), carbon dioxide and cerium(III) are produced quantitatively[26].

Potassium iodide, a useful standard in water, gives two inflections upon oxidation in acetonitrile (Figure I). These inflections correspond to formation of triiodide and iodine[42,43].

$$2 \ Cu^{+2} + 3 \ I^- \rightleftarrows 2 \ Cu^+ + I_3^- \tag{1}$$

$$2 \ Cu^{+2} + 2 \ I_3^- \rightleftarrows 2 \ Cu^+ + 3 \ I_2 \tag{2}$$
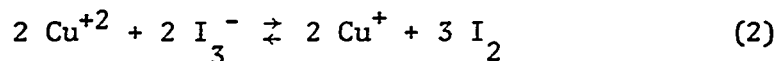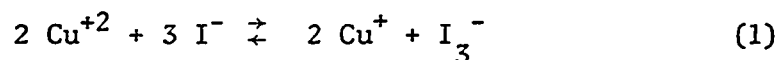
End-point selection is not accurate enough to use potassium iodide as a primary standard because both potential breaks are slightly drawn out and the equivalence points are concentration dependent (Appendix A). However, potassium iodide is acceptable as a standard if an accuracy and precision of one or two parts per thousand can be tolerated.

Thiourea has been used previously to standardize solutions of copper(II) perchlorate in acetonitrile[34]. It reacts in a 1:1 ratio with copper(II) to form a disulfide.

$$2 \ Cu^{+2} + 2 \ \underset{H_2N}{\overset{H_2N}{>}}C = S \rightleftarrows 2 \ Cu^+ + \left[\underset{H_2N}{\overset{H_2N}{>}}C \cdots S - S \cdots C \underset{NH_2}{\overset{NH_2}{<}} \right]^{+2} \tag{3}$$
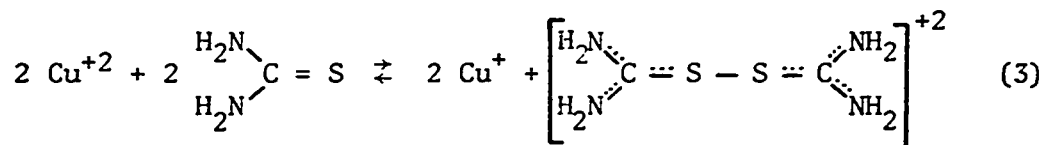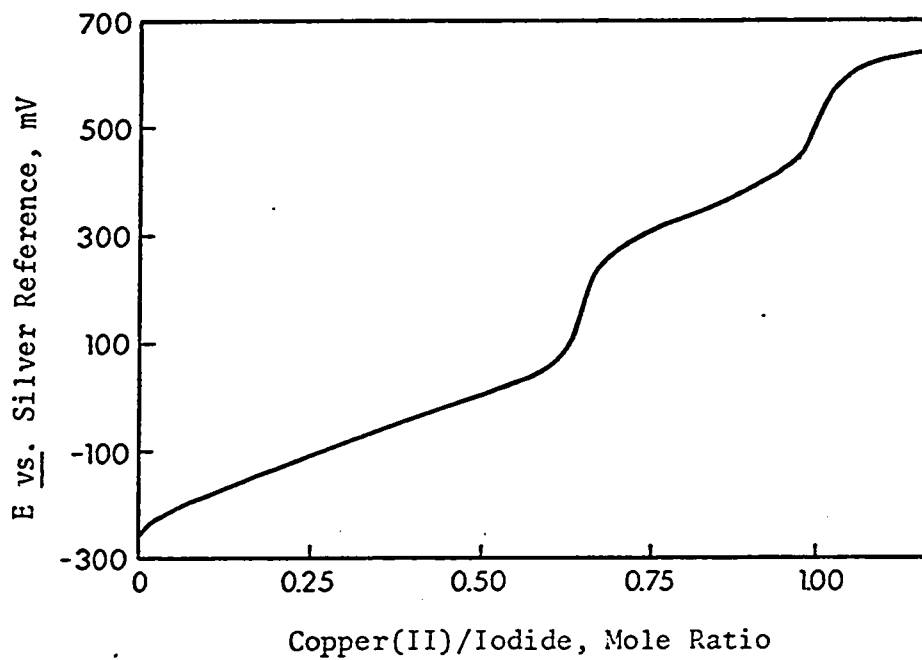
Figure 1. Potentiometric Titration of Potassium Iodide with Copper(II) Perchlorate in Acetonitrile

The titration break is somewhat drawn out, and the potential of the equivalence point is dependent on the concentration of disulfide (Appendix A). Additional disadvantages are that thiourea is somewhat unstable on storage, and that its equivalent weight is rather low.

Hydroquinone has been proposed for standardization of cerium(IV) solutions in acetonitrile[23-26]. It is oxidized by copper(II) in acetonitrile to quinone.

$$2 \; Cu^{+2} + \text{(hydroquinone)} \rightleftharpoons 2 \; Cu^+ + \text{(quinone)} + 2 \; H^+ \tag{4}$$
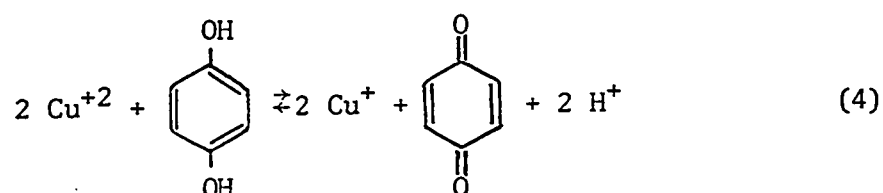
The disadvantages of this compound as a standard are that the equivalent weight is low, the potential break is small and drawn out, the potential at the equivalence point is dependent on the hydrogen ion concentration (Appendix A), and it is unstable on storage. Quinhydrone was also investigated.

$$2 \; Cu^{+2} + \text{(quinhydrone)} \rightleftharpoons 2 \; Cu^{+\cdot} + 2 \; \text{(quinone)} + 2H^+ \tag{5}$$
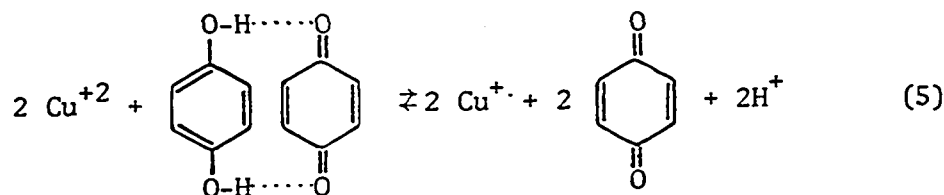
While the equivalent weight is greater than that of hydroquinone, 108 vs. 55, the potential break is still small and drawn out, the potential of the equivalence point is still dependent on

hydrogen concentration, and quinhydrone is difficult to purify and analyze.

Of the substances investigated, ferrocene appeared the most promising as a primary standard for copper(II) perchlorate solutions in acetonitrile. The reaction is

$$Cu^{+2} + Fc \; \rightleftarrows \; Cu^+ + Fc^+ \tag{6}$$
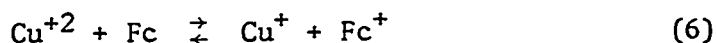
where Fc is ferrocene and Fc^+ is ferricenium ion. The potential at the equivalence point is not concentration dependent, and the potential break is large and symmetric (Figure II). Some of the physical properties of ferrocene are: m.p. by differential thermal analysis, 175.4-175.9°C; density at 25°C, 1.516 g/cc[44]; decomposition temperature, 470°C[45]; vapor pressure in mm Hg (T in degrees Kelvin), $10^{(10.0355 - \frac{3565.1}{T})}$[45]; heat of sublimation, 16.29 kcal/mole[45]; and solubility in acetonitrile, 3.39 weight per cent (0.15M)[46]. Ferrocene obtained from different sources was analyzed as received by titration with copper(II) (Table II) and a range of purity was observed. The material from Arapahoe Chemicals was selected for further purification and study.

An additional reason for investigating the precision and accuracy of this reaction arose from the fact that stoichiometries of electron-transfer reactions in nonaqueous solvents have not been established to better than a few parts
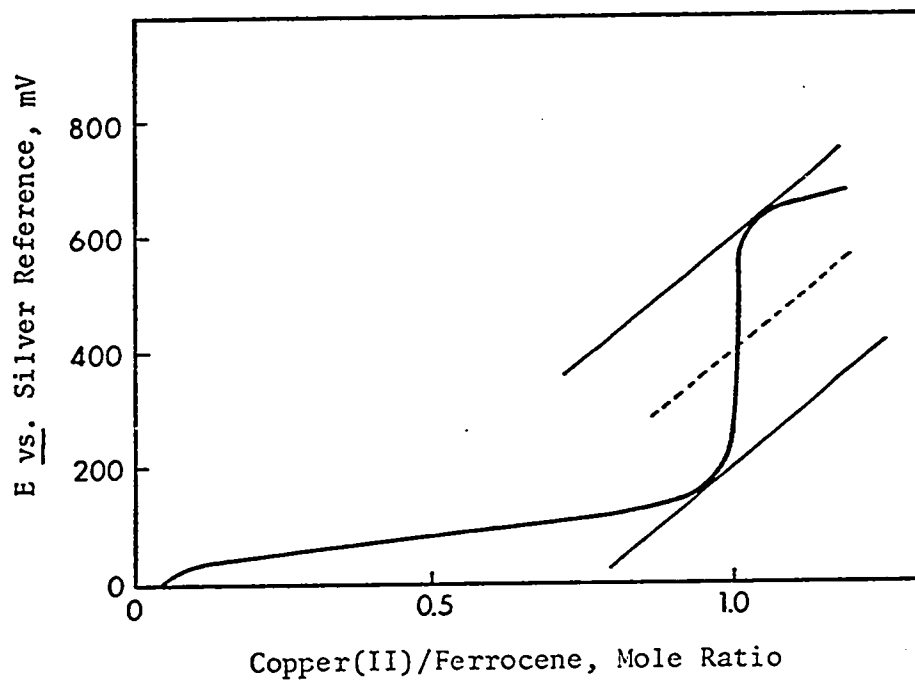
Figure II. Potentiometric Titration of Ferrocene with
Copper(II) Perchlorate in Acetonitrile

Table II. Comparison of Purity of Commercial

Ferrocene from Various Sources

Source	Purity Found by Copper(II) Titration, %	Rel. Std. Dev. for 3 Titrations, p.p.t.
Arapahoe Chemicals	99.4[a]	0.7
J. T. Baker Chemical Co.	99.5	1.0
Alfa Inorganics	98.8	1.7
Eastman Organic Chemicals	95.7	1.7
Matheson, Coleman, and Bell	94.4	2.4

[a]Value taken from Table V.

per thousand. It was therefore of interest to determine whether side reactions might be occurring in reactions of copper(II) in acetonitrile, or whether impurities in the commercial or purified solvent might cause errors. It was also desired to develop a convenient procedure for titrations in nonaqueous solvents with better than part per thousand accuracy.

Experimental

Reagents. Solvents. Technical grade acetonitrile
(Matheson, Coleman, and Bell) was either used as received or
purified by a modification of the method of O'Donnell, Ayers,
and Mann[12]. In the first step, 32 ml of benzoyl chloride
(The British Drug Houses Ltd.) was added to approximately 2.7
liters of technical grade acetonitrile. The mixture was
refluxed for two hours, then distilled at a rate of about 500
ml per hour into a flask that contained 3 to 4 ml of water to
destroy any benzoyl chloride carried over in the distillate.
The last 150 to 250 ml in the still pot were discarded. About
32 g of anhydrous sodium carbonate (Fisher Scientific Co.,
Certified A.C.S.) was added to the distillate. This mixture
was refluxed and distilled in the same manner as in the benzoyl
chloride step; the distillate was collected in a flask that had
been dried at 160°C overnight. A still pot residue of 100 to
150 ml was discarded. To the distillate was added 32 g of
anhydrous sodium carbonate and 48 g of potassium permanganate
(Fisher Scientific Co., USP grade) and a third distillation
performed in the same way as the second. Again a residue of
100 to 150 ml of liquid, containing a large amount of
precipitate, apparently manganese dioxide, was discarded. In
this step the distillate occasionally had an odor of ammonia

and contained a small amount of white precipitate.
Approximately three ml of concentrated sulfuric acid (Canadian
Industries Limited) was added to the distillate. A precipitate
of ammonium sulfate appeared in most cases. Several porcelain
Berl saddles were added as boiling chips and the mixture was
vacuum distilled below 55°C into a dry flask. The distillate
contained more ultraviolet absorbing impurities if distilled at
atmospheric pressure in the presence of sulfuric acid. A
residue of 100 to 300 ml was discarded. Approximately 2.5 liters
of this distillate was distilled through a 30 theoretical plate
column packed with glass helices at 10 ml per hour. Collection
of the distillate was begun when the absorbance at 200 mμ was
less than 0.2 in a 1-cm quartz cell measured in a Unicam SP 800 B
visible-ultraviolet spectrophotometer. At this point the absorbance
above 215 mμ was negligible. The absorbance at 200 mμ decreased
as the distillation progessed, and the last portions had the
best optical purity. The distillation was stopped when about
100 ml remained in the still pot. The water content of the
final product was shown to be less than $5 \times 10^{-3}\underline{M}$ by Karl Fischer
titration. Titrations on the automatic titrator were made using
technical grade acetonitrile, and weight titrations were made
using pure acetonitrile, unless stated otherwise.

All water used was deionized. Technical grade heptane
(Fisher Scientific Co.) was used as received.

Chemicals. Commercial ferrocene was obtained from several sources (Arapahoe Chemicals; Eastman Organic Chemicals; Alfa Inorganics, Inc.; Matheson, Coleman, and Bell; and J. T. Baker Chemical Co.). The material from Arapahoe Chemicals was purified by recrystallization, sublimation, or recrystallization followed by sublimation. Recrystallization was done by saturating 200 to 800 ml of heptane at 50°C with ferrocene, raising the temperature of the solution to 60 to 65°C, filtering through a fine porosity (4-8μ) sintered-glass filter, and evaporating the solvent in a rotary evaporator under partial vacuum while warming with an infrared lamp. A small amount of black residue was left on the filter if the starting material was commercial ferrocene. The solution was allowed to cool until crystals of ferrocene formed. These were collected and dried under vacuum at room temperature for 12 hours or more. The yield was 65 to 80%. Sublimations were performed under vacuum at 60 to 80°C on gram portions of ferrocene. Accumulated sublimate was removed from the water-cooled cold finger every 20 minutes because the product was more crystalline and convenient to work with than when allowed to collect for longer periods. Collection was stopped after 80 to 90% of the material had sublimed. When commercial ferrocene was allowed to sublime to completion there was left a greyish-green residue. Recrystallized ferrocene, when allowed to sublime completely,

left a minute amount of brown residue, less than 0.01% of the original material. The ferrocene designated pure ferrocene in this work is commercial ferrocene from Arapahoe Chemicals that was recrystallized twice from heptane and sublimed once.

Two batches of hydrated copper(II) perchlorate were used. The first was obtained commercially (G. F. Smith Chemical Co.). The second was prepared by the addition of a slight excess of 70% perchloric acid (J. T. Baker Chemical Co.) to a suspension of copper(II) carbonate (Fisher Scientific Co., Certified Reagent) in water, followed by boiling to drive off carbon dioxide and to concentrate the salt in solution. The hydrated copper(II) perchlorate crystals that formed on cooling were collected and dried at room temperature under vacuum. About 1.5 kg of the salt was prepared. The copper content of this material was determined by EDTA titration with murexide as the indicator, and perchlorate was determined by reduction to chloride followed by titration of the chloride with silver nitrate[47a]. The spectrophotometric method for determination of perchlorate by Fritz, Abbink, and Campbell[47b] could not be used because copper(II) interfered. Copper(II) also interfered in the determination of water in the product by Karl Fischer titration. Attempts to eliminate the copper(II) interference by complexation with EDTA were unsuccessful. The acid content was estimated by measurement of the pH of several aqueous solutions of the prepared salt.

Aqueous acid-base titrations of the prepared salt were not
feasible because of the formation of copper(II) hydroxide.
Qualitative tests of the salt for bicarbonate, carbonate,
sulfate, nitrate, and the halides were negative[48]. Results of
carbon-hydrogen analyses were too uncertain to make a positive
statement about the presence of carbon-containing impurities,
although they appeared to be absent, or the amount of hydrogen
present. With the assumption that the only acid present is
perchloric acid, the overall analysis corresponds to the formula
$Cu(ClO_4)_{2.00} \cdot 6.1 \ H_2O \cdot 0.01 \ HClO_4$. Except where specified, this
salt was used for all subsequent work.

Tetrakis(acetonitrile)copper(I) perchlorate was
prepared by adding excess copper powder (Allied Chemical) to a
solution of hydrated copper(II) perchlorate in acetonitrile,
allowing the reduction of copper(II) to go to completion, as
indicated by the disappearance of the blue color, filtering off
the excess copper powder, evaporating the solution to
concentrate the copper(I) salt, cooling, then collecting and
drying the salt under vacuum at room temperature overnight.
The salt was analyzed by oxidation of portions to copper(II)
with nitric acid followed by titration of the copper(II) with
EDTA. The salt was found to be 99.8% pure; the impurity is
probably acetonitrile. (Safety precautions must always be
exercised when handling perchlorate salts.)

The disodium salt of EDTA (British Drug House Ltd.) was

recrystallized from ethanol-water solution according to the method of Blaedel and Knight[49] and dried overnight at 80°C. Potassium iodide (Fisher Scientific Co., Certified A.C.S.) was recrystallized several times from water containing a slight amount of hydriodic acid, then dried under vacuum at 200°C for 10 hours. Hydroquinone (Fisher Scientific Co., Purified) and thiourea (Fisher Scientific Co., Certified Reagent) were recrystallized once from 95% ethanol and dried 8 hours under vacuum at room temperature. Quinhydrone (Eastman Kodak Company, White Label) and oxalic acid (Allied Chemical, Reagent A.C.S.) were used as received. Murexide (J. T. Baker Chemical Co.) was mixed with sodium chloride (Fisher Scientific Co., Certified A.C.S.) to give 0.1% by weight murexide and this mixture used as the indicator. Commercial nitric acid and ammonium hydroxide (Canadian Industries Ltd.) were used as received. Copper wire (Canadian Laboratory Supply, 20-gauge) was cleaned with emery paper just before use. For the salt bridge and reference electrode, anhydrous lithium perchlorate (G. Frederick Smith Chemical Co.) and silver nitrate (Fisher Scientific Co., Purified) were used as received. Aqueous sodium sulfate was prepared from anhydrous sodium sulfate (Allied Chemicals, A.C.S.).

For the studies of the impurities in technical grade acetonitrile, acrylonitrile (British Drug House Ltd.), acetic acid (Canadian Industries Ltd.), acetamide (Allied Chemicals),

lithium acetate dihydrate (Matheson, Coleman, and Bell),
ammonium perchlorate and potassium cyanide (Fisher Scientific
Co., Certified Reagent) and ammonium acetate (Mallinckrodt
Chemical Works) were used as received. For polarographic
studies lithium perchlorate and sodium perchlorate (Fisher
Scientific Co.) were recrystallized from water and dried
overnight under vacuum at room temperature. Tetrabutylammonium
perchlorate was prepared by precipitation through addition of
a saturated solution of sodium perchlorate to a boiling aqueous
saturated solution of tetrabutylammonium iodide (Eastman Organic
Chemicals, Red Label). Deaeration of the iodide solution with
nitrogen was necessary to prevent oxidation to insoluble
tetrabutylammonium triiodide.

    <u>Solutions</u>. For the weight titrations,
approximately 0.03 molal solutions of hydrated copper(II)
perchlorate in acetonitrile (accurate solution concentrations
were determined in units of mmoles of copper(II) per g of
solution) were prepared in 1 or 2 liter amounts by dissolving
portions of the salt in pure acetonitrile. To suppress
hydrolysis of the copper, about 1 ml of 70% perchloric acid was
added per liter of hydrated copper(II) perchlorate titrant. The
solutions were stored in borosilicate bottles with ground-glass
stoppers. In a few specified cases technical grade acetonitrile
was used as the solvent. Approximately 0.09$\underline{M}$ hydrated

copper(II) perchlorate in technical grade acetonitrile was used in the preliminary work and for the investigation of suspected impurities in technical grade acetonitrile. Because of the higher concentration of copper(II), 2 ml of perchloric acid were added per liter of titrant to suppress copper(II) hydrolysis. These solutions were stored in polyethylene bottles with a guard tube of magnesium perchlorate and were used within one to two days of preparation.

Approximately 0.03 molal solutions of EDTA (the actual concentration was determined as mmoles of EDTA per g of solution) were prepared by dissolving portions of the disodium salt in water and were stored in polyethylene bottles.

Approximately 1.9-g portions of copper wire were weighed to the nearest microgram, dissolved in 15 ml of cold nitric acid, and diluted with water to 1000±0.005 g to give standard by weight solutions of copper(II). The concentration of these solutions were also expressed as mmoles of copper(II) per g of solution.

Experimental procedures. Titrations in the preliminary survey of possible standard reducing agents were performed with the Metrohm Potentiograph E436 automatic recording titrator in a 120-ml cylindrical cell (Figure III). In this instrument the titrant could be transferred from the polyethylene storage bottle to the syringe buret without exposure to the atmosphere. The

Indicating Electrode

Silver Wire
(Reference Electrode)

0.01M Silver Nitrate
in Acetonitrile

Teflon Lid

Nitrogen Inlet

Ultra Fine Frits

0.1M Lithium Perchlorate
in Acetonitrile

Pt

Buret

Magnetic Stirring Bar
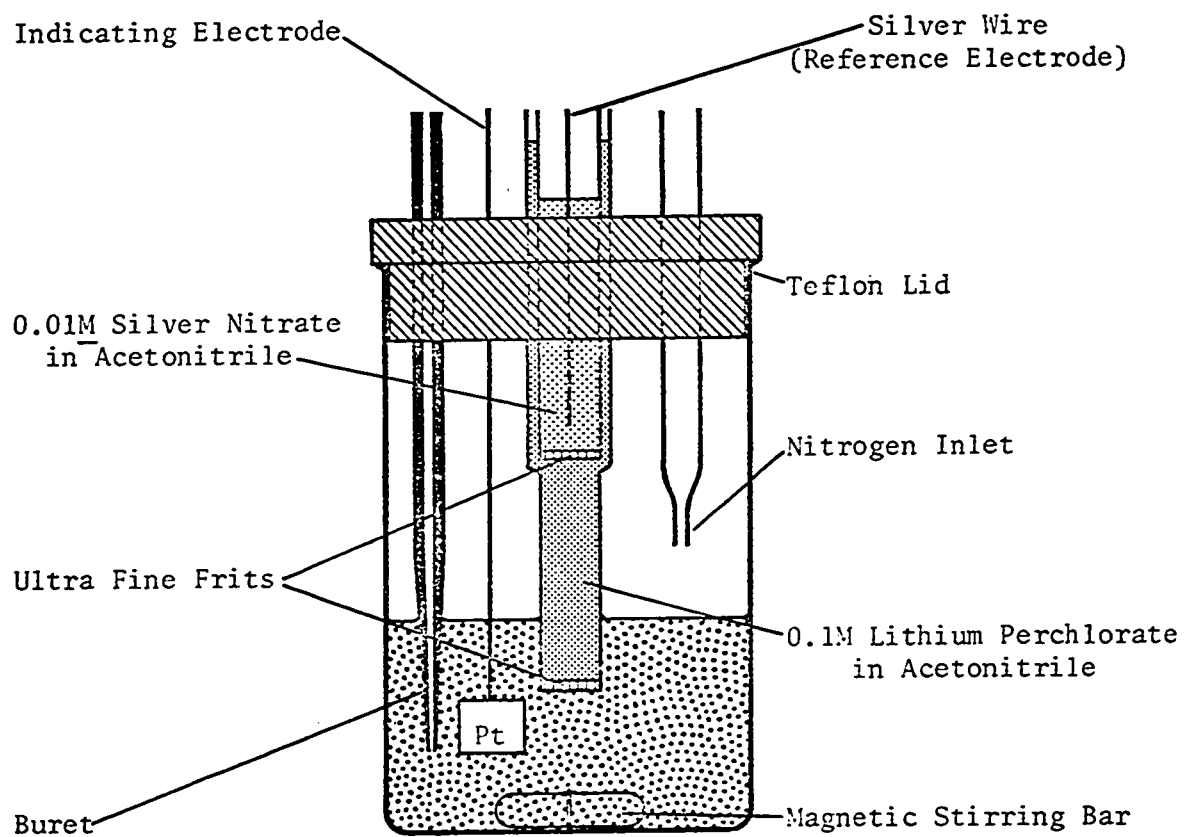
Figure III. Potentiometric Titration Cell

reproducibility of delivery of the titrant and recording of the volume delivered was determined by delivery of several samples of water. These samples were weighed and the calculated volumes compared to the recorded volumes. Delivery was found to be reproducible to ±0.01 ml for all volumes in the range of 5 to 20 ml; the amount of titrant delivered is determinable from the chart paper to ±0.01 ml. The three-way glass stopcock provided on the instrument leaked when acetonitrile was used as the solvent even after lubrication with silicone grease; it was therefore replaced with a Teflon stopcock. Volumes of titrant from 10 to 13 ml were used in typical titrations and were delivered at a constant rate of 1.7 ml per minute for the first part of the titration, with automatic slow-down of the delivery rate in the region of large change in potential (end point region). For part per thousand precision it was necessary to record the temperature of the solution and apply a correction to the volume of titrant used[50]. To protect material being titrated from oxidation by air while in solution, the samples were dissolved in acetonitrile that was deaerated with nitrogen (Linde, Union Carbide Canada Limited) and during the titration nitrogen was passed over the solution. This nitrogen was first bubbled through acetonitrile to prevent evaporation of the cell solution. It was found however, that nitrogen deaeration did not affect the results for any of the substances investigated

in the preliminary survey.

Determinations of the purity of commercial ferrocene from various sources were done as follows. A one-gram portion of the commercial material was mixed in a 20-ml weighing bottle to give a homogeneous sample. About 0.2-g (1.1 mmole) portions of this material were weighed into a cylindrical titration cell and dissolved immediately in 40 to 50 ml of technical grade acetonitrile. Since it was found that air oxidation did not occur to a significant extent, nitrogen purging was not necessary. The titration curve for the ferrocene-copper(II) reaction is symmetric and has a large potential change at the inflection point; therefore the end point was taken as that point of the curve equidistant from two parallel lines drawn tangent to the curve at the potential break region (Figure II).

Other material titrated in the preliminary survey was treated in the same way as the samples of ferrocene, except that preliminary mixing to ensure homogeneity of the bulk samples was omitted, and about 1.1 milliequivalent samples were weighed out such that the equivalence point occurred in the range of 10 to 13 ml of titrant. For samples of potassium iodide the equivalent weight depended on which equivalence point of potassium iodide (Figure I) was being examined.

For accurate work weight titrations of ferrocene with copper(II) in pure acetonitrile were performed in a 120-ml

titration cell similar to that shown in Figure III. However,
to allow access for titrant addition to the cell by syringe,
the Teflon lid was removed and the electrodes were held in
place by clamps. An Orion digital pH meter was used to measure
the potential. Samples of ferrocene (0.5 to 0.6 mmole) were
weighed to the nearest microgram into glass cups about 1.1 cm
in diameter and 1.5 cm deep. The cups were covered to minimize
loss of ferrocene through volatilization; as an added precaution
all samples were titrated within 30 minutes of weighing. The
cups were dropped into 40 to 50 ml of acetonitrile in the
titration cell and magnetic stirring was begun. Approximately
0.03 molal copper(II) perchlorate in acetonitrile was added by
means of a 30-ml hypodermic syringe with a glass capillary tip
attached by an air-tight Teflon sleeve. It was found necessary
to lubricate the syringe plunger with silicone grease after
every four or five titrations to prevent evaporation of titrant
and provide more positive operation. When a potential of 260
to 280 mV vs. the silver reference electrode was reached,
indicating that the titration was about 99.9% complete, an
approximately 0.003 molal copper(II) solution, prepared through
accurate dilution by weight of the stock solution, was delivered
from a 5-ml syringe, fitted with a standard stainless steel
needle, to complete the titration. The syringes were weighed on
an analytical balance before and after delivery of titrant and

were handled with thin cotton gloves during the titration.
Again lubrication of the syringe plunger with silicone grease
was necessary. After each titration of ferrocene a weighed
aliquot of the copper(II) in acetonitrile from the stock
solution, of approximately the same size (17 to 20 g) as
required in the titration of ferrocene, was weighed for
standardization. By alternately titrating ferrocene and taking
weighed aliquots of copper(II) for standardization, errors
caused by any systematic change such as evaporation of
acetonitrile in the stock solution could be minimized.

An expansion of potential vs. equivalent amount of
copper(II) at the potential break for the ferrocene-copper(II)
reaction (Figure IV-A) shows that the end point can easily be
determined by this method to within 0.1 part per thousand
relative. Although the expanded potential break (Figure IV-A)
was not perfectly symmetrical, the end point was determined by
a parallel lines method (Figure II) rather than by a first or
second derivative plot. To offset the unsymmetrical character
of the expanded potential break the point midway between two
points on the titration curve, as determined by the parallel
lines method for two sets of parallel lines two and six cm
apart, was taken as the end point. The difference between the
two points determined by the 2 and 6-cm parallel lines was
always less than 0.005% relative to the total copper(II) used
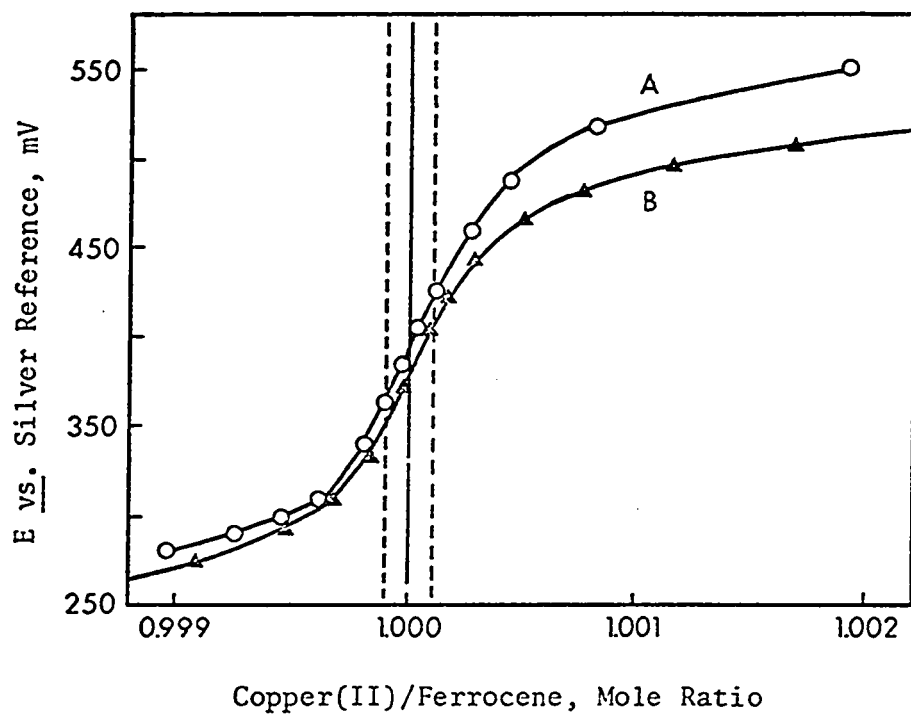
Figure IV. End Point Region of Potentiometric Weight

Titration of Ferrocene with Copper(II) Perchlorate:

(a) 0.2M Water Present; (b) 0.8M Water present. Dotted

lines indicate mole ratio values 0.9999 and 1.0001

in the titration. The differences in the end point volumes for end points determined by the parallel lines method and those determined by the derivative methods was found to be insignificant, so the parallel lines method was chosen for its greater convenience.

The copper(II) solution in acetonitrile was standardized by weight titrations with aqueous EDTA. Weighed aliquots of the solution were evaporated to near dryness before titration with EDTA. Later experiments omitting the evaporation step gave the same results so this step appears unnecessary. About 95% of the stoichiometric amount of approximately 0.03 molal aqueous EDTA was added by 30-ml syringe as described previously, the titration solution was diluted to about 550 ml with water, and the pH adjusted first to 2.0 with dilute nitric acid, then to 7.5±0.1 with dilute ammonia. The dilution minimized interference with the end point by the blue color of the copper(II)-ammonia complex. The two-step pH adjustment provided the needed buffer and adjusted the ionic strength to approximately the same level as for the standard copper(II) solutions. A final pH of 7.5 gives the most reproducible and easily determined end point with murexide[51]. About 0.2 g of diluted murexide indicator was added and the titration continued until the solution just started to change from green to blue-green, at which point the reaction was about 99.8% complete. Then aqueous EDTA, diluted tenfold by

weight from the stock solution, was added from a 5-ml syringe as previously described until the end point, a permanent blue color with no trace of green, was reached. The syringes were used as in the weight titration of ferrocene. The aqueous EDTA in turn was standardized in the same manner against weighed aliquots of standard aqueous copper(II) nitrate solution. Alternation was used in the weight titration of weighed aliquots of the standard aqueous copper(II) and copper(II) in acetonitrile solutions with aqueous EDTA. By using a white background, and through careful matching of end point colors on successive weight titrations, relative standard deviations of better than 0.5 parts per thousand were obtained routinely.

The purity of the copper wire used in preparation of the standard solution was determined by electrodeposition according to the standard ASTM method[52]. The electroanalysis was performed in a 300-ml lipless beaker, with a hollow cylinder of platinum gauze (135 cm^2 area) as the cathode and a platinum gauze (60 cm^2 area) cylindrical electrode as the anode. To eliminate possible errors due to inconsistency of the balance weights, the cathode electrode was weighed, then a 5-g sample of copper wire was added and both were weighed together. Current was supplied by a Model 6206B Hewlett-Packard DC Power Supply. After each run a check for complete deposition of copper from the solution was made by weight titration of the

solution with aqueous EDTA using murexide as indicator. The

aqueous EDTA was standardized against weighed aliquots of

standard aqueous copper(II) which had been treated in the same

way as the electrodeposition solution, that is, large amounts

of nitric and sulfuric acid were added to them. Alternation

was used as before. Though the end point color changes were not

sharp, they were adequate for the values required.

To investigate possible impurities in technical grade

acetonitrile some semiquantitative titrations were performed

on the automatic recording titrator. For these titrations 0.09$\underline{M}$

copper(II) in technical grade acetonitrile was used as titrant

and samples (0.5 to 0.6 mmole) of ferrocene, with possible

impurities added, were titrated in 50 ml of technical grade

acetonitrile. Since the weight titrations of ferrocene by

copper(II) in acetonitrile take about 20 minutes, the titrant

was added by the automatic recording titrator at only 0.4 ml per

minute to give the added materials time to react with the

copper(II).

Coulometric titrations were performed in a cell described

by R. Long[29] with one modification; the silver reference electrode

was separated from the 0.1$\underline{M}$ lithium perchlorate bridge solution

by an ultrafine glass frit rather than a porous Vycor glass plug.

Tetrakis(acetonitrile)copper(I) perchlorate was dissolved either

in pure or technical grade acetonitrile to give the desired

molarity. Before addition of the sample of ferrocene, the solution potential was usually adjusted to a predetermined value vs. the silver reference by coulometric generation of copper(II) (Leeds and Northrup Co., Catalog No. 7960); occasionally a small amount of ferrocene was added before potential adjustment to give a more poised system. The potential vs. the silver reference was measured on the Orion digital pH meter. Ten-milligram samples of ferrocene were weighed as described for the weight titrations, and similarly were titrated within 30 minutes of weighing. A current generation rate of 0.643 mA was used. The data were plotted, and end points determined by the method of parallel lines as described previously.

Polarographic studies were performed with a Leeds and Northrup Type E electro-chemograph using a Sargent synchronous rotator for the rotating platinum electrode (R.P.E.). The perchlorate salts of lithium, tetrabutylammonium and sodium were used as electrolytes at $0.1M$ concentrations. A silver wire in a solution of $0.1M$ silver nitrate in acetonitrile was employed as the counter and reference electrode; it was separated from the polarographic solution by ultrafine frits and a $0.1M$ lithium perchlorate bridge solution as shown for the silver reference electrode in Figure III. The solutions were deaerated with nitrogen before each run; during the runs nitrogen

was passed over the solution. The R.P.E. was cleaned with
nitric acid, followed by 0.1$\underline{M}$ iron(II) sulfate in 1$\underline{M}$ aqueous
sulfuric acid, and rinsed with pure acetonitrile before use.

The concentration of acrylonitrile in technical grade
acetonitrile was determined by the sodium bisulfite method[53].
Pure acetonitrile was used as a blank and pure acetonitrile
with acrylonitrile added was used as a standard.

The concentration of cyanide in technical grade
acetonitrile was determined by the procedure of Murthy and
Viswanathan[54]. In this procedure cyanide is oxidized by
bromine-water and the product in the presence of barbituric
acid gives a solution whose absorbance at 588 mμ is proportional
to the cyanide concentration. The pure acetonitrile blank
did not absorb to any significant extent at 588 mμ. Solutions
of pure acetonitrile with acrylonitrile added when treated
by this method were found to give an absorbance maximum at
588 mμ also; tests with silver nitrate showed that this
absorbance was not due to a cyanide contaminent in the
acrylonitrile. The absorbance produced by the acrylonitrile
impurity in technical grade acetonitrile is only about a third
of that produced by the cyanide impurity in this solvent. Cyanide
added to technical grade acetonitrile gives a lower absorbance
than the same concentration of cyanide in pure acetonitrile. A
volume of 25 ml of technical grade acetonitrile, technical grade
acetonitrile with potassium cyanide added, and pure
acetonitrile with acrylonitrile added were each diluted to 100 ml

with water. These solutions were stirred for several hours to ensure equilibrium. Variations in the acetonitrile to water ratio affected the results, larger amounts of acetonitrile lowering the absorbance significantly. Two 25-ml samples of each of the diluted solutions were analyzed. The relative precision of the absorbance measurements was on the order of 1 to 2%; absorbance readings were stable for at least 20 minutes.

The carbon-hydrogen analysis (Coleman Carbon-Hydrogen Analyzer) of the synthesized hydrated copper(II) perchlorate salt, mass spectroscopy (Metropolitan Vickers MS2) of samples of ferrocene and heptane, and the mass, infrared (Perkins Elmer 421) and neutron magnetic resonance (Varian A-60) spectroscopy of samples of acetonitrile were done by the services groups at the University of Alberta. Visible and ultraviolet spectra were recorded on a Unicam SP 800 B visible-ultraviolet spectrophotometer in 1-cm quartz cells.

Since ferrocene sublimes readily it was not possible to obtain a melting point in an open capillary tube or between cover glasses on a heated block melting-point apparatus. The melting point of pure ferrocene was determined therefore from DTA curves recorded on a DuPont Model 900 Differential Thermal Analyzer using U.S.P. Melting Point Reference Standards sulfapyridine (m.p. 191-3°C) and sulfanilamide (m.p. 164.5-165.5°C). The samples were measured using glass beads as the reference, a temperature rate of increase of 15C° per minute, and a

sensitivity of 0.5C° per inch in the recorder. Endothermic changes at the melting points were very sharp for the ferrocene samples and slightly more drawn out for the two standards.

Results and Discussion

Weight titrations. Preliminary titrations of ferrocene
with copper(II) in acetonitrile were performed on the Metrohm
automatic recording titrator. The end points can be selected
to no better than about a part per thousand with this instrument,
however, and measurements of volume are subject to the large
temperature coefficient of expansion of acetonitrile. Therefore,
weight titrations were used to obtain more precise results.
Increased precision was also obtained by using a solution of the
titrant diluted tenfold by weight in the region of the potential
break. The reaction between ferrocene and copper(II) in
acetonitrile is rapid, and potential drift during titrations
is negligible. However, potentials take 15 to 30 seconds to
stabilize through the equivalence point region, 375 to 475 mV
vs. the silver reference.

The copper(II) in acetonitrile titrant was standardized
against aqueous EDTA by weight titration. This method was
chosen despite the fact that routine standardizations of
copper(II) with aqueous EDTA solutions were considered
undesirable because the standardization is a complexing reaction
in water instead of electron-transfer reaction in acetonitrile.
In using this procedure the assumption was made that solutions
of copper(II) in pure acetonitrile react with the same

stoichiometry in titrations of ferrocene as in aqueous

titrations with EDTA. The aqueous EDTA solutions were in turn

standardized by weight titrations of weighed aliquots of

standard aqueous copper(II) nitrate solutions prepared from

analyzed copper wire. The purity of the copper wire was found

to be 99.957±0.005% (Table III). Buoyancy corrections were

made for all weighings (Appendix B). The results of three sets

of titrations show that weight titrations of pure ferrocene

(recrystallized twice, then sublimed) with copper(II) agree

within 0.3 part per thousand relative with the standardization

of copper(II) by weight titration with aqueous EDTA (Table IV).

Therefore, the assumption that copper(II) in acetonitrile has

the same stoichiometry in titrations with ferrocene in pure

acetonitrile and with EDTA in water appears valid.

Samples of ferrocene dissolved in acetonitrile show no

evidence of air oxidation at the 0.1 part per thousand relative

level after stirring in air for 30 minutes, so protection of the

solutions from air before or during the titration is unnecessary.

Copper(II) solutions prepared from hydrated copper(II)

perchlorate synthesized in the laboratory gave slightly more drawn

out titration curves for ferrocene than solutions prepared from

commercial hydrated copper(II) perchlorate. An analysis of the

commercial material for perchlorate[47a] showed that it contained

about 2.7 moles of perchlorate per mole of copper(II). It was

Table III. Analysis of Copper Wire used for

Standardization of EDTA Solutions

Weight of Wire Taken, g	Weight of Copper Deposited Electrolytically, g	Weight of Copper Remaining in Electrolyte, Determined by Titration with EDTA, mg	Purity, %
5.0043	5.0013	1.1	99.962
5.0038	5.0007	0.8	99.954
5.0020	4.9995	0.2	99.954
		Av.	99.957
		Rel. Std. Dev. in p.p.t.	0.05

Table IV. Concentration of Copper(II) in Acetonitrile as

Determined with Ferrocene and EDTA[a]

	[EDTA][b]	Copper(II) Concentration	
		by Ferrocene	By EDTA
Set I	0.031026	0.028745	0.028780
	0.031027	0.028755	0.028762
	0.031025	0.028766	0.028751
			0.028746
Av.	0.031026	0.028755	0.028760
Rel. Std. Dev., p.p.t.	0.03	0.4	0.5
Set II	0.030047	0.028781	0.028755
	0.030051	0.028781	0.028782
	0.030052	0.028789	0.028778
	0.030047	0.028785	0.028804
	0.030050	0.028776	0.028784
		0.028766	0.028727
Av.	0.030049	0.028780	0.028788
Rel. Std. Dev., p.p.t.	0.08	0.3	0.8
Set III	0.030056	0.028111	0.028117
	0.030060	0.028118	0.028140
	0.030058	0.028125	0.028120
	0.030051	0.028125	0.028125
Av.	0.030056	0.028120	0.028125
Rel. Std. Dev., p.p.t.	0.13	0.2	0.4

[a]All concentrations expressed in units of millimoles of substance per g of solution.

[b]EDTA concentration determined by weight titration of standard aqueous copper(II) solutions.

assumed that the excess 0.7 moles of perchlorate per mole of

copper(II) was present as perchloric acid, which would decrease

hydrolysis of the copper(II) in acetonitrile solution and

thereby sharpen the potential break in the copper(II)-ferrocene

titration. The addition of 1 ml of 72% perchloric acid per

liter of 0.03 molal copper(II) titrant prepared from laboratory

synthesized copper(II) perchlorate improved the sharpness of

the potential breaks, but affected the stability of the potential

near the end point by making the ferricenium ion susceptible to

further oxidation. Qualitative spectrophotometric measurements

on solutions of ferricenium ion in pure acetonitrile indicated

that ferricenium ion decomposes slowly to ferrocene and other

products that were not identified; the addition of water stopped

this decomposition. Also, added water lowered the $E^{\circ'}$ of the

ferrocene-ferricenium couple in acetonitrile. Thus water

appears to interact with ferricenium ion. A combination of

$0.01\underline{M}$ perchloric acid in the titrant plus $0.2\underline{M}$ water in the

solution being titrated gave sharp potential breaks and stable

potentials, and was used in all ferrocene-copper(II) weight

titrations where pure acetonitrile was employed as the solvent.

Technical grade acetonitrile contains sufficient water to stabilize

the ferricenium ion. Higher concentrations of water in the

copper(II) ferrocene titration gave smaller and more drawn out

potential breaks, but did not affect the copper(II)-ferrocene

stoichiometry (Figure IV-B). Since the above combination of acid and water gave satisfactory results, no further study was carried out of the effects of varying concentrations of water and perchloric acid on the copper(II)-ferrocene titration.

Points to consider in using ferrocene as a primary standard for copper(II) in pure acetonitrile under conventional conditions are: (1) the temperature coefficient of expansion for acetonitrile affects volumetric measurements, the relative volume change being about 1.4 parts per thousand per degree C at 25°C; (2) the high vapor pressure of acetonitrile increases the concentration of copper(II) solutions through solvent volatilization and (3) the volatility of ferrocene itself is such that a loss of about one part per thousand occurs in six to seven hours in an open container. None of these points constitutes a serious disadvantage at the part per thousand level if adequate precautions are taken.

<u>Purification procedures for ferrocene</u>. Commercial ferrocene was purified by recrystallization and sublimation. It was found that concentrations of copper(II) obtained by weight titrations with copper(II) in pure acetonitrile of commercial ferrocene recrystallized twice, then sublimed (pure ferrocene), differed negligibly from values obtained by weight titrations with aqueous EDTA (Table IV). The purity of samples of ferrocene, obtained by various combinations of

recrystallization and sublimation, based on weight titrations in acetonitrile by copper(II) which was standardized against aqueous EDTA, is shown in Table V.

The results suggested that the recrystallized material might contain some heptane solvent that is eliminated upon sublimation. Mass spectroscopic measurements on pure ferrocene, twice-recrystallized ferrocene, heptane, and commercial ferrocene did not, however, provide conclusive evidence for the presence of heptane in the recrystallized material.

It was also considered that sublimation alone did not yield a pure product because commercial ferrocene might contain an impurity that would sublime along with ferrocene, but would be removed by recrystallization. Comparison of mass spectra of sublimed and commercial ferrocene indicated that methylferrocene was present in commercial ferrocene to the extent of about a per cent, but was not present in the sublimed material. Methylferrocene could not be detected by mass spectroscopy in twice-recrystallized or pure ferrocene.

When commercial ferrocene was dissolved in heptane, insoluble, paramagnetic black particles were found clinging to the magnetic stirring bar. Since ferrocene is diamagnetic, commercial ferrocene contains in addition to methylferrocene a small amount of paramagnetic iron-containing impurity. Further identification of the impurities was not attempted.

Table V. Comparison of Procedures for

Purification of Ferrocene

Procedure	Purity Found By Copper(II)[a] Titration,%	Number of Titrations	Relative Standard Deviation, p.p.t.
As received	99.37	3	0.3
1 Recrystallization[b]	99.56	3	0.2
1 Recrystallization	99.82	3	0.5
2 Recrystallizations	99.89	4	0.1
3 Recrystallizations	99.91	3	0.2
1 Sublimation	99.91	3	0.2
2 Sublimations	99.93	2	0.0
1 Recrystallization and 1 sublimation	99.99	2	0.2
2 Recrystallizations and 1 sublimation	100.02	13	0.3
2 Recrystallizations and 2 sublimations	100.02	4	0.3

[a]Concentration determined by titration with aqueous EDTA. [b]From technical grade acetonitrile; remainder from heptane.

Stability and hygroscopicity. Commercial ferrocene
recrystallized twice from heptane was divided into three portions.
Samples of the first portion were titrated by weight with
copper(II) in acetonitrile. The second portion was stored in
a brown bottle at room temperature and the third portion was
stored at room temperature in an open container in a desiccator
containing a saturated aqueous solution of sodium sulfate[55].
The relative humidity in the desiccator ranged from 91 to 93%
as measured by a Taylor Humidiguide hygrometer. After six
months, samples of the second and third portions were titrated
by weight with copper(II) in acetonitrile. Twice-recrystallized,
sublimed ferrocene was used to standardize the copper(II) titrant
in each case. Each portion was titrated three or more times and
had a relative standard deviation of less than 0.3 parts per
thousand. The results for the three portions agreed within
0.2 parts per thousand. On the basis of these results ferrocene
appears to be nonhygroscopic and stable on storage at room
temperature in humidities up to at least 90%. It appears also
to be stable on long term exposure to typical laboratory
illumination.

Technical grade acetonitrile as solvent for ferrocene
titrations with copper(II). To assess the effects of impurities
present in technical grade acetonitrile on the stoichiometry of
the copper(II)-ferrocene reaction, two different shipments of

acetonitrile were used as received to prepare the copper(II) titrant and to dissolve samples of pure ferrocene for titration. In one case the concentration of copper(II) as determined by several weight titrations of pure ferrocene was five parts per thousand, and in the other, three parts per thousand, lower than that found by weight titrations with EDTA.

It was first thought that impurities in the 50-ml volume of acetonitrile used to dissolve the samples of ferrocene in the potentiometric weight titration caused the difference in the concentrations of copper(II), since this volume of acetonitrile is not used in the titration by aqueous EDTA. However, the addition of technical grade acetonitrile in amounts ranging from 25 to 100 ml to the weighed aliquots of copper(II) titrant taken for the weight titrations with EDTA did not affect the results.

Two other modes of interference were considered. The first was that an impurity in the technical grade solvent was oxidized by copper(II), so that additional copper(II) titrant was required in the titration of ferrocene. For this error to appear, the copper(I) formed by oxidation of the impurity would have to be quantitatively complexed by EDTA under the conditions used. That the titration of copper(I) by EDTA is quantitative was confirmed by titrations of tetrakis(acetonitrile)copper(I) perchlorate that had been dissolved in acetonitrile and treated

by the same procedure as the copper(II) in acetonitrile aliquot taken for the titration by EDTA.

Copper(I) has an absorptivity of about 1.9×10^4 liter/mole-cm at 206 mμ. Therefore ultraviolet spectrophotometry was considered as a way to detect copper(I) in technical grade acetonitrile to which copper(II) had been added. However, impurities in the technical grade acetonitrile absorb so strongly in the 205 to 220 mμ region that this method is not applicable.

The second mode of interference considered was that an impurity in the technical grade solvent complexed a portion of the copper(II) and prevented oxidation of ferrocene by this portion. In this case also, additional copper(II) titrant would be required to titrate the ferrocene. A complexing impurity of this kind would have to have a formation constant in water of a magnitude that would allow murexide and EDTA to displace it from copper(II) in order to not interfere with the titration of copper(II) by aqueous EDTA.

For either of the above described interferences, the impurity would interfere to only a slight extent. Its concentration in technical grade acetonitrile, assuming complete 1:1 interaction with copper(II), would be only about 2 to $3 \times 10^{-5}\underline{M}$. Pure and technical grade acetonitrile were examined by mass, ultraviolet, visible, infrared, and nuclear magnetic

resonance spectroscopy in a search for an impurity that could be responsible for the titration discrepancy. The only difference between pure and technical grade acetonitrile detected by the above analytical procedures was in the ultraviolet spectra, where an absorbance of 2.0 in the 205 to 220 mμ region was found for technical grade acetonitrile vs. an absorbance of less than 0.1 for the pure solvent in the same range.

The impurities reported to be present in technical grade acetonitrile are acrylonitrile, acetic acid, acetamide, ammonia, and ammonium acetate[20]. Technical grade acetonitrile on dilution with pure acetonitrile gives an ultraviolet spectrum similar to that observed when acrylonitrile is added to pure acetonitrile. The molar absorbtivity of acrylonitrile in acetonitrile could not be determined because the absorption peak fell near the instrument cut-off and did not obey Beer's law. Beer's law also was not obeyed in this wavelength region when technical grade acetonitrile was diluted with pure solvent. Assuming the absorbance between 205 and 220 mμ for technical grade acetonitrile to be due only to acrylonitrile, the estimated concentration present in technical grade acetonitrile is about 0.01 to 0.02$\underline{M}$. A more accurate value for the concentration of acrylonitrile in technical grade acetonitrile was obtained by the sodium bisulfite method[53]. A concentration of 0.007±0.002$\underline{M}$ was found. This is in general agreement with the spectrophotometric estimate. Therefore, the ultraviolet absorbing impurity in

technical grade acetonitrile appears to be predominately

acrylonitrile. Weight titrations of ferrocene with copper(II)

in pure acetonitrile were not affected by

0.2$\underline{M}$ acrylonitrile in the titration solution at the end point,

so acrylonitrile is not the impurity affecting the copper(II)

stoichiometry.

To check the effect of the other possible interferences,

quantities of each were added separately to portions of

technical grade acetonitrile, and these solutions used to

dissolve samples of pure ferrocene in a series of titrations

with copper(II) on the automatic recording titrator (Table VI).

Pure ferrocene dissolved in untreated technical grade

acetonitrile was used to standardize the titrant. To compare

the results with weight titrations in technical grade

acetonitrile, 0.1 g samples of ferrocene were used. This

resulted in an error in end point selection of two to four parts

per thousand because of the small volume of titrant required;

however, this was considered acceptable for survey work. The

results show that acetamide and acetic acid do not affect the

copper(II)-ferrocene titration at concentrations of 0.07$\underline{M}$. This

level is much larger than that expected in technical grade

acetonitrile for either acetamide or acetic acid[20]. Ammonia

and ammonium acetate affect the copper(II)-ferrocene titration

appreciably at 0.013 and 0.031$\underline{M}$ levels, respectively, but

TABLE VI. Effect of Possible Interfering Substances on the

Titration of Ferrocene with Copper(II) in

Technical Grade Acetonitrile

Added Substance	Concentration at End Point, mM	Relative Titration Error, p.p.t.
Acetamide	68	0
Acetic acid	15	0
Acetic acid	73	0
Ammonia	0.8	0
Ammonia	1.0	0
Ammonia	13	370
Ammonium acetate	0.9	0
Ammonium acetate	1.7	0
Ammonium acetate	31	1500
Ammonium perchlorate	15	0
Lithium acetate	1.0	0
Lithium acetate	1.4	5
Lithium acetate	19	450
Potassium cyanide	1.2	13
Potassium cyanide	2.3	37

apparently not at about 0.001M. Titrations with ammonium

perchlorate present show that ammonium ion does not affect the

titration at 0.15M, while a titration in the presence of 0.019M

lithium acetate shows that acetate ion will affect the titration

at this concentration but not greatly at 0.001M These results

show that ammonium acetate might affect the titration as ammonia

or acetate ion at relatively high concentrations, but not as

ammonium ion or acetic acid.

The procedure used for the synthesis of technical grade

acetonitrile is not given by Matheson, Coleman, and Bell. One

source of acetonitrile is as a by-product of acrylonitrile

synthesis[20]. In the production of acrylonitrile from propylene,

ammonia, and oxygen, the principle by-products are hydrogen

cyanide and acetonitrile[56]. The product by this synthesis

contains acrylonitrile, acetonitrile, and hydrogen cyanide in

the proportion 7.3:1.1:1.3, respectively. Therefore, although

hydrogen cyanide generally has not been reported as an impurity

in technical grade acetonitrile, its presence is possible, and

accordingly the effect of added cyanide on the ferrocene-

copper(II) titration was assessed. Cyanide, added to acetonitrile

as potassium cyanide rather than as hydrogen cyanide (for safety

and convenience), interfered in the copper(II)-ferrocene

titration at levels of 0.001 to 0.002M (Table VI).

More precise data on the extent of interference by ammonia,

ammonium acetate, and cyanide were obtained by weight titrations

of ferrocene with copper(II) in pure acetonitrile. The conditions

employed were the same as previously described. In alternate

titrations one of the contaminants was added to the titration solution;

intervening titrations were used to standardize the copper(II)

titrant. No effect on the copper(II)-ferrocene titration was

seen at concentrations of 0.001$\underline{M}$ for ammonia and 0.0015$\underline{M}$ for

ammonium acetate. However, at concentrations of 0.012$\underline{M}$ for

ammonia and 0.010$\underline{M}$ for ammonium acetate, a relative titration

error of about 400 and 800 parts per thousand was introduced

and the potential in both titrations showed considerable

downward drift. Near the end point, addition of approximately

one-half ml portions of 0.03 molal titrant caused the potential

to first rise to over 500 mV $\underline{vs}$. the silver reference, then

fall to below 300 mV during the next few minutes. The potential

became stable after about 5 minutes. Because the determination

of the exact end point by dropwise titrant addition was too

time consuming, the end point was estimated in the following

way. Titrant was added until a stable potential past the

end-point potential in a normal weight titration (Figure IVA)

was obtained. An estimate of the difference between this value

and the end point potential was made by comparison with the potential

curve of a normal weight titration. The relative error in

end point selection by this method was estimated to be no greater

than 0.2%. At the end of the titration in which 0.012M ammonia

had been added, the solution was dark brownish green in color;

for the titration at 0.010M ammonium acetate the solution was

dark green. Neither solution contained a precipitate.

Weight titrations of ferrocene with copper(II) in

acetonitrile in the presence of potassium cyanide at 2.4 and

1.3 x 10^{-4}M also displayed a downward potential drift, but not

nearly as much as was the case with 0.012M ammonia and 0.010M

ammonium acetate. Titrant was again added until a steady

potential past the normal end-point potential (Figure IVA) was

obtained and the end point was estimated as before. However,

in these cases the relative error in end point selection was

only about 0.02% at most because the final potential was much

lower than in the previous titrations. The relative titration

error in the presence of 2.4 x 10^{-4}M potassium cyanide was 8

parts per thousand, and of 1.3 x 10^{-4}M, 2 parts per thousand.

The solutions at the end of the titrations were both dark blue

(the normal ferricenium color).

By polarography it was determined that technical grade

acetonitrile contains less than 5 x 10^{-4}M ammonia and less than

0.010M acetic acid. Attempts to obtain polarographic waves for

0.001M ammonium acetate, in a supporting electrolyte of 0.1M

lithium perchlorate were unsuccessful because of formation of

a precipitate, apparently lithium acetate. Previous work

(Table VI) showed litnium acetate to be quite insoluble in acetonitrile. However, the addition of 0.1$\underline{M}$ lithium perchlorate to technical grade acetonitrile does not give a precipitate, indicating from solubility product consideration that the ammonium acetate concentration must be below $10^{-3}\underline{M}$. Using the method of Murthy and Viswanathan[54] cyanide was found to be about 1 x $10^{-4}\underline{M}$ in one batch of technical grade acetonitrile.

When ammonia, ammonium acetate and potassium cyanide were added in quantities sufficient to affect the weight titration of ferrocene by copper(II), considerable drift was observed in the end point region. In all three cases it appears that the copper(II) reacts quickly with the small amount of ferrocene present near the end point, followed by a slow reaction of the remaining copper(II) with the added species. This might have occurred in the titrations in which smaller amounts of ammonia or ammonium acetate (on the order of $10^{-3}\underline{M}$) were present if additional time to establish equilibrium had been allowed. However weight titrations performed in technical grade acetonitrile came to equilibrium near the end point as rapidly as did those in pure acetonitrile. In titrations of ferrocene in the presence of cyanide, potential drift near the end point may be caused by a slow reaction between copper(II) and cyanide ion, due primarily to a probable high degree of association for potassium cyanide in acetonitrile.

To see whether cyanide interferes in the titration of copper(II) with EDTA, potassium cyanide was added to weighed aliquots of copper(II) in acetonitrile and weight titrations of the mixtures with aqueous EDTA were performed in the normal way. At cyanide concentrations of 0.0001, 0.0005, and 0.001$\underline{M}$ in the weighed aliquots the results obtained were not significantly different from those without added potassium cyanide. Thus cyanide was shown to be the interference in technical grade acetonitrile, for it affects the stoichiometry of the copper(II)-ferrocene reaction, but not that of the copper(II)-EDTA reaction at the concentration of cyanide found in technical grade acetonitrile.

Another approach toward the determination of the nature of the interference is to study the interaction between copper(II) and possible interfering ions by other techniques, such as polarography or ultraviolet spectroscopy. A knowledge of the formation constants for the association of these species would enable prediction of the extent of interference. Acetonitrile purified by the procedure of O'Donnell, Ayers, and Mann is reported not to be oxidized or reduced between +2.0 and -3.0V $\underline{vs}$. the silver reference [12]. However, polarograms of pure acetonitrile in this work showed anodic waves in the region of 0.8V $\underline{vs}$. the silver-0.1$\underline{M}$ silver nitrate reference electrode; this is in the potential region for the copper(II)-(I)

reduction wave. It appears that the electrolytes used, lithium, sodium, and tetrabutylammonium perchlorate, all contained impurities that were not eliminated by recrystallization from water. No further polarographic work was attempted.

Ultraviolet spectroscopy was also investigated as a tool for studying complexes of copper(II) and (I) in acetonitrile. Both species absorb strongly at 205 to 210 mμ. The molar absorptivity for copper(II) in pure acetonitrile is 1.44×10^3 liter/mole-cm at 208 mμ; upon addition of water the wavelength of maximum absorbance shifts to lower wavelength readings and is accompanied by a slight increase in the molar absorptivity. The absorptivity of copper(II) in water is 1.66×10^3 liter/mole-cm at 196 mμ. The concentration of water present in pure acetonitrile as obtained by most reported procedures is usually stated as being less than 0.001$\underline{M}$. At the millimolar level water may affect the absorption spectrum of copper(II), since it would be present at a concentration near that of the copper(II). Therefore, to do quantitative work on the complexes of copper(II) in acetonitrile, the formation constants for copper(II) with water in acetonitrile would have to be determined and the concentration of water in pure solvent known. In addition it would be necessary to know the dissociation constants for the salts of the added ions. Most cyanide, acetate, and ammonium salts would be expected to have appreciable

association.

Qualitatively it was found that ammonia and acetamide both react with copper(II) in acetonitrile to give ultraviolet absorbing complexes. Ammonia forms several complexes, apparently with large formation constants, that absorb in the region of 200 to 250 mμ, and which have molar absorptivities of about 2000 liter/mole-cm. Acetamide forms a very weak complex with copper(II) that has a molar absorptivity of about 4000 liter/mole-cm at 270 mμ. Apparently one or more higher order complexes form also, but slowly. Acetic acid showed no indication of complex formation. Cyanide ion forms a complex whose wavelength of maximum absorbance is slightly longer than that of copper(II) alone in pure acetonitrile; the molar absorptivity is similar.

Copper(I) in acetonitrile shows spectrally no noticable interaction with water, as expected. The ultraviolet spectra for copper(I) with acetic acid, ammonia, and acetamide did not indicate formation of complexes. No other species were investigated with copper(I).

For comparison, the formation constants reported in the literature for copper(II) and (I) in water are [57]: ammonia, copper(I) β_2 = 8.7 to 11.2; copper(II) β_4 = 9.3 to 15.74; cyanide ion, copper(I) β_4 = 27 to 28; copper(II) β_4 = 25; and acetic acid, copper(II) β_2 = 2 to 3. In nitromethane, water as a ligand has for copper(II) β_5 = 7.5. These values indicate that

cyanide is a much stronger complexing reagent for copper(I) and (II) than the other species.

In conclusion, this work shows that ammonia, ammonium acetate, acetic acid, acrylonitrile, and acetamide, the impurities reported present in technical grade acetonitrile, are not responsible for the relative titration error of several parts per thousand in the ferrocene-copper(II) reaction in technical grade acetonitrile. Spectral evidence indicates that cyanide forms a complex with copper(II) in acetonitrile. Cyanide has been found to be present in technical grade acetonitrile at a concentration of about $1 \times 10^{-4}\underline{M}$. The addition of potassium cyanide to give a concentration of $10^{-4}\underline{M}$ at the end point results in a relative titration error of about 2 parts per thousand in the ferrocene-copper(II) reaction. Therefore, the interference in this reaction in technical grade acetonitrile appears to be cyanide ion, most likely present as hydrogen cyanide.

Other methods of analysis for ferrocene. Other methods of analysis for ferrocene were reviewed in a search for an alternate method of checking its purity. Ferrocene and its derivatives have been analyzed primarily by either (a) destruction of the organic portion followed by iron determination[58-62] or (b) by direct titration with an oxidizing agent in a nonaqueous solvent[63-65].

None of the destruction methods reported relative standard

deviations of better than two parts per thousand. The general procedure was investigated therefore to determine whether higher precision could be obtained. The method of Renger and Jenik[62], which used bromine-water to destory the organic portion of ferrocene followed by an EDTA titration of the iron with salicylic acid as the indictor, gave the best reported results and consequently was studied further. When the recommended sample size of 2 to 4 mg of ferrocene was used, the weight of sample is known to only about 0.4 parts per thousand, and therefore, precision better than this level cannot be attained. A sample size of 20-25 mg however, with proportional increases in the other reagents, yields a solution volume so large that selection of the end point becomes uncertain. Also, with larger samples complete destruction of the organic portion of ferrocene becomes more difficult, and an early end point is obtained. Best results were obtained with photometric titrations using 2 to 4 mg samples and a Bausch and Lomb Spectronic 20 Spectrophotometer to detect the end point[66]. The end points were still several parts per thousand early, however, and had relative standard deviations of several parts per thousand, apparently because of incomplete destruction of the organic portion of ferrocene. This method, therefore, does not appear to be satisfactory for the analysis of ferrocene at a precision of better than a part per thousand. Because the direct titration

methods using oxidizing reagents were reported to have standard deviations of no better than two parts per thousand and did not seem to be an improvement on the copper(II) perchlorate in acetonitrile system, these methods were not investigated.

Constant current coulometric titrations of ferrocene also were performed in acetonitrile. Copper(II) was generated from copper(I) perchlorate at a platinum gauze electrode. In pure acetonitrile the potential in the end point region dropped when current generation was stopped; the addition of five to ten drops of water per 30 ml of solution stabilized the potentials. In technical grade acetonitrile the addition of water was not necessary. Most of the coulometric work was done in pure acetonitrile with water added since technical grade acetonitrile had been shown to introduce an error in the weight titrations of ferrocene by copper(II). Potential breaks were drawn out at 0.1$\underline{M}$ copper(I) perchlorate concentrations, and the current efficiency appeared to be less than 100% at 0.01$\underline{M}$ concentrations of copper(I). The best values were obtained at copper(I) concentrations of about 0.05$\underline{M}$; however, the break was not sharp enough for selection of an end point with better than part per thousand precision, and the end points varied randomly over a range of 5 to 10 parts per thousand. These results indicate that potentiometric end point detection in coulometric titrations with this cell are not precise enough for primary standard work.

CHAPTER III   DETERMINATION OF FERROCENE DERIVATIVES BY OXIDATION

WITH COPPER(II) IN TECHNICAL GRADE ACETONITRILE

Background

Analytical methods for determining derivatives of
ferrocene have generally followed one of the two paths previously
outlined for ferrocene: destruction of the organic portion
followed by determination of the iron present[58-62], or direct
oxidation of the ferrocene moiety in a nonaqueous solvent,
usually acetic acid, with one of several oxidizing agents[63-65].
The solubility of ferrocene in water is too low, about $2 \times 10^{-5} \underline{M}$[67],
to make it a useful solvent. The first procedure is slow and
gives erroneous results if iron-containing impurities are
present. The second type involves one of several generally
unstable titrants; the most useful of these appears to be
potassium dichromate in a 3:1 mixture of acetic acid and water[65].
Although this titrant was able to oxidize ferrocene and alkyl-
substituted ferrocenes, derivatives having a carbonyl group
attached to one of the cyclopentadienyl rings were not directly
titratable and had to be reduced to the corresponding alkyl
derivatives with lithium aluminum hydride and aluminum chloride
before titration. Also, both types of procedures report relative
precision no better than two to three parts per thousand.

This chapter shows ferrocene to be a suitable standard for solutions of copper(II) perchlorate in technical grade acetonitrile at the part per thousand relative level, and reports the use of this titrant for the determination of several alkyl and acyl derivatives of ferrocene. Formal reduction potentials for these derivatives were measured and compared with values obtained chronopotentiometrically by other workers. The derivatives are shown to be reversibly oxidized.

Experimental

Reagents. Technical grade acetonitrile (Matheson,
Coleman, and Bell) was either used as received or purified by
the modified method of O'Donnell, Ayers, and Mann[12] described
in Chapter II.

The hydrated copper(II) perchlorate salt was synthesized
as previously described and potassium iodide was prepared as
before. Deionized water was used throughout. Ferrocenecarboxylic
acid, 1,1'-diacetylferrocene, and 1,1'-ferrocenedicarboxylic
acid were obtained from Aldrich Chemical Co.; acetylferrocene
(white label) from Eastman Organic Chemicals; benzoylferrocene,
dibenzoylferrocene, n-butylferrocene, and ferrocenealdehyde
from Alfa Inorganics; and the n-butyryl-, amyl-,
dimethylaminomethyl-, t-butyl-, n-butyl-, dimethyl-, and
di-n-butyl- derivatives of ferrocene from Arapahoe Chemicals.
All the derivatives of ferrocene were used as received.

Ferrocene (Arapahoe Chemicals) was recrystallized twice
from heptane and sublimed once as previously described.

Solutions. Approximately $0.09\underline{M}$ solutions of hydrated
copper(II) perchlorate were prepared by dissolving portions of
the salt in either technical grade or pure acetonitrile and
adding 2 ml of 70% perchloric acid as described

before. The solutions were stored and used as previously described.

Approximately 0.1$\underline{M}$ solutions of ferrocene in technical grade acetonitrile were stored under an atmosphere of nitrogen and used within two days.

Procedures for titrations. Titrations were performed with the same cell arrangement as in Figure III on the automatic recording titrator. Titrant volumes of 10 to 13 ml were delivered at a constant rate of 1.7 ml per minute (slower through the end-point region) for potassium iodide and for all the ferrocene derivatives except ferrocenecarboxylic acid. As ferrocenecarboxylic acid is only slightly soluble in acetonitrile, small samples were titrated at a rate of 0.1 ml per minute to provide sufficient time for reaction. Again the titrant temperature was recorded to take into account the coefficient of expansion of acetonitrile[50].

About 1-milliequivalent samples (except for ferrocenecarboxylic acid and dimethylaminoferrocene) were weighed into a titration cell and dissolved in 40 to 50 ml of deaerated acetonitrile. Because of the low solubility of ferrocenecarboxylic acid 0.2 to 0.4-milliquivalent samples were used, while in the case of dimethylaminomethylferrocene about 0.2 g was taken per titration, the number of milliequivalents not being determinable

from the titration results. When pure acetonitrile was used as the solvent, 0.2 ml of water was added to the sample solution. Air oxidation was minimized by starting the titrations immediately upon dissolution of the samples in deaerated solvent, and by passing nitrogen over the surface of the solutions during the titrations.

It is shown in Appendix A that the first equivalence point for potassium iodide is concentration dependent. The same size of sample and amount of solvent were used in all titrations of this reagent and the end point was chosen by the parallel line method. This method of end point selection satisfactorily shows the consistency of copper(II) oxidation of potassium iodide, although it does not give the true equivalence point for the first inflection. Since the derivatives of ferrocene oxidized by copper(II) undergo one-electron reactions, their end points were determined by the parallel line method also. An exception to the one-electron oxidation was dimethylaminomethylferrocene, for which two inflections at uninterpreted ratios were obtained; the end points for this species were also determined by the parallel lines method.

In some cases an excess of copper(II) perchlorate was added and the excess titrated with a solution of ferrocene in acetonitrile. These titrations were performed in 300-ml beakers using the electrode arrangement shown in Figure III and

an Orion digital pH meter to record the potential. The
derivatives investigated were weighed (0.3 to 0.5 mmole) and
excess 0.09$\underline{M}$ copper(II) in technical grade acetonitrile was
added by means of the syringe buret of the automatic recording
titrator. The solutions were stirred under an atmosphere of
nitrogen for various lengths of time, then back titrated with a
solution of ferrocene in a calibrated 50-ml buret. No
precautions were taken against air oxidation during the
titration. Potential breaks were not sharp in most cases;
however, end points were easily determinable with a relative
accuracy of a few per cent. The solution of ferrocene was
standardized by titration of a standard solution of copper(II)
immediately before use.

Visible spectra was recorded on a Unicam SP800 B visible-
ultraviolet spectrophotometer.

Results and Discussion

Ferrocene as a standard for titrations in technical grade acetonitrile.

Ferrocene recrystallized twice, then sublimed, is shown in Chapter II to be a suitable primary standard for solutions of copper(II) perchlorate in pure acetonitrile. The purification of acetonitrile takes several days and therefore use of this material is inconvenient in routine work. When technical grade acetonitrile was used as the solvent, however, the titer values of solutions of copper(II) standardized with ferrocene were lower than those standardized with EDTA by three to five parts per thousand. It is shown in Chapter II that cyanide in technical grade acetonitrile interferes with the copper(II)-ferrocene titration. Asumming that the cyanide present reacts quantitatively with copper(II), it would be expected to interfere to about the same extent with all copper(II) oxidation as long as similar equivalents of sample and volumes of solvent are used. Therefore, under these conditions ferrocene may be an acceptable standard for copper(II) solutions in technical grade acetonitrile because determinate errors caused by the cyanide would cancel. In addition, the relative effect of cyanide in technical grade acetonitrile on this work will be greater in the weight titrations than in the volume titrations because

larger amounts of copper(II) and smaller amounts of solvent are used in the volume titrations. Thus, the relative error in the amount of titrant used in the volume titrations due to the cyanide interference would be expected to be only about 1 to 2 parts per thousand.

To check this aspect, pure ferrocene was used to standardize solutions of copper(II) in pure and technical grade acetonitrile. These titrants were then used to determine the equivalent weights of potassium iodide (at the first equivalence point only) and several derivatives of ferrocene. The results are shown in Table VII. Since the derivatives of ferrocene were analyzed as received, their purity would not be expected to be 100%. For these titrations derivatives of ferrocene were chosen which had formal reduction potentials both below and above ferrocene because it has been found that the titer values of iron(III) perchlorate in acetonitrile varied according to the ease of oxidation (neglecting kinetic effects) of the compounds being titrated[29]. Potassium iodide was included to compare the oxidation of a system other than that of the ferrocene moiety.

Comparison of the results in Table VII show that ferrocene is an adequate standard at the 1 to 2 part per thousand level in technical grade acetonitrile and that this solvent can be employed for the analysis of other compounds. Weight titrations were not used because the longer titration times that

Table VII. Comparison of Equivalent Weights of Potassium Iodide and Derivatives of Ferrocene Determined by Titration with Copper(II) Perchlorate in Technical Grade and Pure Acetonitrile

Substituent Group	Equivalent Weight Calculated	Equivalent Weight Observed	$E^{\circ\prime}$ in Mv^a	Number of Determinations	Relative Standard Deviation in p.p.t.
Technical Grade Acetonitrile					
H	186.0	186.0[b]	84	3	1.4
Acetyl	228.1	224.0	330	2	1.4
n-Butyl[c]	242.1	240.6	28	3	1.6
Formyl	214.0	209.5	369	3	1.0
1,1'-Di-n-butyl	298.2	291.0	-30	3	1.3
Potassium iodide[d]	249.0	249.2		3	0.7
Pure Acetonitrile					
H	186.0	186.0[b]	83	4	1.1
Acetyl	228.1	223.3	330	2	1.0
n-Butyl[c]	242.1	240.9	25	3	0.0
Formyl	214.0	209.5	368	3	1.6
1,1'-Di-n-butyl	298.2	291.3	-32	3	0.7
Potassium iodide[d]	249.0	249.2		3	1.0

[a]Potential at midpoint of titration; all potentials refer to silver-0.01M silver nitrate in acetonitrile reference electrode.
[b]Used as standard.
[c]Alfa Inorganics.
[d]Obtained from first equivalence point.

were required allowed air oxidation of several of the ferrocene
derivatives. The acyl derivatives were especially susceptible
to air oxidation when dissolved in acetonitrile.

Determination of derivatives of ferrocene. Results of
titrations of several derivatives of ferrocene in technical
grade acetonitrile with copper(II) are given in Table VIII, and
some representative titration curves are shown in Figure V.
All the derivatives determined gave similar symmetrical potential
breaks with the exception of dimethylaminomethylferrocene, which
had two distinct nonsymmetric inflections. The equivalent
weights found are the averages of three or more titrations.
Relative standard deviations ranged from 0.4 to 2 parts per
thousand except for dimethylferrocene and ferrocenecarboxylic
acid, which were 4 and 8 parts per thousand. Commercial
dimethylferrocene appeared heterogeneous, and the slow titration
rates for ferrocenecarboxylic acid allowed opportunity for air
oxidation to occur to varying degrees. Most derivatives gave
lower results if oxygen was not excluded; slow titrations also
gave lower results in many cases, probably because some air
oxidation occurred despite the use of nitrogen.

The formal reduction potentials follow the pattern
expected on the basis of electron withdrawing or donating
capacity of the substituent groups. Since the reduction
potentials of the diacetyl, dicarboxylic acid and dibenzoyl

Table VIII. Oxidation of Derivatives of Ferrocene by Copper(II) in Technical Grade Acetonitrile

Substituent Groups	Equivalent Weight Theoretical	Found	Slope at Midpoint, mV	$E°,a$ in mV^b	Previously Reported $E_{1/4}$ Values, mV^b Ref.(68)	Ref.(69)	Ref.(70)	Ref.(71)
Acetyl	228.1	223.8	59	330	96	282	276	
Amyl	256.1	255.3	58	28				
Benzoyl	290.2	285.6	59	335		280	280	
n-Butyryl	256.1	248.4	58	321				
n-Butyl[c]	242.1	242.1	57	28				
n-Butyl[d]	242.1	240.6	58	27				
t-Butyl	242.1	241.9	57	34				
Carboxylic acid	230.0	212.8	70	310		259	261	
1,1'-Diacetyl	270.1	e				505	508	499
1,1'-Di-n-butyl	298.2	291.0	58	-30				
1,1'-Dibenzoyl	394.3	e						
1,1'-Dicarboxylic acid	274.1	e					477	
1,1'-Dimethyl	214.1	200.6	62	-18	-50			
Dimethylaminomethyl	243.1	163.6	f	(37)g				
		354.4	f	(297)g				
Formyl	214.0	209.5	58	370	333			
H	186.0	186.0	56	85	50	16	24	11

a Potential at midpoint of titration.
b All values refer to the silver-0.01M silver nitrate in acetonitrile reference.
c Arapahoe Chemicals.
d Alfa Inorganics.
e Not determinable by copper(II).
f Not calculable because stoichiometry undetermined.
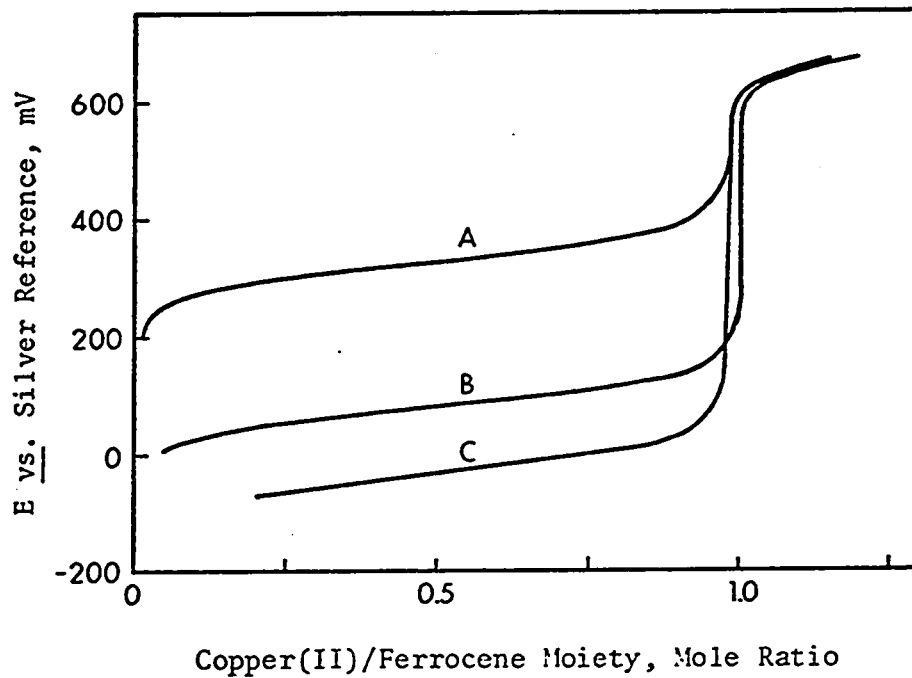g Not true formal reduction potential.

Figure V. Potentiometric Titration of (A) Acetylferrocene,

(B) Ferrocene, (C) 1,1'Di-n-Butylferrocene with Copper(II)

Perchlorate in Acetonitrile

derivatives were too high to give satisfactory titration curves, these compounds are not determinable by this method. However, it was possible to obtain some qualitative results for these species. Titrations of 1,1'-diacetylferrocene indicated that five moles of copper(II) were consumed per mole of compound; the dissolved species was easily air oxidized. Titrations of 1,1'-dibenzoylferrocene indicated a two-electron oxidation was taking place; this species was not as sensitive to air oxidation. 1,1'-Dicarboxylic acid ferrocene did not give a potential break, but upon addition of copper(II) a slow decrease in potential occurred after a quick initial rise, indicating a slow reaction was taking place.

Since the diacyl derivatives gave small or negligible potential breaks, consideration was given to the possibility of differentiating the mono- and diacyl derivatives of ferrocene by copper(II) titration. Titrations of the mixtures benzoyl- and dibenzoyl-, carboxylic acid- and dicarboxylic acid-, and acetyl- and diacetylferrocene gave drawn-out unsymmetrical potential breaks and equivalent weights for the mono derivatives that were 5 to 10% higher than those obtained for the mono derivatives alone. Titrations were also performed on mixtures of dibutylferrocene and ferrocene, and ferrocene and benzoylferrocene. The first mixture gave a single inflection corresponding to the total of the two compounds. The second

gave two inflections, but the resolution was poor, and the results disagreed with those found for the compounds individually by several per cent. Ferrocene and 1,1'-dibenzoylferrocene gave one inflection that, though not symmetrical, was sharp enough to give a few parts per thousand precision and accuracy. t-Butyl- and benzoylferrocene gave two symmetrical potential breaks that permitted end point selection with precision and accuracy comparable to that for the individual components. Therefore, copper(II) in acetonitrile is suitable for the differential or total titration of selected mixtures of ferrocene compounds.

Most of the potentials previously reported for these compounds in acetonitrile are chronopotentiometric $E_{1/4}$ values measured relative to the aqueous saturated calomel electrode (SCE)[68-70]. In Table VIII all values have been referred to the silver-0.01$\underline{M}$ silver nitrate in acetonitrile reference by subtracting 0.291V from the SCE values[72]. Hall and Russell[71] used a silver-0.01$\underline{M}$ silver nitrate -0.2$\underline{M}$ tetraethylammonium perchlorate in acetonitrile reference electrode. For comparison purposes their values were converted to the silver-0.01$\underline{M}$ silver nitrate reference by subtracting 52mV from each. This correction was determined by measurement at 25°C of the potential of the cell

$$Ag \mid 0.01\underline{M}\ AgNO_3,\ 0.2\underline{M}\ Et_4NClO_4 \mid \mid 0.01M\ AgNO_3 \mid Ag$$
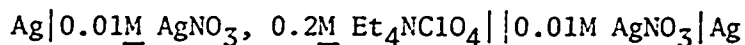
The differences in reduction potentials among the various reports
are probably due to variations in junction potential between the
saturated calomel electrode and the acetonitrile solutions, to
the presence of varying amounts of water in the solutions, or
to the effect of concentration variations on ion activities
in acetonitrile.

As can be seen from Table VIII, all the derivatives
of ferrocene oxidized by copper(II) were found to give
reversible or nearly reversible slopes at the midpoint, with
two exceptions, ferrocenecarboxylic acid and dimethylaminomethyl-
ferrocene. Ferrocenecarboxylic acid, due to the length of
time required for titration, apparently was affected by air
oxidation and values for dimethylaminomethylferrocene, could not be
obtained because the stoichiometries were not determined.

n-Butyl- and t-butylferrocene were the most pure of
the commercial derivatives; they also appeared stable toward
air oxidation during titration. The formyl, carboxy, and
benzoyl derivatives gave end points 5 to 25% earlier when air
was not excluded. The other derivatives showed an effect due
to air oxidation of less than 1%.

Most of the derivatives with a carbonyl functional
group adjacent to one or both of the cyclopentadienyl rings,
besides being more difficult to oxidize, were oxidized slowly
past 1:1 stoichiometry. To determine whether the ferricenium

species of these compounds could be stoichiometrically oxidized to further products, several of these and other derivatives were treated with an excess of copper(II), allowed to stand for varying lengths of time, then the copper(II) remaining was titrated with a standard solution of ferrocene in acetonitrile. Results are shown in Table IX. The ferrocene titrant was stored under nitrogen as a precaution against air oxidation; later work, however, showed that solutions of ferrocene in acetonitrile under normal atmospheric conditions had not changed in titer relative to copper(II) solution after 50 hours. From the results in Table IX it is apparent that excess copper(II) will oxidize most derivatives past the one-electron oxidation seen in the titrations. It appears that 1,1'-ferrocenedicarboxylic acid is only partly oxidized in the presence of excess copper(II).

Ferrocenes as oxidation-reduction indicators. Ferrocene and its derivatives show many of the properties sought in oxidation-reduction indicators. For example, the formal reduction potentials vary over a wide range, most of the derivatives are reversibly oxidized, and all show a color change upon oxidation by copper(II). However, the molar absorptivity of the ferricenium ion at the wavelength of maximum absorption, 617 mμ, is only slightly over 400 liter/mole-cm in pure acetonitrile (this

Table IX. Oxidation Ratio of Ferrocene Derivatives by Back

Titration of Excess Copper(II) with

Ferrocene in Acetonitrile

Substituent Group	Copper(II)/Derivative, Mole Ratio[a]		Time Excess Copper(II) Left in Contact, Hr.
	Added	Consumed	
Benzoyl	4.6	4.5	1.5
Carboxylic acid	3.2	1.8	1.5
	3.4	2.3	12
1,1'-Diacetyl	13.7	7.7	4
	9.7	8.3	12
1,1'-Dibenzoyl	6.2	6.1	4
	9.6	7.4	12
1,1'-Dicarboxylic acid	2.1	0.57	1.5
	4.2	0.55	12
Dimethylaminomethyl	3.8	0.92	1.5
	2.3	0.40	12
Formyl	4.7	4.6	4
	5.8	5.7	12
H	1.5	1.0	1.5
	1.9	1.2	12

[a]Calculated assuming all derivatives 100% pure.

compares to 340 liter/mole-cm at 617 mμ in water[73]) and that of

benzoylferricenium ion at its maximum absorbance, 635 mμ, is

only about 320 liter/mole-cm. Therefore, these oxidized species

do not absorb strongly enough in the visible region to be useful

as indicators.

When water was added to the titration solutions past

the end point, the color of the solutions did not change for the

alkyl derivatives and ferrocene, but the monoacyl-,

1,1'-dicarboxylic acid-, and dimethylaminomethylferrocenes

reverted to the color prior to titration. Water lowers the

reduction potential of the copper(II)-(I) couple, and since all

the species involved in the reactions are reversible, apparently

the lower potential causes the starting material to be formed.

1,1'Dibenzoyl- and 1,1'-diacetylferrocene gave brown colored

solutions past the end points in the titrations with copper(II) that

did not change on addition of water. Since these species have

high reduction potentials the addition of water would be

expected to reverse the color change; since this was not observed,

irreversible degradation of these species must have taken place

during the initial oxidation.

CHAPTER IV SUMMARY

1. By use of weight titrations, the stoichiometry of an electron-transfer reaction in a nonaqueous solvent, the oxidation of ferrocene by hydrated copper(II) perchlorate in acetonitrile, was established with a relative accuracy and precision of a few parts per ten thousand.

2. Weight titrations of aqueous copper(II) with EDTA, using murexide as indicator, were shown to be capable of a relative precision of a few parts per ten thousand.

3. Ferrocene was shown (a) to be obtainable at 100.0% purity by double recrystallization from heptane, followed by sublimation under vacuum, (b) to be stable and nonhygroscopic in air under ordinary conditions, (c) to react stoichiometrically and rapidly with hydrated copper(II) perchlorate in pure acetonitrile, and (d) to have a sufficiently large potential break at the equivalence point in its oxidation by copper(II) to allow precise determination of the end point. It also has the advantage of a high equivalent weight (186.04). Therefore, ferrocene is a satisfactory primary standard for hydrated copper(II) perchlorate solutions in pure acetonitrile.

4. Comparisons of weight titrations using technical grade and pure acetonitrile as the solvent indicate that standardization of copper(II) solutions in acetonitrile by

aqueous titration with EDTA can be used only with pure acetonitrile. It is hypothesized that aqueous titrations by EDTA of copper(II) in acetonitrile give the total amount of copper present in acetonitrile, but not the amount of copper(II) which will function as an oxidant in acetonitrile.

5. Acrylonitrile, acetic acid, ammonia, ammonium acetate, and acetamide, reported contaminants in technical grade acetonitrile, were shown not to interfere at the concentration normally encountered in technical grade acetonitrile in the titration of ferrocene by copper(II). Cyanide was found at a concentration of about $1 \times 10^{-4}\underline{M}$ in the technical grade acetonitrile used in this work. Cyanide added as potassium cyanide at $1 \times 10^{-4}\underline{M}$ levels to pure acetonitrile gave a relative titration error which corresponded to that observed when technical grade acetonitrile was used as the solvent. Therefore, cyanide, most likely present as hydrogen cyanide, appears to be the contaminant in technical grade acetonitrile that interferes with copper(II) as an oxidant.

6. Hydrated copper(II) perchlorate in technical grade acetonitrile was shown to be a suitable titrant for the determination of selected alkyl and monoacyl derivatives of ferrocene when pure ferrocene is used to standardize the titrant. These derivatives were found to be reversibly oxidized by copper(II), with the exception of ferrocenecarboxylic acid and dimethylaminomethylferrocene.

7. Ferrocene in acetonitrile was found to be stable at the part per thousand level for a few days, and can be used as a reducing titrant of moderate strength.
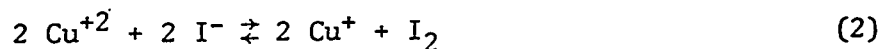
APPENDIX A. DERIVATION OF EXPRESSIONS FOR THE CALCULATIONS

OF POTENTIALS AT THE EQUIVALENCE POINTS

Titration of Potassium Iodide with
Copper(II) in Acetonitrile

The first inflection (Figure I, Chapter II) is the
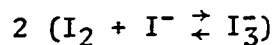oxidation of iodide to triiodide.

$$2 \; Cu^{+2} + 3 \; I^- \rightleftarrows 2 \; Cu^+ + I_3^- \tag{1}$$
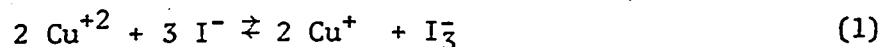
Equation 1 can be considered to occur in two steps, oxidation
of iodide to iodine,

$$2 \; Cu^{+2} + 2 \; I^- \rightleftarrows 2 \; Cu^+ + I_2 \tag{2}$$

followed by formation of triiodide.

$$I_2 + I^- \rightleftarrows I_3^- \tag{3}$$

Equation 3 can be written as the sum of the two half-reactions:

$$3 \; I_2 + 2 \; e \rightleftarrows 2 \; I_3^- \tag{4}$$

$$2 \; I^- - 2 \; e \rightleftarrows I_2 \tag{5}$$

$$\overline{2 \; (I_2 + I^- \rightleftarrows I_3^-)}$$

To simplify all calculations, concentrations will be considered
equal to activities and all potentials will be expressed in V vs.

the silver reference. The potential at equilibrium for

Equations 4 and 5 is

$$E = E^{\circ\prime}_{I_2/I_3^-} + \frac{0.0591}{2} \log \frac{[I_2]^3}{[I_3^-]^2} = E^{\circ\prime}_{I_2/I^-} + \frac{0.0591}{2} \log \frac{[I_2]}{[I^-]^2} \quad (6)$$

Rearranging

$$E = \frac{E^{\circ\prime}_{I_2/I_3^-} + E^{\circ\prime}_{I_2/I^-}}{2} + \frac{0.0591}{2} \log \frac{[I_2]^2}{[I_3^-][I^-]} \quad (7)$$

The values of $E^{\circ\prime}_{I_3^-/I^-}$ and $E^{\circ\prime}_{I_2/I_3^-}$ in acetonitrile are[42]

$$E^{\circ\prime}_{I_3^-/I^-} = -0.248 \quad \text{and} \quad E^{\circ\prime}_{I_2/I_3^-} = 0.396 \quad (8)$$

To solve Equation 7, $K_{f_{I_3^-}}$ for Equation 3 and $E^{\circ\prime}_{I_2/I^-}$ for

Equation 5 must be known or determined. At equilibrium

$$E^{\circ\prime}_{I_2/I_3^-} + \frac{0.0591}{2} \log \frac{[I_2]^3}{[I_3^-]^2} = E^{\circ\prime}_{I_3^-/I^-} + \frac{0.0591}{2} \log \frac{[I_3^-]}{[I^-]^3} \quad (9)$$

$$E^{\circ\prime}_{I_2/I_3^-} - E^{\circ\prime}_{I_3^-/I^-} = \frac{3(0.0591)}{2} \log \frac{[I_3^-]}{[I_2][I^-]} \quad (10)$$

Taking values from equation 8,

$$K_{f_{I_3^-}} = \frac{[I_3^-]}{[I_2][I^-]} = 10^{7.26} \quad (11)$$

At the first equivalence point from equation 3 it is found that

$$[I^-] = [I_2] \tag{12}$$

therefore, $[I^-] = [I_2] = K_{f_{I_3^-}}^{-\frac{1}{2}} [I_3^-]^{\frac{1}{2}}$ (13)

Also, at equilibrium

$$E^{\circ\prime}_{I_2/I^-} + \frac{0.0591}{2} \log \frac{[I_2]}{[I^-]^2} = E^{\circ\prime}_{I_3^-/I^-} + \frac{0.0591}{2} \log \frac{[I_3^-]}{[I^-]^3} \tag{14}$$

$$E^{\circ\prime}_{I_2/I^-} = E^{\circ\prime}_{I_3^-/I^-} + \frac{0.0591}{2} \log \frac{[I_3^-]}{[I_2][I^-]} = -0.033 \tag{15}$$

Substituting Equations 8, 11, 13, and 15 into Equation 7, where E_1 is the potential at first equivalence point

$$E_1 = \frac{0.396 + (-0.033)}{2} + \frac{0.0591}{2} \log \frac{10^{-7.26}[I_3^-]}{10^{-3.63}[I_3^-]^{\frac{1}{2}}[I_3^-]} \tag{16}$$

$$E_1 = 0.074 - \frac{0.0591}{4} \log [I_3^-] \tag{17}$$

Thus the potential at the first equivalence point is dependent on the concentration of triiodide present by the relation shown in Equation 17.

The reaction at the second inflection of the iodide oxidation curve is the formation of iodine according to

$$2 \, Cu^{+2} + 2 \, I_3^- \rightleftarrows 2 \, Cu^+ + 3I_2 \tag{18}$$
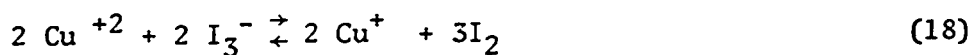
The potential at the second equivalence point is given by

$$E_2 = E^{\circ \prime}_{Cu^{+2}/Cu^+} + 0.0591 \log \frac{[Cu^{+2}]}{[Cu^+]} = E^{\circ \prime}_{I_2/I_3^-} + \frac{0.0591}{2} \log \frac{[I_2]^3}{[I_3^-]^2} \tag{19}$$

$$E_2 = \frac{E^{\circ \prime}_{Cu^{+2}/Cu^+} + E^{\circ \prime}_{I_2/I_3^-}}{2} + \frac{0.0591}{4} \log \frac{[Cu^{+2}]^2[I_2]^3}{[Cu^+]^2[I_3^-]^2} \tag{20}$$

Since the overall reaction of iodide and copper(II) is

$$2\ Cu^{+2} + 2\ I^- \rightleftarrows 2\ Cu^+ + I_2\ , \tag{21}$$

then at the second equivalence point

$$[Cu^+] = 2[I_2] \tag{22}$$

and from Equations 3, 11, and 21

$$[Cu^{+2}] = [I_3^-] + [I^-] = [I_3^-](1 + \frac{1}{10^{7.26}[I_2]}) \tag{23}$$

In this work the concentration of iodine at the second inflection was larger than 0.01 $\underline{M}$, therefore

$$[Cu^{+2}] = [I_3^-] \tag{24}$$

Substituting Equations 22 and 24 into 20
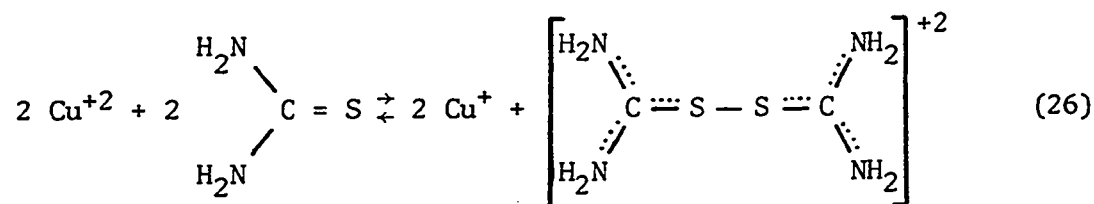
$$E_2 = \frac{0.801 + 0.396}{2} + \frac{0.0591}{4} \log \frac{[I_2]}{4} \tag{25}$$

Thus the potential at the second equivalence point is dependent on the

concentration of iodine present according to Equation 25.

Titration of Thiourea with Copper(II) in Acetonitrile

The potential at the equivalence point for the reaction,

$$2\ Cu^{+2} + 2\ \underset{H_2N}{\overset{H_2N}{\diagdown}}C = S \underset{\leftarrow}{\rightarrow} 2\ Cu^+ + \left[\underset{H_2N}{\overset{H_2N}{\diagdown}}C \doubleequals S - S \doubleequals C \underset{NH_2}{\overset{NH_2}{\diagup}} \right]^{+2} \tag{26}$$

is $E_{e.p.} = \dfrac{E^{\circ\prime}{Cu^{+2}/Cu^+} + E^{\circ}{Tu_2^{+2}/Tu}}{2} + \dfrac{0.0591}{2} \log \dfrac{[Cu^{+2}]^2 [Tu_2^{+2}]}{[Cu^+]^2 [Tu]^2}$ (27)

where Tu is thiourea and Tu_2^{+2} is the disulfide ion.
At the equivalence point

$$[Cu^{+2}] = [Tu] \qquad \text{and} \qquad [Cu^+] = 2[Tu_2^{+2}] \tag{28}$$

Therefore Equation 27 becomes

$$E_{e.p.} = \frac{0.801 + E^{\circ\prime}{Tu_2^{+2}/Tu}}{2} - \frac{0.0591}{2} \log\ (4[Tu_2^{+2}]) \tag{29}$$

The potential at the equivalence point is dependent, therefore, on the concentration of the disulfide ion according to the relation shown in Equation 29.

Titration of Hydroquinone and Quinhydrone
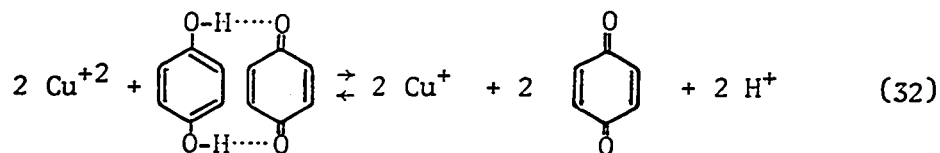### by Copper(II) in Acetonitrile

The potential at the equivalence point for the reaction,

$$2\ Cu^{+2} + \text{(hydroquinone, OH...OH)} \rightleftarrows 2\ Cu^{+} + \text{(quinone, O...O)} + 2\ H^{+} \tag{30}$$
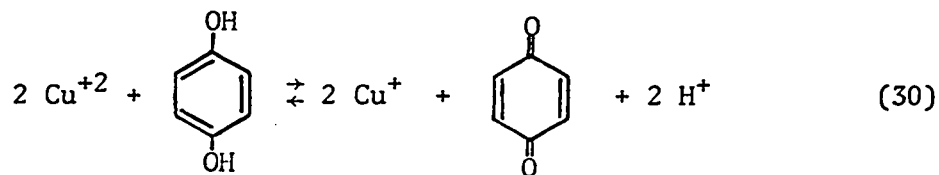
$$\text{is } E_{e.p.} = \frac{E^{\circ\prime}_{Cu^{+2}/Cu^{+}} + 2E^{\circ\prime}_{Q/H_2Q}}{3} + \frac{0.0591}{3} \log\,[H^{+}]^2 \tag{31}$$

where Q is quinone and H_2Q is hydroquinone.

This potential is difficult to obtain precisely because the concentration of hydrogen ion in acetonitrile cannot be easily obtained. Furthermore, it has been reported that in acetonitrile quinone is protonated after hydroquinone is oxidized[74] which would complicate the determination of $E_{e.p.}$ even more. The potential at the equivalence point for the reaction,

$$2\ Cu^{+2} + \text{(quinhydrone, O-H}\cdots\text{O / O-H}\cdots\text{O)} \rightleftarrows 2\ Cu^{+} + 2\ \text{(quinone, O...O)} + 2\ H^{+} \tag{32}$$

$$\text{is } E_{e.p.} = \frac{E^{\circ\prime}_{Cu^{+2}/Cu^{+}} + 2E^{\circ\prime}_{Q/H_2Q}}{3} + \frac{0.0591}{3} \log\,(2[H^{+}]^2) \tag{33}$$

assuming in solution that quinhydrone disassociates to hydroquinone and quinone. Again this potential would be difficult to obtain precisely due to the difficulties mentioned above.

APPENDIX B BUOYANCY CORRECTIONS FOR WEIGHT TITRATIONS

Densities

Air. For the following calculations a value of

0.00109 g/cc was used for the density of air. For relative

humidities of 0 to 100%, atmospheric pressures in the range of

685 to 710 mm of mercury[75], and temperatures in the range of 20.0

to 26.0°C, the maximum and minimum values for the density of air

are 0.001125 and 0.001049 g/cc[76]. Therefore, the uncertainty in

the value 0.00109 due to these factors is no greater than

0.00004 g/cc. When this uncertainty is taken into account in the

buoyancy calculations for (a) the concentration of copper(II) in

acetonitrile as determined by titration of ferrocene, (b) the

concentration of aqueous EDTA as determined by titration of

standard aqueous copper(II) nitrate, and (c) the concentration

of copper(II) in acetonitrile as determined through titration

by standard   aqueous EDTA, the relative errors obtained

will be no larger than 0.03, 0.04, and 0.05 parts per

thousand for the concentrations of (a), (b), and (c). The

uncertainty in the density of air due to changes in relative

humidity, atmospheric pressure, and temperature therefore can be

neglected since the resulting relative error in the concentrations

is negligible.

Other materials. The density of ferrocene is

1.516 g/cc[44]; the weights used in the balances are brass, for

which a density of 8.4 g/cc was taken. The densities of the

solutions were determined at 25°C by pycnometer; the values

obtained were: 0.786 g/cc for a solution of copper(II)

perchlorate in acetonitrile containing 0.03 mmoles of copper(II)

per g of solution; 1.0005 g/cc for an aqueous copper(II) nitrate

solution containing 0.03 mmoles of copper(II) per g of solution;

and 1.0011 g/cc for an aqueous EDTA solution containing 0.03

mmoles of EDTA per g of solution. The relative standard

deviations for these three values, based on two determinations

each, were all less than two parts per thousand. This uncertainty

has a negligible effect on the buoyancy corrections.

Absolute Buoyancy Correction for the Apparent Concentration of Copper(II) in Acetonitrile as Determined by Titration of Ferrocene

For all calculations, concentrations are given in units

of mmoles of substance per gram of solution. The symbol $[X]^A$

is used for the apparent concentration of X, that is, the

concentration calculated without buoyancy corrections, and W_X

is the apparent weight of X in grams.

The value used for the density of the balance weights is

unimportant for overall absolute buoyancy corrections if the same

value is used throughout. However, for completeness this factor is

included in the calculations. In all these weighings a fraction of

the total weight is derived from an optical scale. Since the optical

scale is calibrated with conventional weights, it requires a buoyancy

correction of the same nature as these conventional weights.

The absolute buoyancy error for the weight of ferrocene, $\Delta E_{W_{Fc}}$, is given by

$$\Delta E_{W_{Fc}} = W_{Fc}(\text{Density of Air})$$

$$(\frac{1}{\text{Density of Ferrocene}} - \frac{1}{\text{Density of Balance Weights}})$$

$$\Delta E_{W_{Fc}} = W_{Fc}(0.00109 \text{ g/cc})(\frac{1}{1.516 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}})$$

$$\Delta E_{W_{Fc}} = W_{Fc}(0.00059)$$

The absolute buoyancy error for the weight of copper(II) perchlorate-acetonitrile solution used to titrate ferrocene, $\Delta E_{W_{Cu-Fc}}$, is given by

$$\Delta E_{W_{Cu-Fc}} = W_{Cu-Fc}(0.00109 \text{ g/cc})(\frac{1}{0.786 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}})$$

$$\Delta E_{W_{Cu-Fc}} = W_{Cu-Fc}(0.00126)$$

The absolute buoyancy correction for the apparent copper(II) concentration as obtained in the titration of ferrocene by copper(II), $\Delta E_{[Cu^{+2}]_{Fc}^A}$, is given by

$$\Delta E_{[Cu^{+2}]_{Fc}^A} = (\text{True Concentration}) - (\text{Apparent Concentration})$$

$$\Delta E_{[Cu^{+2}]_{Fc}^A} = \frac{(\frac{W_{Fc} + \Delta E_{W_{Fc}}}{\text{g of Fc/mmole}})}{W_{Cu-Fc} + \Delta E_{W_{Cu-Fc}}} - \frac{(\frac{W_{Fc}}{\text{g of Fc/mmole}})}{W_{Cu-Fc}}$$

$$\Delta E_{[Cu^{+2}]^A_{Fc}} = \left\{ \frac{W_{Fc}(1 + 0.00059)}{\overline{g \text{ of Fc/mmole}}} \right\} \cdot \left(\frac{W_{Fc}}{\overline{g \text{ of Fc/mmole}}} \right) - \frac{W_{Fc}}{W_{Cu-Fc}}$$

$$\Delta E_{[Cu^{+2}]^A_{Fc}} = \frac{\left(\frac{W_{Fc}}{\overline{g \text{ of Fc/mmole}}} \right)}{W_{Cu-Fc}} (-0.00067)$$

$$\Delta E_{[Cu^{+2}]^A_{Fc}} = [Cu^{+2}]^A_{Fc}(-0.00067)$$

Absolute Buoyancy Correction for Apparent Concentration of Aqueous EDTA Determined by Titration of Standard Aqueous Copper(II) Nitrate

The absolute buoyancy error for the weight of copper wire, $\Delta E_{W_{Cu-Wire}}$, is expressed as

$$\Delta E_{W_{Cu-Wire}} = W_{Cu-Wire}(0.00109 \text{ g/cc}) \left(\frac{1}{8.9 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}} \right)$$

$$\Delta E_{W_{Cu-Wire}} = W_{Cu-Wire}(-0.00001)$$

The absolute buoyancy error for the total weight of standard aqueous copper(II) nitrate solution, $\Delta E_{W_{Cu-H_2O-Total}}$, is given by

$$\Delta E_{Cu-H_2O-Total} = W_{Cu-H_2O-Total}(0.00109 \text{ g/cc}) \left(\frac{1}{1.005 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}} \right)$$

$$\Delta E_{W_{Cu-H_2O-Total}} = W_{Cu-H_2O-Total}(0.00095)$$

The absolute buoyancy error for the weighed aliquots of standard aqueous copper(II) nitrate solution, $\Delta E_{W_{Cu-H_2O-Aliq}}$, is expressed by

$$\Delta E_{W_{Cu-H_2O-Aliq}} = W_{Cu-H_2O-Aliq}(0.00109 \text{ g/cc})(\frac{1}{1.005 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}})$$

$$\Delta E_{W_{Cu-H_2O-Aliq}} = W_{Cu-H_2O-Aliq}(0.00095)$$

The buoyancy error for the weight of aqueous EDTA used to titrate the weighed aliquots of standard aqueous copper(II) solution, $\Delta E_{W_{EDTA-Cu-H_2O}}$, is given by

$$\Delta E_{W_{EDTA-Cu-H_2O}} = W_{EDTA-Cu-H_2O}(0.00109 \text{ g/cc})(\frac{1}{1.0011 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}})$$

$$= W_{EDTA-Cu-H_2O}(0.00096)$$

The overall absolute buoyancy correction for the apparent concentration of aqueous EDTA, $\Delta E_{[EDTA]A}$, is given by

$$\Delta E_{[EDTA]}^A = \frac{(W_{Cu-H_2O-Aliq} + \Delta E_{W_{Cu-H_2O-Aliq}}) \left\{ \dfrac{(\dfrac{W_{Cu-Wire} + \Delta E_{W_{Cu-Wire}}}{g \text{ of copper/mmole}})}{W_{Cu-H_2O-Total} + \Delta E_{W_{Cu-H_2O-Total}}} \right\}}{W_{EDTA-Cu-H_2O} + \Delta E_{W_{EDTA-Cu-H_2O}}}$$

$$- \frac{(W_{Cu-H_2O-Aliq}) \left\{ \dfrac{(\dfrac{W_{Cu-Wire}}{g \text{ of copper/mole}})}{W_{Cu-H_2O-Total}} \right\}}{W_{EDTA-Cu-H_2O}}$$

$$\Delta E_{[EDTA]}^A = \frac{(1.00095)(\dfrac{0.99999}{1.00095})}{1.00096}[EDTA]^A - [EDTA]^A$$

$$\Delta E_{[EDTA]}^A = (-0.00097[EDTA]^A$$

Absolute Buoyancy Correction for Apparent Concentration of Copper(II) in Acetonitrile as Determined by Titration with Standard Aqueous EDTA

The absolute buoyancy error for the weighed aliquots of copper(II) in acetonitrile, $\Delta E_{W_{Cu-AN-Aliq}}$, is given by

$$\Delta E_{W_{Cu-AN-Aliq}} = W_{Cu-AN-Aliq}(0.00109 \text{ g/cc})(\frac{1}{0.786 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}}$$

$$\Delta E_{W_{Cu-AN-Aliq}} = W_{Cu-AN-Aliq}(0.00126)$$

The absolute buoyancy error for the weight of aqueous EDTA used to titrate the weighed aliquots of copper(II) in acetonitrile, $\Delta E_{W_{EDTA-Cu-AN}}$, is given by

$$\Delta E_{W_{EDTA-Cu-AN}} = W_{EDTA-Cu-AN}(0.00109 \text{ g/cc})(\frac{1}{1.0011 \text{ g/cc}} - \frac{1}{8.4 \text{ g/cc}})$$

$$\Delta E_{W_{EDTA-Cu-AN}} = W_{EDTA-Cu-AN}(0.00096)$$

The overall absolute buoyancy correction for the apparent copper(II) concentration as obtained by titration with EDTA, $\Delta E_{[Cu^{+2}]^A_{EDTA}}$, is given by

$$\Delta E_{[Cu^{+2}]^A_{EDTA}} = \frac{W_{EDTA-Cu-AN} + \Delta E_{W_{EDTA-Cu-AN}})([EDTA]^A + \Delta E_{[EDTA]^A})}{W_{Cu-AN-Aliq} + \Delta E_{W_{Cu-AN-Aliq}}}$$

$$- \frac{(W_{EDTA-Cu-AN})[EDTA]^A}{W_{Cu-AN-Aliq}}$$

$$\Delta E_{[Cu^{+2}]^A_{EDTA}} = \left\{ \frac{(1.00096)(0.99903)}{1.00126} - 1 \right\} [Cu^{+2}]^A_{EDTA}$$

$$\Delta E_{[Cu^{+2}]^A_{EDTA}} = [Cu^{+2}]^A_{EDTA}(-0.00127)$$

These calculated absolute buoyancy corrections were applied to the data of the weight titrations to give actual concentrations.

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