CERIC SULFATE

The Use of Standard Ceric Sulfate as Modern Analytical Chemistry's Most Recently Developed Widely Applicable Oxidizing Agent

VOLUME I

Third Edition, with extensions
(August, 1935)

Published by
The G. Frederick Smith Chemical Company
P. O. Box 1611
Columbus, Ohio

Data Compiled by
G. Frederick Smith, Ph. D.,
Associate Professor, University of Illinois
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Laboratory Procedures—

NOTE.—This third edition is merely a republication of the second edition, due to wide demand for the booklets, previous editions being exhausted.

PREFACE

The second edition of this booklet "Ceric Sulfate" represents an extension and improvement of the first issue demanded principally as a result of recent new developments greatly extending the application of ceric sulfate and simplifying the methods of its use. The G. Frederick Smith Chemical Company was the first manufacturer of reagent chemicals to market stock reagents to fill the need for a satisfactory raw material to be used in the preparation of ceric sulfate solutions for use as a volumetric oxidizing agent. This was done in two ways, first by the preparation of ceric sulfate solutions to market as such ready for standardization and analytical application, and second by supplying hydrated ceric oxide of such form as to be sufficiently soluble after digestion with sulfuric acid to serve as a convenient raw material for preparation of standard solutions.

The distribution of ceric sulfate solutions containing sulfuric acid is not entirely satisfactory because of the necessity for glass stoppered containers and the inconvenience of packing and shipping as a result of the presence of sulfuric acid. This method has, however, one advantage particularly attractive to the incidental small consumer, namely, that the solution is ready for standardization or can be supplied with a standard oxidation factor since such solutions are permanently stable. The distribution of hydrated ceric oxide eliminates the objection that a solution is involved but has other slight disadvantages. Hydrated ceric oxide varies in its acid solubilities very markedly depending chiefly upon the conditions under which it is ignited to bring about its partial dehydration. When dehydrated to a point lower than $CeO_2 \cdot 2H_2O$, it is difficultly soluble in acid. When the temperature of ignition is too low, the product is often low in Ce^{IV}. In this wise the conflict in advantages associated with its preparation results in a finished product often undesirable. The last objection to hydrated ceric oxide consists in the fact that it undergoes partial reduction when treated with hot sulfuric acid to convert it to sulfate.

In view of these facts, the need was quite evident for the preparation of ceric sulfate as a dry reagent which would be freely soluble in dilute sulfuric acid giving a clear solution ready for immediate standardization and use as a volumetric oxidizing agent. This goal has been attained and it is a matter of keen satisfaction to the writer that this method was made possible through the use of perchloric acid as an oxidizing agent. The preparation of ceric sulfate by the new method, a detailed description of which is a portion of the subject matter of this booklet, gives a ceric sulfate which is easily soluble in dilute sulfuric acid and the rare earth materials other than cerium ordinarily associated with it have no undesirable effect. This regagent is supplied in the dry form as $(Ce(SO_4)_2$. Starting with hydrated ceric oxide which is easily soluble in hydrochloric acid, ceric sulfate can be readily prepared by the purchaser following the directions given. The ceric oxide for this process is now available. This considerably extends the facilities with which solutions of ceric sulfate are prepared. The method given has the advantage as well that the resulting product is obtained at the minimum of cost. Crystalline ceric ammonium sulfate, easily soluble in dilute sulfuric acid, is now available which provides the simplest method for the preparation of standard solutions.

Originally, investigation proved that many applications in the use of ceric sulfate as a volumetric reagent were dependent upon the use of the potentiometric end point determination. The use of the indicators, erio-glaucine and erio-green, introduced by Furman and Wallace proved to be a great advantage in the standardization of ceric sulfate using iron as either primary or indirect standard. Other indicators are suitable for this standardization, for example, diphenylbenzidine, diphenylamine sulfonic acid, or diphenylamine with practically as good results as in the case of the erio indicators. The desire to make ceric sulfate reactions applicable without applying the potentiometric end point has led to important contributions by Willard and Young as yet not off the press but which through the courtesy of Professor Willard have been made available in this booklet. These results were made possible by the study of the use of ortho-phenanthroline ferrous complex as indicator as described by Walden, Hammett and Chapman (reference (44)* in bibliography). This indicator has been shown by Willard and Young(45) to serve as an internal oxidation and reduction indicator suitable for most ceric sulfate reactions for which potentiometric determination of the end point was previously used exclusively.

These developments place ceric sulfate in a distinctive strategic position to justify the claim that it substitutes for permanganate as a standard volumetric reagent having many material advantages. The chief disadvantage, that ceric sulfate does not serve well as its own indicator, has been overcome by the use of the ortho-phenathroline ferrous complex. This indicator with its high oxidation potential serves admirably in most of the common reactions. Ceric sulfate solutions being permanently stable have a distinct advantage over permanganate solutions and can be standardized using the same standards of reference with equally satisfactory visual end point determination. The raw materials for making ceric sulfate solutions are getting cheaper and the methods of manipulation simpler. The supply of ortho-phenanthroline indicator is available from the stock of reagents supplied by The G. Frederick Smith Chemical Company as are also the ceric salts for the preparation of the solutions.

This preface would not be complete without the statement that all methods resulting from the research work developed at the G. Frederick Smith Chemical Company in the manufacture of their products are given in full detail either by publications promoted by this company and distributed gratis or in current issues of the best chemical journals. This service may be said to be unique and original. It is not paralleled, so far as is known to the writer, at the hands of any existing manufacturer of reagent chemicals. The advantage to the trade is at once apparent. The character of the reagent supplied is not a matter of conjecture; its scientific application at the hands of the consumer is materially facilitated who may duplicate the work with a minimum of effort. These facts undoubtedly work to the slight disadvantage of the company supplying the information. The cost of supplying the data adds somewhat to the price of products. There is the firm conviction, however, which our experience has amply justified as a fact, that a conscientious scientific effort has nothing to fear from the dissemination of scientific information and full development publicity. The manufacturer's surety lies in perpetual and intensive research and not in mysticism, in most cases imaginative, or secrets, selfishly and in most cases superficially guarded.

At the close of this booklet a new service is presented. Short, precise and accurate details of procedures involving the standardization of ceric sulfate as a volumetric standard reagent are given. By the transcription of these methods to the plant laboratory procedure files the same may be easily expanded or, better, this booklet may be made a permanent addition to the laboratory procedure files. This service, as an innovation, is provided to meet the fair criticism that the bulk of the material of this booklet is in such scientific detail that the laboratory manipulator is confused by its complexity. This feature will be extended under separate cover in future releases. Suggestions for additional improvements or modifications are welcomed and questions relative to this work will be given prompt attention.

G. Frederick Smith.

Urbana, Illinois, and Columbus, Ohio.
July, 1933.

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*These numbers refer to a bibliography at the end.

CERIC SULFATE

The Use of Standard Ceric Sulfate as Modern Analytical Chemistry's Most Recently Developed Widely Applicable Oxidizing Agent

The systematic study of the use of ceric sulfate as an improved standard oxidizing agent to be used in substitution for the less desirable reagents, potassium premanganate or dichromate, was, by a peculiar coincidence, taken up simultaneously by the well-known authorities, H. H. Willard(26—38) and N. H. Furman(5—17). In the brief interval since the introduction of these separately conducted series of analytical research projects, first appearing in 1928, a large number of studies in the application of ceric sulfate to volumetric oxidation reactions have accumulated. The more general industrial and research applications of the quantitative methods thus originated by Willard and by Furman and their collaborators have, perhaps, not properly materialized due to the absence of prepared solutions of ceric sulfate from the usual trade channels. Acting upon the suggestion of both Professor H. H. Willard and Professor N. H. Furman, The G. Frederick Smith Chemical Company has undertaken the task of making directly obtainable ceric sulfate solutions of proper strength, stability, and purity to fill a scientific need and to further the already popular use of analytical chemistry's most modern and outstanding developments.

Besides preparing ceric sulfate solutions for use in the methods described, there are in addition available for distribution, hydrated ceric oxide, $CeO_2{\cdot}2H_2O$, and anhydrous ceric sulfate, $Ce(SO_4)_8$. The preparation of ceric sulfate solutions starting with ceric ammonium sulfate is very convenient and the salt for this purpose is also available. The most important individual contribution to the field of ceric sulfate analysis is that of Walden, Hammett and Chapman. The preliminary announcement of the application of ortho-phenanthroline ferrous complex as internal indicator for ceric sulfate reactions is therefore taken from reference 44 and is quoted in full in the following section. By use of this new indicator ceric sulfate reactions are virtually free from the inconvenience of a required potentiometric end point determination.

A Reversible Oxidation Indicator of High Potential Especially Adapted to Oxidimetric Reactions

"The ferrous-ortho-phenanthroline complex ion discovered by Blau (46) may be used as a reversible oxidation indicator of high potential and is ideally suited for many oxidimetric titrations. It is of an intense red color, which oxidation to the ferric complex converts to a blue of less intensity. Once formed by reaction of phenanthroline and ferrous sulfate in aqueous solution, the complex is not appreciably decomposed in several hours at room temperature by strong acids, although these do prevent its formation. The ferric complex is resistant to acids and to the action of permanganate, dichromate or ceric ions in acid solution. By electrometric titration with ceric sulfate we have found the indicator system to be of high mobility and perfect reversibility and to have a molar potential of 1.14 volts. It may, therefore, be used for any titration of an active reducing agent with ceric sulfate in the cold. This valuable and extremely stable oxidizing agent has been available for titrations hitherto only by the use of an electrometric end-point or of an indicator of potential not really suited to the titration and susceptible to side reactions and decompositions. We have found that high precision may be attained in the titration of ferrous ion and ceric ion when the amount of indicator used has an oxidation equivalent of 0.01 cc. of 0.1 normal solution. We have furthermore found that a similar precision may be obtained in titrations of ferrous ion and dichromate ion in sulfuric or hydrochloric acid solution, and that the above-named quantity of indicator gives an entirely satisfactory end-point in spite of the color of the chromic and ferric compounds. When titrating dichromate with ferrous salt the color change is instantaneous; in the reverse titration it is necessary to wait for a few seconds after each addition when near the end-point. The standardization of a ferrous sulfate solution against purified potassium dichromate using this indicator agrees excellently with that obtained against sodium oxalate by way of permanganate. The use of this valuable ultimate standard in oxidimetry is thus made simpler than previously possible. The presence of other common metallic ions, including notably mercuric ion, was not found to affect the precision of ferrous-dichromate titrations. The ferrous-dipyridyl complex was found to be a less satisfactory indicator because of its more rapid reactions with acids."

General Characteristics of Ceric Sulfate as a New Analytical Oxidizing Agent

At first thought ceric sulfate as a standard reagent for any routine analytical reaction might be considered too difficult to purify and, therefore, too expensive to be employed extensively. Pure preparations of ceric sulfate are not, however, required. Other cerium group rare earth materials do not interfere. Expensive, pure ceric salts are not needed, therefore, in the preparation of suitable ceric sulfate solutions for standardization and subsequent use. The finished product cannot, it is true, be sold at a price to compete with potassium permanganate or dichromate required for an equal amount of oxidizing solution. The price of ceric sulfate can be maintained well within the limits set by virtue of its manifold and diversified advantages.

"An extensive development of analytical methods based upon the use of ceric salt as volumetric reagents would have been difficult before the advent of the potentiometric method of determining an end-point. Though a visual change or an internal indicator may be used in some cases, the end-point in many of the titrations must be determined electrometrically. Since the oxidation potential of the most powerful oxidizing agents such as that of permanganate in acid solutions is very close to that of ceric compounds in a similar medium, the latter should prove to be very strong oxidizing agents and should behave in many reactions in a manner similar to permanganate." This quotation from reference (26) has indeed been substantiated as to the number of possible applications as indicated by the bibliography following. The need for the application of the electrometric determination of the end-point has become less and less essential through the introduction of numerous satisfactory internal indicators. In some cases ceric sulfate like potassium permanganate serves as its own indicator.

By the use of the ortho-phenanthroline ferrous complex indicator described above it can now be said without reservation that ceric sulfate takes a position of undisputed equality with potassium permanganate as a standard volumetric reagent. The standards of reference, sodium oxalate, arsenious oxide and Mohr's salt or electrolytic iron serve as equally good comparison standards for ceric sulfate as for potassium permanganate. Ceric sulfate can be used in the determination of arsenic, antimony, iron, hydrogen peroxide, ferrocyanide, uranium, nitrite, thallium, etc., with equal ease and accuracy as compared to potassium permanganate. Solutions of ceric sulfate from 0.01 N to 0.1 N or stronger are stable both hot and cold indefinitely and indicators and raw materials are now easily available. These points are increasingly clear from an examination of the following list of advantages.

List of Advantages

A list of advantages derived from the use of ceric sulfate as a standard oxidizing agent is apparent by reference to the various papers cited in the bibliography. The list follows:

1. The stability of standard ceric sulfate solution has been proven over a wide range of sulfuric acid solutions (10-40 cc. conc. H_2SO_4 per liter.)

2. Ceric sulfate may be used in the determination of reducing agents in the presence of high concentration of hydrochloric acid. This is in sharp distinction to the similar use of potassium permanganate.

3. Ceric sulfate solutions can be standardized by practically the same methods as those employed when working with potassium permanganate. Thus, sodium oxalate or oxalic acid may be used in sulfuric, hydrochloric, perchloric, or acetic acid solution. Phosphoric acid may be present when ceric sulfate is used as standard solution, but, since ceric phosphate is insoluble, phosphates must be absent during the titration of ceric salts with standard reducing agents except when practically all the ceric salt has been reduced. Ferrous sulfate solutions, Mohr's salt, pure iron, or standard iron ores may be used to standardize ceric sulfate solutions in sulfuric, hydrochloric, or other acid solutions. Stannous chloride and mercuric chloride may be used in the quantitative reduction of iron preparatory to the comparison with ceric sulfate. For these reactions the following indicators can be employed: diphneylamine, diphenylbenzidene, methyl red, methylene blue, erio glaucine, and erio green as well as in some cases the color of ceric iron itself and, in all cases, the electrometric end-point.

4. High normal oxidation-reduction potentials result in the case of ceric salt reactions.

5. The valence change is simple. One change only is possible, $Ce^{++++} + e \longleftrightarrow Ce^{+++}$.

6. Ceric salts are almost unique among the stable powerful oxidizing agents in having a cation as the primary active constituent(9).

7. Ceric ion is not too highly colored to obstruct vision when reading the meniscus of its tenth normal solution in burets, flasks, and pipets as is often the case with potassium permanganate.

8. The cerous ion is colorless. This is similar to the manganous ion but unlike the case of the chromic ion from potassium dichromate.

9. The solution of ceric sulfate and ceric salts from which it is made can now be readily purchased at a moderate price. (The G. Frederick Smith Chemical Company.)

10. Ceric sulfate is a versatile standard oxidizing agent. A partial list of elements and products that are determined follows: Oxalates, hydrogen peroxide, iron, chromium, vanadium, uranium, thiosulfate, arsenic, antimony, ferrocyanide, calcium, hydroquinone, iodide, organic acids, thallium, mercury, and tellurium.

11. The Walden indicator, ortho-phenanthroline ferrous complex in the form of its 0.025 M solution, can now be purchased or the compound ortho-phenanthroline monohydrate in crystalline form from which the indicator solution is made can be purchased. (The G. Frederick Smith Chemical Company.) This indicator virtually eliminates potentiometric end-point determination as a required procedure in many determinations using standard ceric sulfate.

12. A new method is now available for the easy preparation of ceric sulfate from low grade, cheap cerous salts. This method does away with the inconvenient methods formerly employed using ceric oxide of variable and uncertain properties and the appreciable loss in oxidation value followed by the preparation from ceric oxide.

For at least these twelve reasons, the analytical chemist of the routine or research laboratory who attempts to keep abreast of the modern developments in this field should place into immediate practice many of the methods described.

Rapid and Accurate Volumetric Methods for the Determination of Cerium in the Presence of Other Rare Earths

Section A. Oxidation of Cerium Using Sodium Bismuthate

The material of this section was rewritten based upon the paper of F. J. Metzger, reference (52).

Principle of the Method

The basis for the method described may be briefly stated as follows: Cerous sulfate in sulfuric acid solution is converted quantitatively to ceric sulfate by means of sodium bismuthate. The excess of sodium bismuthate is then removed by filtration, a known excess of ferrous sulfate added to reduce the ceric compound, the excess of ferrous sulfate being titrated with potassium premanganate.

The reactions are:

$$2Ce_2(SO_4)_3 + 2\ NaBiO_3\ \text{(excess)} + 6\ H_2SO_4 = 4\ Ce(SO_4)_2 + Na_2SO_4 + Bi_2(SO_4)_3 + 6H_2O$$

Filter off excess of bismuthate.

$$2\ Ce(SO_4)_2 + 2\ FeSO_4\ \text{(slight excess)} + (H_2SO_4) = Ce_2(SO_4)_3 + Fe_2(SO_4)_3$$

Colorless solution indicates complete reduction of ceric to cerous salt.

$$10\ Fe(SO_4)\ \text{(excess)} + 2\ KMnO_4 + 8\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8\ H_2O$$

End point determined by the first appearance of pink color of permanganate.

Solutions Required

1. Potassium permanganate solution approximately N/40 since the equivalent weight of cerium is high and a weak solution of ferrous sulfate only is required.

2. Ferrous sulfate, 10 grams of Mohr's salt and 50 ml. conc. H_2SO_4 per liter, making N/40 solution approximately.

The Method

The cerous salt in the form of sulfate in sulfuric acid (1 volume conc. H_2SO_4 to 4 volumes of water) in 100 ml. of solution is treated with 2 grams of ammonium sulfate $(NH_4)_2SO_4$ and 1 gram of sodium bismuthate is added and the solution heated to boiling. Cool somewhat and add 50 cc. of two percent H_2SO_4. Filter through a Gooch crucible (or substitute) and wash with 100-150 cc. of two percent H_2SO_4. Add standard ferrous sulfate in excess (as shown by the change from yellow to colorless) and titrate the excess of ferrous iron with permanganate. Ammonium sulfate is used to prevent retention of ceric ion by the undissolved excess of sodium bismuthate.

Accuracy of Method

Samples of C. P. cerium salts were proven as to purity by precipitation as cerous oxalate and ignition to ceric oxide. Samples of these salts were converted to cerous sulfate by evaporation with excess of sulfuric acid and analyzed as indicated above. The results were calculated on the basis of the CeO_2 content of the original salts taken and the data follow:

Sample CeO_2	CeO_2 found
g.	g.
0.1901	0.1897 and 0.1907
0.2102	0.2103 and 0.2104
0.1928	0.1928 and 0.1922

The method is rapid, requiring 15 to 20 minutes after the solution has been prepared for precipitation. The metals Th, La, Nd, Pr, Y, Er, Zr, Sm, Gd, and Ti do not interfere. By this method 0.2 mg. of CeO_2 in 100 ml. can be qualitatively detected by means of the yellow color (more intense when the solution is hot). This process is therefore one of the most delicate qualitative tests for cerium.

This procedure can be simplified by titration of the ceric sulfate solution directly to an end-point using standard ferrous sulfate if ortho-phenanthroline ferrous complex is used as internal indicator. Before titrating the filtrate from the sodium bismuthate oxidation of cerium, add two drops of the 0.025 M indicator solution. The red color of the indicator is destroyed and as the ferrous sulfate solution is added, the yellow of ceric ion is gradually taken away. A few drops before the end-point, the red color of the phenanthroline indicator is restored then dispelled and finally with the first drop excess of ferrous sulfate the solution becomes a permanent pink. The possibility of this modification to the method as originally described by Metzger has been suggested by Walden, Hammett and Chapman (44).

Section B. Oxidation of Cerium Using Ammonium Persulfate in Presence of Silver Nitrate

The material of this section was rewritten based upon the paper of Willard and Young (46).

Principle of the Method

The basis of the method described may be briefly stated as follows: Cerous sulfate in sulfuric acid solution is converted quantitatively to ceric sulfate by boiling 15 minutes with an excess of ammonium persulfate using silver nitrate as catalyst. The solution of ceric sulfate containing excess sulfuric acid and silver nitrate is titrated with standard ferrous sulfate using ortho-phenanthroline ferrous complex as indicator. The reactions are:

$$\begin{aligned}
&H_2S_2O_8 + Ce_2\ (SO_4)_3 + [AgNO_3] \longrightarrow 2Ce\ (SO_4)_2 + H_2SO_4 \\
&2Ce\ (SO_4)_2 + 2FeSO_4 + [H_2SO_4] \longrightarrow Ce_2(SO_4)_3 + Fe_2(SO_4)_3 \\
&FeSO_4\ \text{(first drop excess)} + \text{leuco-indicator} \longrightarrow \text{Color indicator (red)}
\end{aligned}$$

Reagents and Solutions Required

1. Silver nitrate catalyst. Dissolve 2.5 g. of crystals in 1000 ml. of water.

2. Standard ferrous sulfate solution, 0.05 N. Standardize using $KMnO_4$ solution compared with sodium oxalate. Store under hydrogen in the Zintl and Reinäcker apparatus. The ferrous sulfate may be made from Mohr's salt. 19.607 g. of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ dissolved in 20 ml. of sulfuric acid (sp.gr. 1.84) diluted to 200-300 ml. with water. Finally dilute to 1000 ml. exactly.

3. C. P. ammonium persulfate, $(NH_4)_2S_2O_8$

The Method

The cerous sulfate to be analyzed, estimated to contain 0.15 to 0.25 grams of cerium, is dissolved in 5 ml. of sulfuric acid, sp.gr. 1.84, diluted to 200 ml. and 5 ml. of silver nitrate solution added. Two grams of crystals of ammonium persulfate are added to the mixture contained in a 400 ml. beaker and the solution gently boiled in a covered beaker for 10 minutes. Cool to room temperature and titrate with 0.05 N ferrous sulfate electrometrically using a silver chloride-platinum electrode system. The "break" at the end point is 200–250 millivolts.

Cerous salts may be analyzed in nitric acid solution as above, using 5 ml. of nitric acid, sp.gr. 1.42, in place of sulfuric acid. Results by both of these methods are shown in Table I.

TABLE I.

Oxidation of Cerium with Persulfate, Silver Nitrate as Catalyst. Titration with Ferrous Sulfate Electrometrically.

Acid ml.		$(NH_4)_2S_2O_8$ g.	$AgNO_3$ cc.	Ce Taken g.	Ce Found g.
2.5	H_2SO_4 (sp.g. 1.84)	1	5	0.1860	0.1863
2.5	"	0.5	5	.1860	Low
2.5	"	1	5	.1116	.1118
2.5	"	3	5	.3720	.3722
2.5	"	2	5	.3720	.3719
10.0	"	2	10	.1860	.1859
10.0	"	4	10	.1860	.1860
10.0	"	5	5	.1860	.1858
10.0	"	5	2.5	.1860	.1856
5.0	"	2	2.5	.1860	.1860
5.0	"	4	2.5	.3720	.3722
5.0	HNO_3 (sp.g.1.42)	2	2.5	.1860	.1858
10.0	"	4	2.5	.1860	.1849

This method can be applied directly as described without the use of the potentiometric titration of the ceric ion with ferrous sulfate. This possibility was first suggested by Walden, Hammet and Chapman (see page 10). Their predictions are substantiated by trial. Instead of titrating the oxidized cerium with ferrous sulfate as above outlined add 2 drops of ortho-phenanthroline ferrous complex and titrate with 0.05 N ferrous sulfate until the yellow solution is decolorized and slowly dropwise thereafter until the solution is permanently pink. This method is approved following the study of Willard and Young (45).

A new method for use in the determination of cerium following oxidation by a mixture of perchloric and sulfuric acids is now being studied by the author. Preliminary results indicate the method to be possible with certain advantages. This new method is applied to the preparation of anhydrous ceric sulfate and ceric ammonium sulfate as described in this booklet in the pages immediately following.

MIXED PERCHLORIC AND SULFURIC ACIDS AND THEIR ANALYTICAL APPLICATIONS

II. THE PREPARATION OF CERIC SULFATE FROM CEROUS SALTS

By G. Frederick Smith

Introduction

The increase in the number of practical quantitative applications in the use of ceric sulfate as a standard oxidizing agent justifies studies having as objective improved methods in its preparation. The most common starting material is hydrated cerous oxalate which is as well the cheapest source. The common method consists in the conversion of this material by ignition in air to form ceric oxide followed by conversion to ceric sulfate by digestion with hot concentrated sulfuric acid. This method is not generally satisfactory due to incomplete solubility of the ceric sulfate thus formed in dilute sulfuric acid. Hydrated ceric oxide corresponding to the formula $CeO_2 \cdot 2H_2O$ has been used to advantage because more easily soluble after treatment with sulfuric acid but is more expensive. The most soluble salts of the cerous series are the chloride, nitrate, and perchlorate, the use of the last named for some reasons being more suitable than either of the preceding. The present method has proven highly efficient in the preparation of ceric sulfate starting with cerous oxalate working through the nitrate or chloride to the perchlorate with final conversion and oxidation using a mixture of perchloric and sulfuric acids. The method has the advantages of speed and ease of manipulation together with the advantage that low grade raw materials give equally as good results as better quality reagents and the reactions are carried out in the wet way throughout. Rare earth impurities generally associated with cerium have been shown to have no undesirable effect.

Perchloric Acid as Oxidizing Agent in the Conversion of Cerous to Ceric Salts

Perchloric acid in strength from 70 to 85 percent when heated with cerous perchlorate does not form ceric perchlorate although this product has been shown to exist through the work of Fichter and Jenny(47). They showed that a 25 percent solution of serous perchlorate in 20 percent perchloric acid can be practically quantitatively oxidized to ceric perchlorate by electrolytic oxidation. As will be shown in the present paper, 70 to 72 percent perchloric acid can be used in the quantitative oxidation of cerous to ceric sulfate. The reason for the failure of perchloric acid alone to oxidize cerous perchlorate consists in the fact that it is reduced as fast as formed by the simultaneous formation of hydrogen peroxide, a reaction which is catalyzed by the presence of cerium in solution. The study of this per-acid property of perchloric acid was the subject of the first paper in this series (48). The attempt of Fichter and Jenny to obtain ceric perchlorate by concentration of its solution in perchloric acid resulted in its decomposition to cerous perchlorate in accordance with the same principles. Ceric sulfate may be prepared by electrolytic oxidization of cerous sulfate as shown by Hengstenberg (49). Ceric sulfate is quantitatively insoluble in 70 to 72 percent perchloric acid mixtures with 75 to 80 percent sulfuric acid. By reason of this fact, cerous sulfate can be quantitatively oxidized to ceric sulfate by heating at suitable temperatures, with these mixed acids. The cerous sulfate which is appreciably soluble in the mixed acids is oxidized to ceric sulfate by the hot perchloric acid and precipitates from the solution, in which case the oxidizing agent is not catalyzed in its reduction to hydrogen peroxide and the conversion is complete. The insoluble ceric sulfate is separated from the mother liquor by centrifuging and decantation, washed with several portions of 75 to 80 percent sulfuric acid to eliminate perchloric acid and is finally dissolved by the addition of water to the residue moist with sulfuric acid under which conditions it is rapidly and easily soluble and can be diluted to convenient strength for use as a volumetric oxidizing agent.

Preparation and Properties of Hydrated Ceric Oxide

Hydrated ceric oxide varies in composition from CeO_2 to $CeO_2 \cdot 4H_2O$ depending upon the temperature at which the higher hydrate is ignited. Cerous chloride is precipitated as a cerous hydroxide and a suspension of this product is oxidized to hydrated ceric oxide using alkali hypochlorite or bromite which is then dried or ignited depending upon the degree of dehydration desired. At a temperature of 200° C the dehydration gives the composition $CeO_2 \cdot 2H_2O$, stable up to approximately 600° C. Above this temperature anhydrous ceric oxide is formed (50). The di-hydrated ceric oxide is soluble in nitric acid forming ceric nitrate and in concentrated hydrochloric acid with the evolution of chlorine forming cerous chloride. It is soluble in concentrated sulfuric acid after heating and dilution, some oxygen being evolved, leaving 93 to 95 percent as soluble ceric sulfate as shown by Carnelley and Walker (51). The completely dehydrated material ignited at temperatures between 600° and 800° C is practically insoluble in nitric, hydrochloric or perchloric acid and can be only partially dissolved in these acids even with the addition of hydrogen peroxide. Hot concentrated sulfuric acid converts it to ceric sulfate with slight reduction to cerous sulfate and the product thus obtained is soluble to a greater or less extent in dilute sulfuric acid depending upon purity and the extent of reduction to cerous sulfate, 5 to 8 percent. The most desirable form of hydrated ceric oxide for use in the preparation of sulfuric acid solutions of ceric sulfate is therefore the composition corresponding to the formula $Ce(OH)_4$. Any of the forms described above may be sufficiently well converted to cerous perchlorate for use in the present method of digestion with nitric or hydrochloric acid in the presence of hydrogen peroxide followed by fuming with perchloric acid. It is better, however, to use as starting material hydrated cerous oxalate.

Preparation of Cerous Perchlorate from Hydrated Cerous Oxalate

As starting material a sample of hydrated cerous oxalate of selected poor grade was obtained from monazite sand by the usual process. The samples were supplied by the Division of Inorganic Chemistry through the courtesy of Professor B. S. Hopkins. Samples were ignited at 1000° C and the residue of impure CeO_2 found to be 46.35 percent of the weight of cerous oxalate as the mean of two closely agreeing duplicates. Theory for $Ce_2(C_2O_4)_3 \cdot 9H_2O$ corresponds to 48.72 percent. The impure ceric oxide thus obtained was digested with hot concentrated sulfuric acid for 10 minutes at 200° C, cooled, diluted, and the ceric sulfate solution thus obtained was titrated with standard ferrous sulfate using erio-glaucine as indicator according to the process described by Furman and Wallace (13). The result indicated the presence of 21.69 percent of CeO_2, theory for hydrated cerous oxalate being 48.74 percent. Since it has been shown (51) that this process of preparing ceric sulfate gives slightly low results because of partial reduction to cerous sulfate by treatment with hot concentrated sulfuric acid, solution of a sample of the same ceric oxide obtained as above described was analyzed following the oxidation of the sulfuric acid solution using sodium bismuthate according to the process of Metzger (52) The result indicated the presence of 22.08 percent CeO_2 which indicates approximately 2 percent reduction of ceric to cerous sulfate during solution of the sample. The ignited cerous oxalate was chocolate brown instead of white, although the cerous oxalate from which it was prepared had but a slight pink color. The samples of cerous oxalate used for the following preparation of ceric sulfate were therefore extensively impure due to the presence of rare earth oxalates to the amount of more than 45 percent of the sample. A second sample of cerous oxalate analyzed 30.40 percent CeO_2 and was therefore 62 percent pure.

The Oxidation of Cerous Perchlorate Using Hot Perchloric and Sulfuric Acid Mixtures

As previously stated, cerous perchlorate in perchloric acid solution is not oxidized to ceric perchlorate at any concentration of the acid nor at the boiling point. The hot concentrated perchloric acid reverses the reaction due to the formation of hydrogen peroxide. The presence of sulfuric acid forms cerous sulfate from the perchlorate which is relatively insoluble in the hot acid mixture and under these conditions is rapidly oxidized and precipitated. The study was therefore made of these reactions; acid concentration, temperature and time being studied as variables.

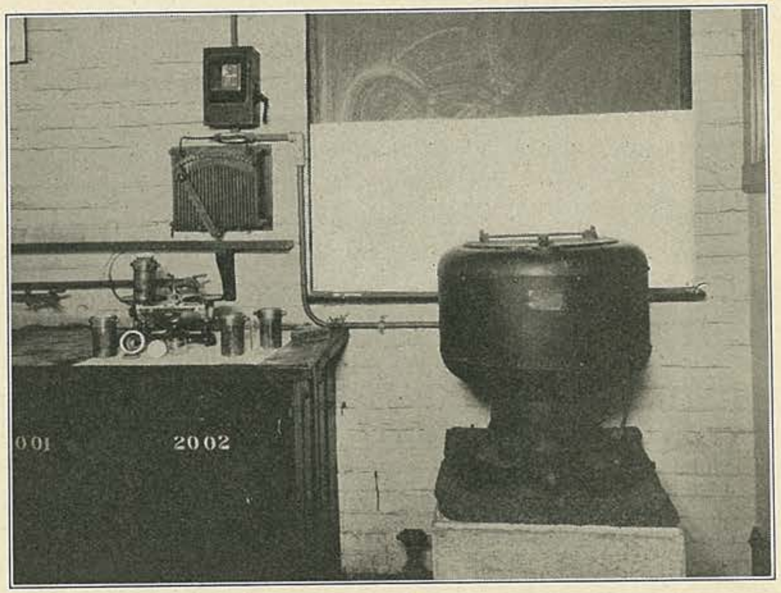

FIG. 1

Forty or sixty gram samples of the hydrated cerous oxalate described above were placed in 600 ml. pyrex beakers and dissolved in 75 ml. of concentrated nitric acid at or near the boiling point of the resulting solution. When brown fumes were no longer evolved, 40 to 50 ml. of 70 to 72 percent perchloric acid were added and the mixture concentrated to fumes from the acid. Forty to sixty ml. of 75 to 85 percent sulfuric acid were then added and the paste of sulfates thus formed heated to various temperatures for various times and the oxidized ceric sulfate paste thus obtained was cooled rapidly to room temperature. The products of the reaction were centrifuged at 1000 to 1500 R. P. M. at approximately 8.5 inches radial distance from the center of rotation, the samples being contained in centrifuge bottles having the top removed to make beaker shapes. (See Figure 2.) The super-natant acid mixture of perchloric and sulfuric acids was removed by decantation and the residue of ceric sulfate was washed twice with 20 ml. of 75 percent sulfuric acid using centrifugal separation as before. The ceric sulfate paste was then dissolved by the addition of water and final dilution to 500 ml. in a graduated flask from which a measured portion was withdrawn for analysis. The samples thus obtained were easily soluble in water without the addition of sulfuric acid other than that left after centrifuging. A sintered glass Buchner funnel may be substituted for the centrifugal filtration but it is not as satisfactory. The results under various conditions are shown in Tables I and II.

TABLE I

Oxidation of Cerous to Ceric Sulfate Using 72 Per Cent Perchloric Acid and 80 to 85 Per Cent Sulfuric Acid

Hydrated cerous oxalate, 22.08 pct. CeO_2 = 40 g.
Ceric oxide (impure) present = 19.5 g.
Excess $HClO_4$ used = 13.5 g.
Excess H_2SO_4 used = 9 to 10 g.
Calculated cerium value for total sample = 46.72 ml. Normal $Ce(SO_4)_2$

H_2SO_4 Per Cent	Temperature Degrees, C.	Time Min.	Normal Ce^{IV} found, ml.	Oxidation Per Cent
80	190	5	33.91	72.5
85	190	5	22.19	47.5
80	160-180	15	33.41	71.5
80	160-170	30	46.16	98.8

TABLE II

The Oxidation of Cerous to Ceric Sulfate Using 72 Per Cent Perchloric Acid and 75 Per Cent Sulfuric Acid.

Hydrated cerous oxalate, 30.4 pct. CeO_2 = 60 g.
Ceric oxide (impure) present = 31.1 g.
Perchloric acid used = 50 ml. (72 pct.)
Sulfuric Acid used = 50 ml. (75 pct.)
Calculated cerium value for total sample = 88.00 ml. Normal $Ce(SO_4)_2$

Temperature, Degrees, C.	Time, Min.	Volume Normal Ce^{IV} ml.	Oxidation Per Cent
170 - 180	5	51.4	58.4
130 - 140	30	64.15	72.9
150 - 160	15	88.06	100.0
150 - 160	30	92.11	>100.0

Discussion of Results

From Table I is observed that at 190° C with 80 percent sulfuric acid, oxidation is incomplete. With 85 percent sulfuric acid at the same temperature, the reaction is less complete. The 85 percent sulfuric acid concentrates the perchloric acid present by its dehydrating effect, and the reduction of cerium results from the increase in formation of hydrogen peroxide. By lowering the temperature to 160-180° C. and increasing the time, using 80 percent sulfuric acid, the oxidation is still incomplete. Using the same strength of sulfuric acid at 160-170°, the reaction is almost complete in 30 minutes.

From the results of Table I, it was concluded that a decrease in sulfuric acid strength from 80 to 75 percent would be desirable at somewhat lower temperatures. Sulfuric acid of 75 percent strength (sp.gr. 1.675) mixed with 72 percent perchloric acid causes no dehydration of the latter. Ceric sulfate is insoluble in this acid mixture and at 150-160° C. no hydrogen peroxide is formed to reverse the oxidation of cerium. By examination of Table II, the time required for complete oxidation lies between 15 and 30 minutes. Higher temperatures and shorter time or lower temperatures at equal time intervals give incomplete oxidation. The last result in Table II indicates that due to the partial solubility of the ceric oxide produced from the ignition of cerous oxalate used as raw material, the analysis after dissolving in sulfuric acid gave low results. The process described is proposed as a method to be followed in the quantitative determination of cerium and the method is being studied to this end.

Cost in the Preparation of Ceric Sulfate Solutions

One pound of hydrated cerous oxalate which analyzes 45 percent CeO_2 (theory, 48.72 percent) results in the preparation of approximately 12 liters of N/10 ceric sulfate. This preparation required 1.5 lbs. of 70 percent perchloric acid which should be technical grade. At 55 cents per lb. for cerous oxalate and 70 cents per lb. for technical perchloric acid and allowing 20 cents as the cost of the technical sulfuric and nitric acids used, the cost of the finished solution is calculated to be 15 cents per liter. This estimate is maximum since the cost of sulfuric acid is less than assumed.

Preparation of Crystalline Ceric Sulfate Soluble in Dilute Sulfuric Acid

Ceric sulfate prepared in a mixture of 70 percent perchloric acid and 75 percent sulfuric acid after removal of the excess acids by centrifugal partition and decantation is washed with the addition of water. The removal of the excess acid also following centrifugal partition leaves a product which can be dried at 190° C. to remove excess water and sulfuric acid. The canary-yellow colored ceric sulfate thus obtained is ground in a mortar and the free flowing powder thus obtained is found to be completely soluble in warm dilute sulfuric acid which solution can be further diluted and will remain clear. Analysis of the product thus obtained using the material described in Table II showed the powdered ceric sulfate to be 50 percent $Ce(SO_4)_2$. The ceric sulfate obtained from the wash water removed after centrifuging was found after drying at 190° C. to be 86.4 percent $(Ce(SO_4)_2$. This is one of the best known forms in which to market ceric sulfate for use in the perparation of solutions for standardization.

It has been proposed to use ceric ammonium sulfate as a solid reagent easily soluble in dilute sulfuric acid as raw material with which to prepare ceric sulfate solutions. Two ceric ammonium sulfates are described in the literature with the following formulae: $2Ce(SO_4)_2 \cdot 3(NH_4)_2SO_4 \cdot 3H_2O$ and $Ce(SO_4)_2 \cdot 3(NH_4)_2SO_4 \cdot 3H_2O$. The average of these two molecular species is $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ which is the formula ascribed to the double ceric ammonium sulfate by Willard and Furman (53). This double ceric ammonium sulfate may be prepared by adding to the dilute sulfuric acid solution of ceric sulfate described in the foregoing material the proper molecular ratio of ammonium sulfate and concentrating until the solution deposits the orange crystals of the mixed salt and the supernatant solution is but slightly colored. These crystals are filtered and redissolved and recrystallized. The final crystal crop is dried at 100° C. or less and is found to be easily soluble in dilute sulfuric acid and from 80 to 90 percent pure even starting with a cerium material containing no more than 60 percent cerium. It could possibly be made more pure with small loss by repeated recrystallization. This salt has the advantage that it is more easily soluble in dilute sulfuric acid than is anhydrous ceric sulfate but has the disadvantage that more is required for a definite volume of equal strength standard ceric sulfate. Centrifuge equipment for the filtration of ceric ammonium sulfate is shown in Figures 1 and 2. A Buchner funnel and suction filter flask may be substituted for the method using centrifugal drainage.

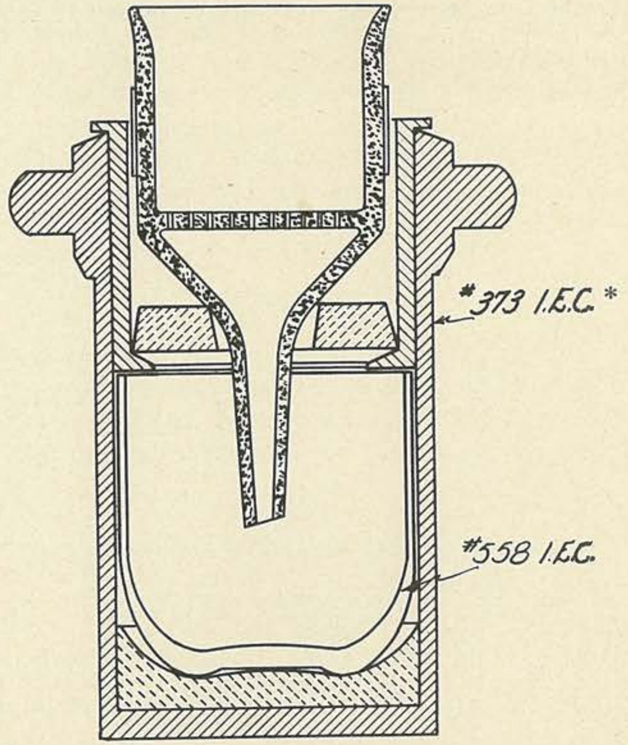

FIG. 2

*Numbers refer to International Equipment Company catalogue.

Summary

1. A method is described for the preparation of solutions of ceric sulfate in dilute sulfuric acid using cerous oxalate as raw material and

a mixture of 70-72 percent perchloric acid and 75 percent sulfuric acid as oxidizing agent.

2. Samples of only moderate purity in terms of cerium are satisfactory for the process described and the ceric sulfate prepared from such samples is readily soluble in dilute sulfuric acid after removal of the perchloric acid used in the oxidation.

3. A study has been made of the variation in the results obtained using different strengths of the mixed acids for the oxidation as well as the time and temperature factors.

4. The process described has been studied in the light of the influence of the per-chemical properties of perchloric acid upon the results obtained.

5. The cost for the preparation of 1 liter of N/10 ceric sulfate by the process described has been shown to be approximately 15 cents.

PREPARATION AND STABILITY OF CERIC SULFATE SOLUTIONS

This section consists of a complete reprint (34).

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT

IX. PREPARATION AND STABILITY OF SOLUTIONS

By H. H. Willard and Philena Young

Introduction

The method used by the authors to purify U. S. P. cerous oxalate and to prepare a large supply of ceric sulfate has been described in the first paper in this series.(26) From subsequent work, (27—32) especially from that dealing with the determination of vanadium and of chromium, it seemed important to investigate more thoroughly the grades of ceric oxide available in order to find the most convenient and inexpensive materials for use. Information concerning the stability of ceric sulfate solutions has also been obtained.

Experimental

Solutions were prepared from four samples of ceric oxide. The approximate amount of the oxide required for a liter of 0.1 *N* solution was taken, treated with sufficient sulfuric acid of the density indicated in Table I to make the final solution 0.5 or 1 *M* in sulfuric acid, and the paste heated at the proper temperature until the conversion into ceric sulfate appeared complete. This material, when cool, was added to about

TABLE I

Preparation and Cost of Ceric Sulfate Solutions

Material	Sp. Gr. of H_2SO_4 Used	H_2SO_4 in the $Ce(SO_4)_2$ Soln., Molar	G. of Oxide per Liter of 0.1 *N* Soln.	Cost of Oxide per Liter of 0-1 N Soln. Based on Price per 500 G.
1 High grade, anhydrous	1.83	0.5	19.2	$0.17
	1.83	1.0	18.9	.17
2 High grade, hydrated	1.5	0.5	22.5	.15
	1.5	1.0	22.3	.15
	1.3	0.5	24.0	.16
3 Commercial, hydrated	1.5	.5	46.9	.05
	1.3	.5	47.3	.05
4 Commercial, anhydrous	1.5	.5	57.9	.10

500 cc. of water, the liquid heated to 70—80° and filtered. The normality of the solution was determined with standard ferrous sulfate, and from this factor the weight of material required for a liter of 0.1 *N* solution was calculated as well as the cost of the ceric oxide for a liter of such a solution, based on the price per 500 g. In large quantities the cost would be 20—30% less.

With Material 1, a temperature of 150—160° was maintained for a half hour to convert the oxide into sulfate. A small amount of the oxide was not attacked. Sample 2 was converted very rapidly by dilute sulfuric acid into ceric sulfate, a temperature of 130—135° being required with acid of sp. gr. 1.5 and 105—110° with acid of sp. gr. 1.3. The ceric sulfate in the former case dissolved in water to give an almost clear solution; in the latter case there was a small amount of unattacked oxide. Sample 3, when treated with acid of sp. gr. 1.5, was heated to 120—125°, and to 110° if treated with acid of sp. gr. 1.3. Sample 4, the commercial anhydrous material, was not satisfactory. The commercial hydrated oxide contained iron and phosphate and a considerable amount of precipitate settled out in solutions prepared from it. The solution decanted from this precipitate was found entirely satisfactory for chromium determinations (33) in which an excess of ceric sulfate was used as the oxidizing agent, the excess being destroyed by sodium azide or by sodium nitrite followed by urea (33) before the titration of the chromic acid with ferrous sulfate. Since the oxide for a liter of such a solution costs only four or five cents, depending upon whether the price per one-half kilo or per fifty kilos of oxide is used, the cost of the reagent for a single chromium determination is very small. There seems to be no reason why this commercial hydrated material cannot be used in all the methods described by the authors (26—33) except in the case of the titration of iodide where the ferric salt might cause trouble. Even when the high grade, hydrated oxide is used, the cost of the reagent is not excessive, being only ten to fifteen cents per liter, depending on the quantity of material purchased.

Stability of Ceric Sulfate Solutions

Furman has given data over a period of twelve weeks on the stability of ceric sulfate solutions containing free sulfuric acid.(5). Table II contains data over a longer period obtained by the authors on four different solutions.

Solutions I and III were 0.5 *M* in sulfuric acid, II and IV, 1.0 *M*.

Twenty liters each of I and II and 2 liters of III were prepared, and the stock bottles were opened a number of times during the periods indicated. Only with Solution IV is the normality expressed in terms of weight normality. The values for this solution are the most accurate indication of the stability of ceric sulfate, for the portion tested after a 33-week interval had been standing during that time in a sealed flask in a well lighted room. These data indicate that ceric sulfate solutions are far more stable than permanganate solutions, the latter oxidizing agent being the only one which is of the same relative oxidizing power as ceric sulfate.

TABLE II

Stability of Ceric Sulfate Solutions Over an Extended Period

Time, Weeks	Normality			
	I	II	III	IV
0	0.09493	0.1043	0.05012	0.09410
10	.09488	.1042	.05009	....
16	....	....	.04996	....
20	.09497	....	....	....
27	.09480	....	....	....
33	....	.1044	....	0.09400
40	....	.1042	....	....

A number of experiments were made to test the stability of ceric sulfate solutions on boiling. In each case 25 cc. of 0.1 *N* solution was diluted with acid and water to a volume of 100 cc. This solution was boiled gently under a reflux condenser for the stated time, cooled to room temperature and titrated electrometrically with standard ferrous sulfate. The values for the normality after such treatment are given in Table III.

TABLE III

Stability of Ceric Sulfate Toward Heat

	Acid per 100 cc., cc.	Time of Boiling, Hours	Normality of $Ce(SO_4)_2$
H_2SO_4, sp. gr., 1.5	15	0	0.09322
	10	2	.09322
	20	2	.09322
	20	5	.09322
HNO_3, sp. gr., 1.42	10	1	.09111
	5+10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09328
	10+10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09288
$HClO_4$, 70%	5+10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09322
	10+10 cc. H_2SO_4 (sp. gr., 1.5)	1	.09310

These results show that ceric sulfate solutions containing free sulfuric acid, or sulfuric acid with moderate amounts of nitric or perchloric acid, are extremely stable toward heat. Such solutions, because of their strong oxidizing power, great stability, utility in a hydrochloric acid solution(27), ease of preparation and small cost, should find extensive use in analytical work.

Summary

1. The type of ceric oxide available for the preparation of ceric sulfate have been investigated. A high grade, hydrated material meets the most exacting requirements, but the commercial, hydrated product is satisfactory in nearly all cases.
2. The cost of such solutions has been shown to be very small.
3. The normality of a ceric sulfate solution containing free sulfuric acid has been found to be practically constant over a period of forty weeks. Such a solution is not sensitive to light or air.
4. The normality of a ceric sulfate solution containing free sulfuric acid, or sulfuric acid with a little nitric or perchloric acid, is not changed by boiling the solution for an hour or longer, but the solution loses oxygen if a high concentration of either of the two latter acids is present.

STANDARDIZATION OF CERIC SULFATE SOLUTIONS

The following section consists of a reprint of part of the paper (26) by H. H. Willard and Philena Young.

Since it is very desirable to use a primary standard for this purpose, a study was made of the titration of sodium oxalate in hot solution, with ceric sulfate, the reaction being

$$Na_2C_2O_4+2Ce(SO_4)_2=Na_2SO_4+2CO_2+Ce_2(SO_4)_3$$

Portions of a standard solution of sodium oxalate from the U. S. Bureau of Standards were acidified with sulfuric acid, heated nearly to boiling and titrated electrometrically with 0.1 *N* ceric sulfate prepared from the ignited oxide containing 85.1% of CeO_2. Two cc. of sulfuric acid were contained in the ceric sulfate used. In all of this work a silver chloride-platinum electrode system was used. The silver chloride electrode in 0.1 *N* potassium chloride was placed directly in the liquid to be titrated. The results are shown in Table I.

These data indicate that concordant results may be obtained when the volume of the solution is varied from 100-300 cc. (larger variations in volume were not studied) and when the weight of sodium oxalate is changed over wide limits. The end-point equilibrium is quite rapid if not more than 2.5 cc. of conc. sulfuric acid is present per 100 cc. of solution at the time of titration. The high result obtained in the last experiment is probably due to the low acid content of the solution. No

TABLE I

Effect of Sulfuric Acid

$Na_2C_2O_4$, g.	Initial Vol., cc.	H_2SO_4, Sp. Gr. 1.83, at Beginning, cc.	$Ce(SO_4)_2$, Normality	Character of End-point
0.2679	200	0	0.1067	Rapid
.2679	200	5	.1067	Fairly rapid
.2679	200	10	.1067	Slow
.2679	300	0	.1067	Rapid
.2679	300	7.5	.1068	Fairly rapid
.2679	300	15	.1068	Slow
.2679	100	0	.1067	Rapid
.2679	100	2.5	.1067	Slow but usable
.2679	100	5	.1068	Too slow
.1339	300	7.5	.1067	Rapid
.5358	300	0	.1067	Rapid
.1339	300	0	.1081	Fairly rapid

acid was added before the titration and only 1.85 g. of sulfuric acid was present in the ceric sulfate. It is probable that not quite all of the cerous oxalate was dissolved. In the other experiments in which no acid was added, a considerable quantity of cerous oxalate precipitated on the addition of the first portion of ceric sulfate and then dissolved as more of the reagent was added.

Experiments showed that the equilibrium at the end-point was reached too slowly in all cases if the temperature of the solution at the end of a titration was below 70°. At or above this temperature results were as indicated in Table I.

The results were identical no matter whether the ceric sulfate solution was added slowly to the oxalate, as would be necessary in a permanganate titration, or rapidly from a pipet.

Portions of a standard solution of sodium oxalate were acidified with hydrochloric acid, heated nearly to boiling and titrated electrometrically with 0.1 *N* ceric sulfate. The equilibrium at the end-point was rapid in all cases. The results are shown in Table II.

TABLE II

Effect of Hydrochrolic Acid

NaC_2O_4, g.	Initial Vol., cc.	HCl. Sp. Gr. 1.18, at beginning, cc.	$Ce(SO_4)_2$, Normality
0.2679	200	0	0.1043
.2679	200	5	.1043
.2679	200	20	.1042
.2679	200	40	.1043
.2679	200	60	.1043
.2679	100	10	.1042
.2679	300	30	.1042
.1339	300	30	.1041
.5358	300	30	.1043

It is seen that ceric sulfate may be used with no special precautions in strong hydrochloric acid solutions and thus has a decided advantage over permanganate. The end-point break in the above experiments averaged about 175-200 mv. per 0.02 cc. of 0.1 *N* ceric sulfate, and fifteen minutes after the completion of a titration not the slightest decrease in potential had occurred.

Experiments similar to those made in Tables I and II showed that as much as 60 cc. of 73% perchloric acid or 50 cc. of glacial acetic acid per 200 cc. of solution could be used instead of sulfuric or hydrochloric acid and the end-point equilibrium was rapid. The presence of even 5 cc. of conc. nitric acid in this same volume, however, gave too high a value for the ceric sulfate, showing that this acid had a slight effect on the oxalate. Phosphoric and hydrofluoric acids must be absent, even if considerable hydrochloric acid is present, as they cause the formation of insoluble cerium salts. In the titration of ferrous ion in hydrochloric acid solution with ceric sulfate, which is described later, the presence of a moderate amount of phosphoric acid causes no interference, probably because this reaction is a more rapid one than the oxalate-ceric sulfate reaction. Experiments using ceric sulfate solution prepared from pure CeO_2 gave the same results.

Since in the titration of oxalate the solution is colorless until an excess of ceric sulfate is present, the possibility of using a visual end-point was investigated. An initial volume of 200 cc. containing 10-20 cc. of conc. hydrochloric acid, was used. If an equal volume of water is taken as a comparison liquid, the slightest change in color at the end-point is easily seen. A blank determination made at 70° on 200 cc. of water containing 20 cc. of conc. hydrochloride acid and 3-5 cc. of conc. sulfuric acid (the volume in the ceric sulfate added) showed that 0.05 cc. of 0.1 *N* ceric sulfate was required to give a pale yellow color. Unless sulfuric acid was added, the ceric sulfate was reduced. When this amount was subtracted from the volume of ceric sulfate used in a titration the normality corresponded exactly to that obtained electrometrically.

Quantitative results were obtained in the reverse titration of ceric sulfate with sodium oxalate in hot solution when as much as 5 cc. of conc. sulfuric acid were present per 200 cc. of solution. If more sulfuric acid was used, the equilibrium at the end point was too slow. Twenty-five cc. of perchloric acid (73%) or 5-20 cc. of conc. nitric acid in the same volume gave quantitative results with a fairly rapid end-point equilibrium. Hydrochloric acid had a reducing effect on the ceric sulfate present in the hot solution. The end-point breaks amounted to 150-200 mv. per 0.03 cc. of 0.1 *N* sodium oxalate except in the nitric acid solutions where they were about half this magnitude. It was found that this electrometric titration with oxalate could be used after a bismuthate oxidation, but the equilibrium in the region of the end-point was quite slow, due to the large amount of acid present.

Iodine Chloride as Catalyst

Later work which showed the value of certain iodine compounds as catalyst in the reaction between arsenite and ceric salt suggested the possibility of titrating oxalate at room temperature in the presence of such a catalyst. It was found that the titration of oxalate in hydrochloric acid solution containing iodine chloride proceeded rapidly and quantitatively at room temperature. Iodine chloride was chosen, although iodine or iodate worked equally well, because it necessitated no blank correction in the volume of ceric sulfate used, since the final form of the catalyst in all cases was iodine chloride. The catalytic action of the iodide or iodate seemed a little slower than that of iodine chloride and the blank required for either was an objection.

The action of the catalyst in this reaction is not clear. It was found that iodine chloride is not reduced at all by oxalate in hydrochloric acid solution in thirty minutes, nor does it catalyze at room temperature the action of oxalate in hydrochloric acid solution with (1) potassium permanganate, (2) potassium dichromate, or (3) potassium iodate. Its catalytic action seems to be confined to the ceric salt titration and this suggests the possibility that the ceric ion is an important factor, since cerous salt was found not to catalyze the action between the iodine chloride and oxalate. This same conclusion was drawn from work with the arsenite titration. This subject is being investigated.

The iodine chloride solution was prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and adding all at once 250 cc. of conc. hydrochloric acid. The solution thus obtained was 0.005 *M* in iodine chloride. It was adjusted electrometrically by adding the proper amount of dilute potassium iodide or iodate.

Measured portions of a standard solution of sodium oxalate were acidified with hydrochloric acid. Iodine chloride was added and water to a total volume of 100 cc. The end-point was determined electrometrically. The results are shown in Table III. In the lower acid range (first experiment) the reaction is at first more rapid than in the higher acid range (third experiment), but the equilibrium at the end-point is slower. The addition of 15-25 cc. of conc. hydrochloric acid per 100 cc. of solution, not considering the acid present in the iodine chloride solution, gives the most favorable conditions for a titration. The values of the blanks in the last two experiments, +0.49 cc. and —0.46 cc. correspond very closely with the volumes of ceric sulfate theoretically required, +0.48 cc. and —0.46 cc., to convert either of the catalysts into iodine chloride. The potential at the beginning of a titration is approximately 625-675 mv., but drops to 400-450 mv. during the addition of the first few cubic centimeters of oxidizing solution. At the end-point the break in potential averaged 200-250 mv. per 0.03 cc. of 0.1 *N* ceric sulfate.

TABLE III

Titration of Oxalate, Iodine Chloride as Catalyst

$Na_2C_2O_4$, 0.1 *N*, cc.	HCl, Sp. Gr. 1.18, at Beginning, cc.	ICl, cc.	Ce $(SO_4)_2$ 0.1 *N*, cc.	Character of End-point
10	10	10	9.98	Slow
10	15	10	9.99	Rapid
10	25	10	9.98	Rapid
10	20	5	9.99	Rapid
10	15	20	9.99	Rapid
50	15	10	49.94	Rapid
50	25	10	49.90	Slow
10	20	10 cc. 0.0025 *M* KI	10.49	Rapid
10	15	5 cc. 0.0025 *M* KIO_3	9.54	Fairly slow

Methylene blue has been proposed by Sinnatt (42) instead of starch in iodimetric titrations, and Atack (43) has discussed its use as a volumetric reagent in oxidation-reduction reactions. This dye was found to give an excellent end-point in the titration of oxalate with ceric salt in the presence of iodine chloride as catalyst, provided that certain rather narrow experimental conditions were maintained.

During this titration the solution is pale yellow, and as the end-point is approached becomes a deeper yellow, due to the presence of free iodine. As the last portion of ceric sulfate (0.2-0.3 cc.) converts this into iodine chloride, the yellow color gradually fades out. In a titration in which the end-point equilibrium is rather slow, the electrometric break in potential is indicated when the solution is still somewhat yellow and two or three minutes or longer may be required for this color to bleach out. The color disappears much more quickly when conditions are such that the end-point equilibrium is rapid. Experiments have shown that methylene blue cannot be added until within 0.4 cc. of the end-point, and the color change is much sharper if it is not added until within 0.2-0.3 cc. Therefore conditions for a rapid end-point equilibrium must be chosen. When 2 drops of the indicator are added to a pale yellow solution, the solution turns green, and with each succeeding drop of ceric sulfate becomes more blue until a final drop or two of the oxidizing agent causes the whole liquid to turn a deep pink color, which in five to ten seconds changes to a permanent blue shade. Under some conditions the entire solution will not become pink, in which cases, as well as in the above, the end-point is taken as the reading for the last drop which caused the appearance of any pink color in the solution.

Measured portions of a standard solution of sodium oxalate were taken. Iodine chloride and hydrochloric acid were used after sufficient water had been added to make the total volume of the solution 100 cc. at the time of titration. Two drops of a 0.1% solution of methylene blue in water were added when within 0.2-0.3 cc. of the end-point. The results are shown in Table IV.

TABLE IV

Titration of Oxalate—Methylene Blue Indicator

$Na_2C_2O_4$ 0.1 *N*, cc.	HCl, Sp. Gr. 1.18, at Beginning, cc.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Character of End-point Color Change
10	15	10.01	Satisfactory
10	20	9.98	Excellent
10	25	9.99	Excellent
10	35	?	Not satisfactory
25	10	24.99	Fairly satisfactory
25	15	24.97	Satisfactory
25	20	24.99	Excellent
25	25	?	Not satisfactory
50	20	49.83	Satisfactory
50	15	49.90	Excellent

The amount of iodine chloride was varied, but 10 cc. were found to give the best results.

Titrations of Ferrous Iron with Ceric Sulfate

To be able to compare the titrations of ceric sulfate against (1) oxalate and (2) ferrous sulfate as a further check on this method of standardizing a ceric salt, the conditions necessary for the ferrous iron-ceric salt reaction were determined.

$$2FeSO_4+2Ce(SO_4)_2=Fe_2(SO_4)_3+Ce_2(SO_4)_3$$

The same volume of ceric sulfate was required in each of 6 titrations of 40 cc. of 0.1 *N* ferrous sulfate in which the volume was varied from 100-300 cc. and the sulfuric acid, sp. gr. 1.83, from 0-25 cc. per 100 cc. of solution. The end-point was determined electrometrically; the end-point equilibrium was rapid in every case and the break in potential amounted to 250-300 mv. per 0.02 cc. of 0.1 *N* ceric sulfate.

Similar results were obtained when hydrochloric or perchloric acid was used. With as much as 40 cc. of conc. hydrochloric acid or 40 cc. of perchloric acid (73%) per 100 cc. of solution, the end-point equilibrium was rapid and the break in potential large. Nitric acid, however, was detrimental and the presence of 5 cc. of it per 100 cc. of solution caused a decided decrease in the volume of ceric salt used.

The titration of ceric salt with ferrous sulfate went smoothly when considerable sulfuric or perchloric acid was present. Five cc. of conc. hydrochloric acid per 100 cc. of solution containing 25 cc. of 0.1 *N* ceric sulfate caused no interference if the titration was made without delay. If the solution was allowed to stand for five to fifteen minutes before titration, the reducing action of the acid became evident. Quantitative results were obtained with the use of as much as 30 cc. of conc. nitric acid per 100 cc. of solution.

Comparison of Standardizations against Oxalate and Iron

A weight buret was used for the ceric sulfate solution. The samples of sodium oxalate were from the Bureau of Standards and the impurities in the electrolytic iron had been accurately determined. In the titrations of oxalate, in one series, 0.35-0.40 g. samples were dissolved in 200 cc. of water, 10 cc. of conc. hydrochloric acid added and the solutions heated nearly to boiling before titration; while in the second series the samples were dissolved in 75 cc. of water, 15 cc. of conc. hydrochloric acid and 10 cc. of iodine chloride before titration. In the third series, the samples of electrolytic iron were dissolved in hydrochloric acid, and ferric chloride reduced with a slight excess of stannous chloride, the cooled solution diluted to 150 cc., 10 cc. of saturated mercuric chloride solution added and the solution titrated(27). The electrometric method was used in all cases. During the titration an atmosphere of carbon dioxide was maintained above the solution to prevent any oxidation of the ferrous iron by air. Later work showed that if this precaution was not taken there was an error of approximately one part in a thousand.

TABLE V

Weight Normality of Ceric Sulfate by Different Methods

Against	(1) Electrolytic Fe, 99.97% Fe	(2) $Na_2C_2O_4$ in Hot Soln.	(3) $Na_2C_2O_4$ at Room Temp. with ICl as Catalyst
	0.09410	0.09410	0.09406
	.09414	.09416	.09409
	.09408	.09407	.09409
	.09409	.09406	.09404
Average	.09410	.09410	09407

CERIC SULFATE IN THE VOLUMETRIC DETERMINATION OF IRON

The following section consists of a reprint of part of the papers by H. H. Willard and Philena Young (27) and by N. H. Furman and J. H. Wallace, Jr. (13).

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT
II. DETERMINATION OF IRON

By H. H. Willard and Philena Young

The possibility of titrating ferrous iron with ceric sulfate has been investigated by the authors (26) and has been found to give quantitative results in either hydrochloric, sulfuric or perchloric acid solution. Furman(7) has also studied this reaction in sulfuric acid solution. It seemed important to study the application of this titration to the analysis of iron ores in which the iron was reduced in hydrochloric acid solution with stannous chloride, the excess of the latter being removed with mercuric chloride, because some of the present methods for titrating the iron after such a reduction have certain undesirable features. If permanganate is used as the oxidizing agent, the concentration of hydrochloric acid must be small because of its reducing action. Manganese sulfate is added but even with this precaution the end-point obtained is fleeting, and some experience with the method is required for accurate results. This end-point has been determined electrometrically. If the titration is made with dichromate, potassium ferricyanide may be used as an external indicator, an inconvenient process, or diphenylamine as an internal indicator (40), the change in color being from a green to a deep blue shade. Many persons find it difficult to obtain a sharp color change in this latter case. The determination of the end-point electrometrically is very satisfactory.

Experimental

A standard iron solution was made by dissolving electrolytic iron (99.97% Fe) in hydrochloric acid. The ferrous chloride was largely oxidized by the addition of potassium chlorate. To 20 cc. of this solution, containing 0.3032 g. of iron, 5 cc. of hydrochloric acid, sp. gr. 1.18 were

added and the reduction carried out with stannous chloride in the usual way. The solution was cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride and the indicated volume of hydrochloric acid added, and the solution titrated with ceric sulfate which had been standardized against sodium oxalate. Experiments similar to those above, in which 35 mg. of arsenic as sodium arsenite, or 15 mg. of manganese as manganese sulfate or both, were added to the iron solution before reduction with stannous chloride showed that neither of these elements caused any interference. Such would not be the case with arsenic in some other methods.

TABLE I

Results Obtained Electromerically

HCl, Sp. Gr. 1.18 Added before Titration, cc.	Error, Mg. Fe	Remarks
0	—0.1	Very slight HgCl ppt.
0	— .4	Heavy HgCl ppt.
15	— .2	Very slight HgCl ppt.
15	— .3	Heavy HgCl ppt.
30	— .2	Heavy HgCl ppt.
50	?	No permanent break in potential at end-point. Solvent action of HCl on HgCl and reducing action of latter probably responsible.

Since diphenylamine has been used as internal indicator in the ferrous iron titration with dichromate and the present authors have found that diphenylbenzidine gave similar results, it seemed probable that either of these indicators might be applicable in the ferrous iron-ceric sulfate titrations. Such was found to be the case, and the color change at the endpoint with this latter oxidizing agent was far superior in sharpness to that obtained in a dichromate titration. This might be expected because the ceric salt is a stronger oxidizing agent than dichromate and also because the change from a green chromic salt color to a deep purple is much more difficult to see than that from a colorless cerous solution to the same deep purple shade.

The standard iron solution was reduced as described above. To the 150 cc. of solution were added 15 cc. of phosphoric acid, sp. gr. 1.37 (prepared by diluting acid of sp. gr. 1.75 with an equal volume of water), the stated volumes of hydrochloric acid and 0.1% diphenylamine (d. p. a.) or dphenylbenzidine (d. p. b.), after which it was titrated with ceric sulfate which had been standardized against sodium oxalate.

In the last two experiments the volume of the solution was 400 cc.

at the beginning of the titration. The data in Table II show that no blank correction is required for 0.8 cc. of either indicator, the amount used to obtain a sharp end-point, but that a correction is necessary with larger amounts of diphenylamine. If the end-point in a titration is overstepped it is possible to add a slight excess of standard ferrous sulfate solution, and after a few moments titrate to the end-point with ceric sulfate. The change in the color of the indicator in the reverse titration is much slower in the strong acid solution than is the development of the color with the first drop excess of ceric salt—too slow to use it in the determination of cerium.

TABLE II

Results Obtained with a Visual End-Point

HCl, Sp. Gr. 1.18, cc.	Indicator 0.1%	Error Mg. Fe.	Character of Color Change
0	0.8 cc d. p. b.	—0.3	Very sharp
15	0.8 cc. d p. b.	— .3	Satisfactory
30	0.8 cc. d. p. b.	— .3	Satisfactory
0	0.8 cc. d. p. a.	— .2	Very sharp
15	0.8 cc. d. p. a.	— .3	Satisfactory
30	0.8 cc. d. p. a.	— .3	Satisfactory
5	1.6 cc. d. p. b.	— .4	Satisfactory
5	3.2 cc. d. p. b.	— .4	Not so sharp as preceding one
5	1.6 cc. d. p. a.	± .0	Sharp
5	3.2 cc. d. p. a.	+ .8	Not so sharp
0	0.8 cc. d. p. a.	± .0	Development of color much slower
0	0.8 cc. d. p. b.	— .3	Development of color much slower

This consistent error of 0.2-0.3 mg. iron for 0.3 g. present or approximately one part in a thousand, appearing in Tables I and II, might easily be caused by oxidation by the air. The addition of 1 g. of cerous sulfate to the ferrous solution caused no increase in this error, so that its catalytic action, if any, is very slight. This error was found to disappear when the titrations were made in an atmosphere of carbon dioxide. A weight buret was used here. Because of the constancy of this error, it is possible in the analysis of iron ores either to standardize the ceric sulfate solution against an iron ore of known value or electrolytic iron, using the same experimental technique as employed in the unknown ore analyses.

Three Bureau of Standards iron ores were analyzed and a summary of the results obtained is given in Table III. Four-tenths to six-tenths g. samples were treated with 5 cc. of water and 25 cc. of conc. hydrochloric acid, and the material kept just below the boiling point until all of the ore was decomposed. The insoluble residue was filtered off, decomposed with hydrofluoric and sulfuric acids, and the salts remaining were taken up with dilute hydrochloric acid and returned to the main filtrate. Ore No. 29 contained so much silica that after treatment with hydrofluoric and a drop of sulfuric acids the material was evaporated to dryness, a small amount of sodium carbonate added and the mixture fused for 3-4 minutes. The fusion was dissolved in dilute hydrochloric acid and added to the main solution. After evaporation to 10-15 cc. the solutions were heated to boiling, reduced with a slight excess of stannous chloride, cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride solution were added and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of indicator were added before the titration. In these analyses as well as in the standardization of the ceric sulfate against electrolytic iron (99.97% Fe) no carbon dioxide was used.

TABLE III

Summary of Analyses of Iron Ores

Ore	Electrometric	Indicator D. P. A.	D. P. B.
B. of S. No. 27	69.21	....	69.25
69.26% Fe	69.27	....	69.26
	69.28	....	....
	69.23	....	....
B. of S. No. 26	58.57	58.54	....
58.62% Fe	58.54	58.57	....
B. of S. No. 29	55.75	55.73	....
55.75% Fe	55.80	55.70	....

Diphenylamine was found to be a much more satisfactory indicator than diphenylbenzidine. When ceric sulfate was added to an iron ore solution containing the latter indicator, a rather heavy, white precipitate formed which dissolved slowly. This difficulty was not encountered with diphenylamine.

Analyses were made of B. of S. ore No. 27, following the directions for the stannous chloride method through the fuming of the siliceous residue with hydrofluoric and sulfuric acids and the returning of this material to the main filtrate. Four cc. of conc. sulfuric acid were added to the solution and it was evaporated to fumes of SO_3 to remove all hydrochloric acid. Twenty-five cc. of water were added to the moist residue and the liquid heated a few moments until a clear solution was obtained. Pieces of pure aluminum were added and the solution was boiled for ten minutes after it had become colorless. The aluminum was removed, the solution diluted to 150 cc., and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of 0.1% diphenylamine were added before the titration. With the electrometric end-point the percentage of iron found was 69.20% and with the indicator 69.24%, both of which agree very well with the B. of S. value of 69.26%.

Summary

1. Standard ceric sulfate may be used to titrate the iron in iron ores after a stannous chloride reduction in hydrochloric acid or a reduction with aluminum or zinc in sulfuric acid solution.

2. Arsenious acid does not interfere in the method.

3. The end-point in the titration may be determined electrometrically or with diphenylamine as internal indicator.

4. Analyses of three Bureau of Standards ores show that this method of titrating the ferrous iron is a very accurate one.

5. Because of the constancy of the slight error due to oxidation of the ferrous iron by air during a titration, the ceric sulfate solution may be standardized against sodium oxalate and a very small correction factor applied, or against a standard iron ore or electrolytic iron of known purity, using the same experimental technique as employed in the analyses.

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VIII. USE OF METHYL RED, ERIO-GLAUCINE AND ERIO-GREEN INDICATORS IN THE REACTION BETWEEN CERIC AND FERROUS IONS

By N. Howell Furman and John H. Wallace, Jr.

Introduction

A number of applications of ceric sulfate in volumetric analysis have been described recently(1—38). The use of various organic substances, for example, methyl red, methylene blue, and methyl orange, as irreversible oxidation-reduction indicators in the titration of trivalent antimony with ceric sulfate was proposed by Rathsburg(18). We have shown that methyl red may be used as an indicator in the titration of hydroquinone with ceric sulfate(12).

We have found that methyl red is an excellent indicator in the titration of ferrous salt with ceric sulfate or *vice versa.* Upon titration of a ferrous solution with ceric sulfate, the ferrous salt is oxidized first; a slight excess of ceric sulfate oxidizes the methyl red to a substance that is brownish in concentrated solution and yellow in very dilute solution. The oxidation product is destroyed upon standing in contact with an excess of ceric sulfate.

When ceric sulfate is being titrated with ferrous sulfate solution, the latter is added rapidly until the color of the ceric ion has almost disappeared. Methyl red is added, and is oxidized to the yellowish product. Upon further addition of ferrous salt, there is a transition from yellow to violet when a slight excess of ferrous salt is present. If phosphoric acid be added, the color change agrees well with the potentiometric end-point. The color change of methyl red is much more rapid than that of diphenylamine under the same conditions. In agreement with Willard and Young(27) we find that the use of diphenylamine is unreliable in the determination of cerium with ferrous sulfate.

During the progress of our work with methyl red there appeared two publications by Knop(39) in which he suggested the use of two triphenylmethane dyes, erio-glaucine and erio-green, as reversible oxidation-reduction indicators in the titration of ferrocyanide with permanganate. We have found that these indicators are excellent for certain titrations with, or of, ceric sulfate.

Experimental

Ceric sulfate solutions of approximately 0.1 or 0.05 *N* oxidizing power and 1 *N* in sulfuric acid were prepared from commercial hydrated ceric oxide (45% CeO_2) and were standardized potentiometrically against pure sodium oxalate (26).

Methyl Red as Indicator.—Two-tenths g. of Kahlbaum preparation was treated with 100 cc. of 6 *N* sulfuric acid. Nearly all of the material dissolved, and the slight residue was filtered off; 0.05 cc. of the solution is adequate for a titration.

Titration of Ferrous Iron with Ceric Sulfate.—The data are presented in Table I.

TABLE I

Titration of Approximately 0.1 *M* Mohr's Salt Solution with 0.1120 *M* Ceric Sulfate

Ferrous soln., cc	25	25	25	25	50	50	10	10
Initial vol., cc	50	100	235	50	150	200	50	100
H_2SO_4 concn., N	0.3	0.2	0.75	3.6	1.2	1.0	0.6	0.3
Ceric soln. used	22.36	22.38	22.34	22.35	44.64	44.62	8.92	8.93
Ceric soln. calcd	22.32	22.32	22.32	22.32	44.64	44.64	8.93	8.93

The calculated values are based on the average of four concordant potentiometric determinations. In each case 0.05 cc. of indicator was used. If the solution is stirred vigorously by hand, there is a sharp end-point even when the indicator is added at the start of the titration. It is desirable, however, to add the indicator when the ceric sulfate has begun to be consumed slowly. The determinations of Table I do not show clearly what correction, if any, should be applied when 0.1 *N* solutions are used. From the results with 0.05 *M* solution it seems safe to apply a correction of 0.03 cc. to be subtracted from the buret reading in the titration of 0.1 *M* solution, this correction being approximately half of that found in Table II.

In Determinations 1-4 the ceric solution was 0.0593 *N*, and in Nos. 5-8, 0.0552 *N*. The calculated values are based on sets of four concordant potentiometric determinations. On the average 0.05 cc. of ceric sulfate needs to be subtracted from the buret reading in order to make the indicator values coincide with the potentiometric ones. When hydrochloric acid is present, the color change is not as sharp as in sulfuric acid solution, but the change is very distinct.

The methyl red end-point is satisfactory in solutions which have been reduced with stannous chlorides in excess, the excess being destroyed with mercuric chloride. A solution of ferric alum in dilute sulfuric acid required per 25 cc.: 21.69, 21.70, 21.68 cc. of 0.0948 *N* ceric solution after stannous chloride reduction, and 21.70, 21.73, 21.71 cc. of the ceric solution after passage of 25-cc. portions through a Jones reductor.

TABLE II

Titration of Approximately 0.05 *M* Ferrous Solution with 0.05 **M** Ceric Sulfate

	1	2	3	4	5	6	7	8
Initial volume, cc.	100	110	150	100	35	60	200	125
Initial acid concn., *N*	0.5	0.7	0.3	0.6	0.2	0.2	0.3	1.2
Acid used	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	H_2SO_4	HCl	H_2SO_4
Ceric soln. used, cc.	41.24	41.25	16.48	16.47	8.03	20.01	20.00	39.98
Ceric soln. calcd., cc.	41.20	41.20	16.42	16.42	8.00	19.96	19.96	39.92

If Mohr's salt is used as a secondary standard, the correction of 0.03 cc. of 0.1 *N* ceric solution brings the methyl red end-point in good agreement with the potentiometric.

Ceric sulfate vs. sodium oxalate, *N*	0.1079	0.1081	0.1080
Mohr's salt used, g.	1.0502	1.3260	1.0072
Ceric solution uncorrected	24.85	31.33	23.82
Normality	0.1077	0.1079	0.1078
Applying 0.03 cc. corr., $N =$	0.1079	0.1080	0.1080

TABLE III

Titration of 0.1073 *N* Ceric Sulfate with Ferrous Sulfate

Series I

Ceric sulfate used, cc.	25	25	25	10	10	10	Av. per 25 cc.
Ferrous sulfate, cc.							
Methyl red	29.80	29.83	29.79	11.94	11.92	11.91	29.81
Potentiometric	29.87	29.85	29.85	11.96	11.93		29.86
Diphenylamine	29.85	29.89		11.90	11.91		29.81

Series II

Ceric solution used, cc.	25	25	25	25			
Ferrous sulfate, cc.							
Methyl red	30.02	30.04	30.03	30.02			30.03
Potentiometric	30.01	30.05	30.06				30.04
Diphenylamine	30.08	30.07	30.11	30.07			30.08

Titration of Ceric Sulfate with Ferrous Sulfate.—The ferrous sulfate is added until the solution is pale yellow (slight excess of ceric ion), 0.05 cc. of methyl red is added, and immediately afterward 25 cc. of the sulfuric-phosphoric acid mixture (150 cc. of each concentrated acid per liter) which is used in Knop's (40) diphenylamine method. The yellow color of the solution becomes much less intense, but no precipitation of cerium phosphates occurs. The ferrous sulfate is added slowly until the solution suddenly becomes pale violet. Upon standing the violet color deepens. Some results are presented in Table III.

Five one-hundredths cc. of methyl red or 0.05 cc. of 1% diphenylamine was used. The behavior of diphenylamine is erratic, and the position of the end-point depends upon the speed of titration at the end-point.

Behavior of Methyl Red on Oxidation and Reduction.—This study is still in a preliminary stage as far as the mechanism of the reaction is concerned. A brief resumé of some qualitative experiments may be of interest. Ceric sulfate appears to be the only oxidizing agent which gives the intermediate oxidation product of methyl red under the conditions used in volumetric analysis. Bromate, permanganate, and chlorine carry the oxidation so far that no colored product is formed on reduction with ferrous salt. The violet-colored substance is formed when the reduction is carefully performed with stannous chloride; sulfite, on the other hand, carried the reduction to a colorless stage.

Methyl red shows the same oxidation-reduction behavior after recrystallization from glacial acetic acid as before purification.

The violet-colored reduction product is extracted from aqueous solution by ether to give an orange-red solution, and by benzene to give a violet-red solution. In the latter solvent methyl red forms an orange or yellow extract, although largely present in the red form in the strongly acid aqueous layer. Thus far it has not been possible to obtain the violet substance in a form pure enough for analysis.

Erio-Glaucine and Erio-Green Indicators.—Erio-Glaucine A (Schulz No. 506) and Alkali Fast (erio) Green A were obtained from the National Aniline and Chemical Company, New York; 0.1% aqueous solutions were prepared, and 0.5 cc. of either solution was used for a single titration. Knop (40) states that the compositions of the rose-colored oxidation products are not known. Either indicator forms a greenish yellow color in acid solution; in pure water the colors are blue and green, respectively. A very slight excess of ceric sulfate colors either indicator rose or red; in the presence of a ferric salt the color is orange or pale rose. There is a short time interval necessary for the development of the full color change at the end-point; the danger of over-titration is slight. The results are summarized in Table IV.

The determinations were made as closely together as possible, in point of time, with alternation of indicator and potentiometric determinations.

TABLE IV

Use of Erio-Glaucine and Erio-Green in Titration of Ferrous Sulfate with 0.0948 *N* Ceric Sulfate

Erio-Glaucine Indicator

Ferrous sulfate, cc.	25	25	25	25	50	50	Av. per 25 cc.
Initial acid concn., *N*	0.7	3.0	0.35	3 *N*	2	2	
Acid	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	
Initial volume, cc.	25	50	50	50	75	75	
Ceric sulfate, cc.	23.05	23.04	22.99	23.00	45.99	45.98	23.01
Erio-Green Indicator							
Ferrous sulfate	25	25	25	25	50	50	
Initial acid concn., *N*	0.7	3.0	3.0	0.75	2.0	2.0	
Acid	H_2SO_4	H_2SO_4	HCl	HCl	H_2SO_4	HCl	
Initial volume, cc.	25	50	50	100	75	75	
Ceric solution, cc.	22.98	23.01	23.03	22.98	45.97	45.91	22.98
Potentiometric							
Ferric solution, cc.	25	25	25	25	50	50	
Ceric solution used, cc.	22.99	23.03	23.00	23.03	45.98	45.89	22.99

There does not appear to be any correction to be applied in working with 0.1 *N* solutions.

TABLE V

Titration of 0.1028 *N* Ceric Sulfate with Ferrous Sulfate

Erio-Glaucine Indicator

Ceric solution, cc.	10	10	10	25	25	Av. per 25 cc.
Initial H_2SO_4 conc., *N*	1	0.67	0.7	1.4	1	
Initial volume, cc.	40	65	100	60	85	
$FeSO_4$ used, cc.	11.97	12.00	11.98	29.95	29.98	29.96
Erio-Green Indicator						
Ceric solution, cc.	10	10	10	25	25	
Initial H_2SO_4 conc., *N*	1	0.67	0.7	1.4	1	
Initial volume, cc.	40	65	100	60	85	
$FeSO_4$ used, cc.	11.99	11.96	11.98	29.95	29.95	29.94
Potentiometric						
Ceric solution, cc.	10	10	25	25	25	
$FeSO_4$ used, cc.	11.99	11.98	29.99	29.99	29.95	29.98

The reverse titration was studied. It was found that either indicator could be added immediately before the start of a titration. The color was initially orange; when nearly all of the ceric ion had been reduced the rose tint predominated. At the end-point there was a sharp transition to yellow with a slight time interval needed for the color change.

Within the limits of error of these determinations there appears to be no indicator correction.

It seemed of interest to determine whether the presence of calomel and mercuric chloride would interfere with the functioning of the indicators. A solution of ferric alum, acidified with sulfuric acid, was prepared, and aliquot portions were reduced by the stannous chloride method with subsequent addition of excess of mercuric chloride. Portions of the solution were reduced by the Jones reductor, and an average of 23.09 cc. of 0.0945 *N* ceric sulfate were required per 25 cc. of alum solution.

TABLE VI

Titration; After Reduction with Stannous Chloride

Erio-Glaucine Indicator

Alum solution, cc.	25	25	25	10	10
Ceric solution found, cc.	23.05	23.13	23.09	9.23	9.22
Error, cc.	—0.04	+0.04	±0.00	±0.00	—0.01

Erio-Green Indicator

Alum solution, cc.	25	25	10	10
Ceric solution found, cc.	23.11	23.08	9.22	9.24
Error, cc.	+0.02	—0.02	—0.01	+0.01

A number of other uses of erio-glaucine and erio-green in titrations with ceric sulfate are being studied.

Summary

Methyl red in dilute sulfuric acid solution may be used as indicator in the titration of ferrous iron with ceric, or *vice versa.* In the latter case the indicator must be added near the end-point, and phosphoric acid must be present. A correction must be applied in the former titration.

A new behavior of methyl red upon mild oxidation-reduction treatment has been described.

Erio-glaucine and erio-green are excellent indicators for the titration of ferrous ion with ceric, or *vice versa.* No correction need be applied in either case with a 0.1 *N* standard solution.

The three indicators are satisfactory in hydrochloric acid solution as well as in sulfuric, and in the presence of calomel and excess of mercuric chloride.

FURTHER APPLICATIONS IN THE USE OF CERIC SULFATE AS A STANDARD OXIDIZING AGENT

The bibliography following gives a list of publications dealing with the use of ceric sulfate in a multitude of applications which attest to the versatility of this valuable analytical reagent. Numerous further applications will undoubtedly continue to appear from time to time in the current literature. The purchase of approximately one-tenth and five-hundredths normal ceric sulfate solutions ready for standardization or already standardized can be made in 1 lb. (approx. 470 cc.), 2 lb. and 4 lb. glass stoppered bottles or in larger amounts in glass stoppered carboys.

The data of this booklet and the following bibliography are in part reviewed in Chapter XVII of *Volumetric Analysis* by Kolthoff and Furman, John Wiley and Sons, Inc., New York City, 1929, Vol. II, pp. 491-495.

The data assembled in this booklet were arranged by

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The Preparation of Solution of Ceric Sulfate for Standardization

Materials:

1. Hydrated ceric oxide, $CeO_2 \cdot 2H_2O$, M. W. 208.16.
2. This product is generally approximately 60 percent CeO_2, and an equivalent weight being in practice approximately 347 grams or 34.7 g. for 1000 ml. of N/10 Ce^{IV}.
2. Anhydrous ceric sulfate, $Ce(SO_4)_2$, M. W. 332.25.
   Since this product may not be completely anhydrous and since it contains other rare earths, an average purity of 50 percent $Ce(SO_4)_2$ is common. The apparent molecular weight is taken as 664 which is the equivalent weight or 66.4 grams for 1000 ml. N/10 Ce^{IV}.
3. Ceric Ammonium Sulfate, $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$, M. W. 628.53.
   Since this salt is generally about 80 percent pure, the approximate weight is obtained by the use of approximately 80 grams of the salt per 1000 ml. for N/10 Ce^{IV}.
4. Concentrated H_2SO_4, sp. gr. 1.84-1.85.

Procedure.—(A) 35 g. of hydrated ceric oxide are weighed into a 600 ml. beaker and 46 ml. of concentrated H_2SO_4 are added. Add cautiously 50 ml. of water and with cover glass in place digest for 5 minutes at the boiling point. Cool somewhat and add cautiously 450 ml. of water and stir and digest until all has dissolved. If not quite all is dissolved allow to cool and settle out and decant the clear orange solution into a 1000 ml. graduated flask and filter the remaining solution and precipitate. Wash the filter, which should be C.S. and S. No. 589, Blue Ribbon, or its equivalent with 2 percent H_2SO_4 solution. Finally dilute to 1000 ml. and the solution is ready for standardization. This solution is roughly 0.5 molar in H_2SO_4.

(B)—Weigh 66-67 grams of anhydrous ceric sulfate into a 600 ml. beaker and add 28 ml. of concentrated H_2SO_4. Dilute with 28 ml. of water and stir with frequent additions of water and heating until all the salt is dissolved. Transfer to a 1000 ml. flask and dilute to the mark. The ceric sulfate is slow to dissolve because it is anhydrous. The solution is generally complete. The resulting solution is approximately N/10 ceric sulfate and is approximately 0.5 molar in free sulfuric acid.

(C)—Dissolve 80 grams of ceric ammonium sulfate in a 600 ml. beaker by the addition of 28 ml. of H_2SO_4 diluted to 500 ml. with water. Stir until all is dissolved and transfer to a 1000 ml. flask and dilute to the mark. The solution thus formed is approximately N/10 Ce^{IV} and 0.5 molar in free sulfuric acid.

The Preparation of Iodine Monochloride Solution for Use as Catalyst in Ceric Sulfate Reactions

Materials:

1. Potassium iodate, C.P., KIO_3, M.W. 214.02.
2. Potassium iodide, C.P., KI, M.W. 166.02.
3. Dilute solution 0.005 M KIO_3 (1.07 g. dissolved in 1000 ml. of water).
4. Dilute solution, 0.01 M KI, (1.66 g. dissolved in 1000 ml. of water).
5. Chloroform.
6. Hydrochloric acid, sp. gr. 1.18-1.19.

Procedure.—Dissolve 10 grams of potassium iodide and 6.74 grams of potassium iodate in 90 ml. of water. The solution should not liberate iodine. Add 90 ml. of concentrated hydrochloric acid and stir well. The reaction is as follows:

$$2\ KI + KIO_2 + 6\ HCl \rightarrow 3\ KCl + 3\ ICl + 3\ H_2O.$$

If potassium iodide has been added in slight excess this must be reacted by addition of just the correct amount of potassium iodate. The solution will be orange colored and by the addition of 5 ml. of chloroform and stirring, if the potassium iodide has been added in slight excess, the chloroform will be colored faintly red. Add a few drops at a time of the dilute potassium iodate until the color of the chloroform is very faint. By the various treatments with the balancing solutions the proper quantities of reagent are determined. The solution thus obtained is 0.5 molar in iodine monochloride. 10 ml. of this solution diluted to 1000 ml. are employed in 5-10 ml. portions as catalyst for ceric sulfate reactions subsequently described. Solutions of iodine monochloride should be stored in glass stoppered bottles in the dark. These solutions in the 0.5 molar strength are available to the consumer or the ingredients can be supplied for their preparation as described. Literature reference 41 describes this preparation. The reaction between iodine and potassium iodate is as follows:

$$2\ KI + KIO_2 + 6\ HCl \rightarrow 3\ KCl + 3\ ICl + 3\ H_2O.$$

The Walden, Hammett and Chapman Indicator

Preparation of Ortho-Phenanthroline Ferrous Complex Indicator Solution.

Materials:

1. Ortho-phenanthroline monohydrate, $C_{12}H_8N_2\ H_2O$, M. W. 198, m. p. 102° C.
   14.85 g. for 1000 ml. of solution under (2) below.
2. Ferrous sulfate, 0.025 Molar solution.
   6.95 g. $FeSO_4 \cdot 7H_2O$ in 1000 ml. of solution. Make fresh as needed.

Procedure.—Dissolve the ferrous sulfate and add the ortho-phenanthroline monohydrate and stir until all is dissolved giving a dark red solution. One drop of this indicator serves for each titration in a volume of 100-150 ml. 1000 ml. of indicator solution should serve for use in 15,000 to 20,000 titrations. The original cost of the indicator bears no appreciable relation to the cost for an individual titration. The ortho-phenanthroline monohydrate or solutions of the same as 0.025 molar ortho-phenanthroline ferrous complex are available for distribution.

STANDARDIZATION OF CERIC SULFATE SOLUTIONS

A. Standardization against Iron. Method of Willard and Furman(53).

Materials:

1. Electrolytic iron wire and concentrated hydrochloric acid, sp. gr. 1.18.
2. Approximately N/10 ceric sulfate in 0.5 molar H_2SO_4.
3. Stannous chloride, 62.5 g. of $SnCl_2 \cdot 2H_2O$ in 150 ml. conc. HCl, dilute to 1000 ml. This solution is 0.5 normal.
4. Saturated solution of mercuric chloride in water.
5. Phosphoric acid, sp. gr. 1.37, prepared by mixing one volume of syrupy phosphoric acid, sp. gr. 1.70 with an equal volume of water.
6. Barium salt of diphenylamine sulfonic acid, 0.01 M. diphenylamine sulfonate used as indicator is prepared by dissolving 0.32 g. of the barium salt in 100 ml. of water. Five tenths of a gram of sodium sulfate is added and the clear solution decanted from the barium sulfate.

Procedure.—Weigh 0.25-0.30 g. samples of electrolytic iron into 400 ml. beakers and add 5 ml. of water and 10 ml. of conc. hydrochloric acid. Warm the solution until the iron has dissolved; then heat the solution to boiling and add 0.5 N stannous chloride one drop at a time, rotating the liquid constantly and keeping it hot, until all ferric chloride is reduced and one drop of the reducing agent causes the color to change from yellow to colorless or very pale green. Then add 2 drops excess of stannous chloride. Add immediately 5 ml. of conc. hydrochloric acid, rinse down the sides of the beaker and cover and dilute the solution with cold water to 250 ml. Add 5 ml. of saturated solution of mercuric chloride to oxidize the excess of stannous chloride. A slight white precipitate of mercurous chloride is formed after 1-2 minutes. A heavy precipitate should not be formed and will give inaccurate results. In case no precipitate is formed or the precipitate is too heavy, the solution should be rejected.

Add 10 ml. of phosphoric acid, sp. gr. 1.37, and 0.3 ml. of indicator solution (solution 6 above.) Titrate with the unknown srtength of approximately 0.1 N ceric sulfate. During the titration of the ferrous salt with ceric sulfate the solution is practically colorless so that the end-point, as shown by the appearance of a purple oxidation product of diphenylamine sulfonic acid, is very sharp. The reaction between the indicator and the ceric sulfate is rapid but not instantaneous. Therefore the titration should be carried out more slowly towards the end.

If exactly 0.2234 grams of pure iron were taken as sample there would be required 40 ml. of ceric sulfate if it is exactly N/10 in Ce^{IV}. If it required 50 ml. of ceric sulfate the solution would be 0.08 N. The standard value of the unknown ceric sulfate is thus easily calculated. For each 0.05584 grams of pure iron taken, 10 ml. of exactly N/10 ceric sulfate would be required. Otherwise the calculation is as follows:

$$\frac{\text{Volume Mohr's salt}}{\text{Volume unknown ceric sulfate}} = \frac{\text{X (normality of Ce}^{\text{IV}}\text{)}}{0.1}$$

$$\text{X} = \frac{\text{Volume Mohr's salt}}{\text{Volume ceric sulfate}} \times 0.1$$

B. Standardization against Mohr's Salt. Method of Furman and Wallace (13).

Materials:

1. Mohr's salt, $\text{Fe(NH}_4\text{)}_2\text{(SO}_4\text{)}_2\cdot 6\text{H}_2\text{O}$, M. W. 392.14.
2. Approximately N/10 ceric sulfate in 0.5 molar H_2SO_4.
3. Erio-glaucine A. Schultz No. 506. 1 gram of the dye is dissolved in 1000 ml. water.
4. Sulfuric acid, sp. gr. 1.84-1.85 (96 percent H_2SO_4) diluted with an equal volume of water.

Procedure.—Prepare a 0.1 N solution of ferrous ammonium sulfate by dissolving 39.214 g. of Mohr's salt in 200-300 ml. of water and add 20 ml. of diluted sulfuric acid (material 4 above) with constant stirring. Dilute to 1000 ml. in a graduated flask giving an exact N/10 solution of ferrous iron.

Take 25.00 ml. of the approximately N/10 solution of ceric sulfate in 0.5 molar sulfuric acid using a pipet to transfer the solution to a 250 ml. beaker. Dilute by the addition of 25 ml. of water and add 2-3 ml. of dilute sulfuric acid (material 4 above). Titrate with the standard Mohr's salt solution until the ceric ion color is almost all bleached out and add 0.5 ml. of erio-glaucine (material 3 above). The color of the solution is now red. Add the ferrous iron solution dropwise slowly until the red solution turns a permanent yellow or yellowish green with the first drop excess of ferrous iron. No indicator correction is required.

For the standardization the ferrous sulfate solution stored under hydrogen in the Zintl and Reinäcker apparatus may be employed after standardization using the process previously described.

If 25 ml. of 0.1 N Mohr's salt solution are required for titration of 25 ml. of the unknown ceric sulfate, the latter is also N/10 in Ce^{IV}. Otherwise the calculation is as follows:

$$\frac{\text{Volume Mohr's salt}}{\text{Volume unknown ceric sulfate}} = \frac{\text{X (normality of Ce}^{\text{IV}}\text{)}}{0.1}$$

$$\text{X} = \frac{\text{Volume Mohr's salt}}{\text{Volume ceric sulfate}} \times 0.1$$

C. Standardization against Sodium Oxalate. Method of Willard and Young (45).

Materials:

1. Iodine monochloride catalyst prepared as described on page 53.
2. Ortho-phenanthroline ferrous complex prepared as described on page 54.
3. Ceric sulfate solution prepared as described on page 52.
4. Sodium oxalate. U. S. Bureau of Standards' sample for standardization.
5. Concentrated hydrochloric acid (sp. gr. 1.18).

Procedure.—Weigh accurately 0.1675 grams of sodium oxalate and place in a 400 ml. beaker and dissolve by addition of 20 ml. of hydrochloric acid diluted with water to 95 ml. Stir until dissolved and add 5 ml. of 0.005 M iodine monochloride and heat to 50° C. Use a thermometer as stirring rod and, after the addition of one drop of 0.025 M ortho-phenanthroline ferrous complex as indicator, titrate with the ceric sulfate until the solution is pale blue in color and there is no return of any pink color after an interval of one minute. If the temperature falls below 45° C., reheat the solution to 50° C. Calculation of normality is as in sections A and B. The oxalate used is equal to 25.00 ml. of N/10 $\text{Na}_2\text{C}_2\text{O}_4$.

D. Standardization against Arsenious Oxide. Method of Willard and Young (45).

Materials:

1-5. Same materials as under section C with the addition of a standard arsenite solution.

6. Dissolve 4,947 grams of U. S. Bureau of Standards' As_2O_3 in a 600 ml. beaker by the addition of 5 grams of sodium hydroxide pellets and 200 ml. of water. Add 13 ml. of conc. hydrochloric acid and follow with the addition of 10 grams of sodium bicarbonate, keeping the beaker covered to prevent loss by spray. Dilute the solution thus obtained to 1000 ml. in a graduated flask. The resulting solution is N/10 in As^{III}.

Procedure.—Pipet 25.00 ml. of N/10 sodium arsenite solution into a 400 ml. beaker. Add 15-20 ml. of conc. hydrochloric acid, sp. gr. 1.18, and 2.5 ml. of 0.005 M iodine chloride and dilute to 100 ml. Add one drop of 0.025 M Ortho-phenanthroline ferrous complex and titrate at room temperature with ceric sulfate until the brown color of the indicator returns slowly after the addition of each drop of oxidizing agent. Heat the solution to 50° C. using a thermometer as stirring rod and continue adding ceric sulfate very slowly until there is no return of the brown color of the indicator within a minute. The calculation of the results is the same as in sections A and B.

IMPROVED TECHNIQUE IN THE STANDARDIZATION OF LABORATORY REAGENTS NOT PERMANENT IN STORAGE

By G. Frederick Smith

Two of the most frequently required standard laboratory reagents are normal solutions of potassium permanganate and ferrous sulfate. Both substances are altered in value as oxidizing or reducing agents and decrease in strength as a result of storage. Potassium permanganate is generally prepared in solutions of approximately tenth normal strength in considerable quantity and standardized at frequent intervals using sodium oxalate as reference standard. More dilute solutions of standard permanganate require more frequent restandardization. Solutions of ferrous sulfate acidified with sulfuric acid are standardized most conveniently by titration with standard permanganate. This frequent comparison of the two most commonly employed laboratory reagents may become unnecessarily burdensome unless measures are taken to eliminate frequent restandardization of one of the two directly comparable solutions.

The most common process which is employed to this end consists in the preparation of a stable solution of an oxidizing agent which is standardized and used at frequent intervals to restandardize the ferrous sulfate solution which has been altered by atmospheric oxidation. Such stable solutions of oxidizing agents are potassium dichromate and ceric sulfate. The former can be prepared suitable for standardization by direct weight but suffers from the disadvantage that unless it is compared with ferrous sulfate electrometrically the results are somewhat unsatisfactory using either diphenylamine or diphenylbenzidine but are satisfactory using erio-glaucine(13) or orthophenanthroline ferrous complex(44). Ceric sulfate solutions cannot be standardized by direct weight but like permanganate are best standardized by comparison with sodium oxalate thus making the value determined most directly comparable to the standardization of potassium permanganate. In this case, however, the electrometric determination of the end-point of the reaction may be used or the phenanthroline indicator end-point is preferred(45). In comparing ceric sulfate with ferrous sulfate, however, the internal indicator, erio-glaucine, is more satisfactory than the use of diphenylamine or benzidine in the dichromate-ferrous sulfate reaction.

The most satisfactory process to be employed in the standardization of solutions of potassium permanganate and comparison with ferrous sulfate consists in the preparation and storage of the latter under conditions preventing its alteration by atmospheric oxidation. The standardization of the ferrous sulfate is then accomplished by comparison with potassium permanganate once standardized using sodium oxalate and subsequently the permanganate of altering strength is always compared with the stable ferrous sulfate solution. None of the reactions involved need be carried out electrometrically, no internal indicators are required, and a third solution of stable oxidizing agent is not necessary.

The storage of sulfuric acid solutions of ferrous sulfate resulting in an unalterable reducing value has been described by Zintl and Reinäcker(54). A transfer buret is described by these authors and a photograph of the assembled apparatus is shown in Figure 3. The same device in modified form is shown schematically in Figure 4 which adapts the process to the use of large capacity storage bottles with simplification of the buret design also providing easy transfer of a solution from storage reservoir to titration beaker either for direct use of the ferrous sulfate for titration or for the measurement of known volumes of the reagent to be used in standardizing the permanganate solution under discussion. The principle involved is the storage of ferrous sulfate out of contact with air and in an atmosphere of hydrogen.

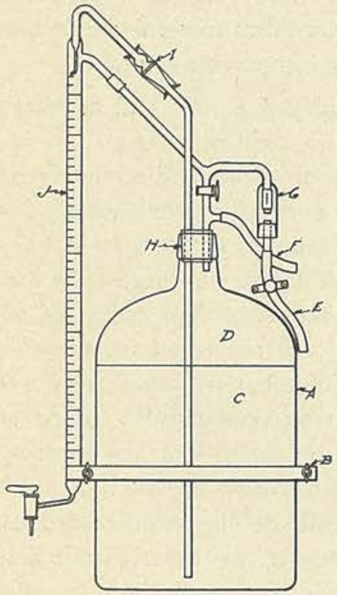

FIGURE 4

A—14 Liter Bottle
B—Buret—Bottle Clamp
C—Standard Solution Mohr's Salt
D—Hydrogen Gas
E—Gum Tubing Aspirator
F—Gum Tubing to Kipp Generator
G—Bunsen Valve
H—Two Hole Stopper
I—Ground Glass Tension Joint
J—50 ml. Buret

Zintl and Reinäcker Standard Storage Bottle and Buret,
Ref. *Z. Anorg. Allgem. Chem.* 155, 84 (1926)

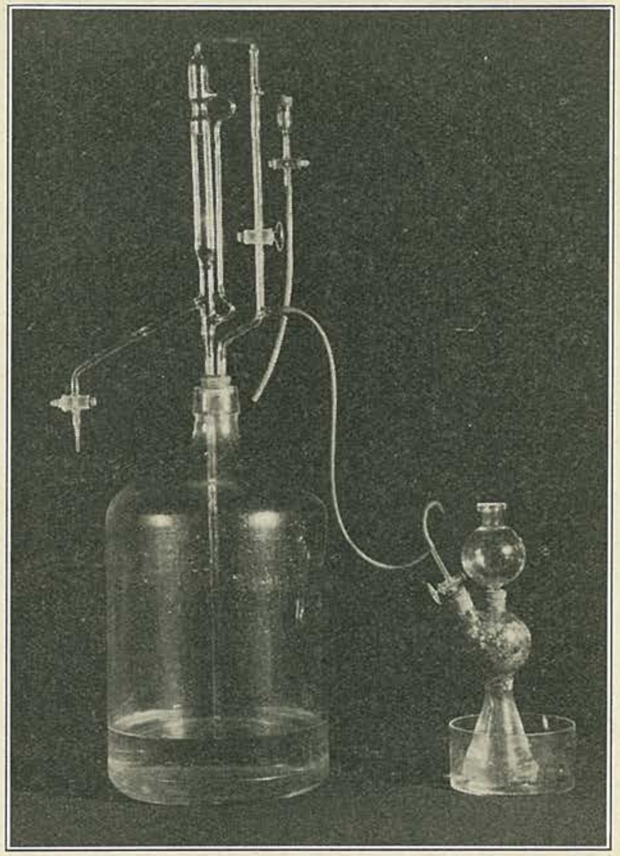

FIGURE 3

The object of the present discussion consists in the demonstration of the permanence of ferrous sulfate solutions stored under these conditions and the value of the process in restandardization of permanganate solutions obviously less tediously than by continuous comparison with sodium oxalate.

Experimental

14-liter bottles of approximately tenth normal solutions of potassium permanaganate and ferrous sulfate were prepared in the customary manner and the ferrous sulfate solution stored as shown in Figure 4. Two solutions of ferrous sulfate reagent were prepared and the permanganate solution standardized by comparison with sodium oxalate in the proper manner on widely different dates and the corresponding standard factor obtained recorded. The data are shown in Table 1. The ferrous solutions were then standardized electrometrically using potassium dichromate with the same time interval in storage and the strength of the ferrous sulfate shown to be unaltered. The data are given in Tables 1 and 2.

TABLE 1

Standardization of Potassium Permanganate Solutions Using Sodium Oxalate and Comparison With Ferrous Sulfate Stored 45 Days Under H$_2$.

Volume Buret			Weight Buret		
$Na_2C_2O_4$ g.	$KMnO_4$ g.	Factor Found Normality	$Na_2C_2O_4$ g.	$KMnO_4$ g.	1 g. $KMNO_4$ = Normal Oxidizing Value in ml.
0.1833	33.26	0.08226	0.0988	19.425	0.07595
0.2643	47.77	0.08258	0.2554	50.294	0.07597
0.2680	48.67	0.08219			
0.1804	32.62	0.08255			
	Average	0.0824		Average	0.07596

Standardization of Ferrous Sulfate Using Standard Permanganate as Reference.

$FeSO_4$ ml.	$KMnO_4$ ml.	Std. Factor Normaiity	$FeSO_4$ ml.	$KMnO_4$ ml.	Std. Factor Normality
25.00	28.52	0.09400	25.00	30.891	0.09387
25.00	28.51	0.09397	25.00	30.921	0.09395
25.00	28.52	0.09400	25.00	30.900	0.09389
25.00	28.53	0.09403			
	Average	0.0940		Average	0.0939

It will be observed from the examination of Table 1 that the ferrous sulfate stored under hydrogen in the Zintl and Reinäcker apparatus has not changed in strength for a period of 45 days. The second and subsequent standardizations of potassium permanganate of Table 1 is thus shown to be unnecessary using sodium oxalate, which condition represents a distinct simplification of the standard process. The solutions of potassium permanganate of Table 1 were not the same, so that the difference in oxidizing value does not show actual decrease in normality with storage. This is further substantiated from the data of Table 2.

TABLE 2

Standardization of Ferrous Sulfate Before and After Storage Forty Days Under H$_2$.
Reference Standards: $KMnO_4$ — $Na_2C_2O_4$ and $K_2Cr_2O_7$ as Primary Standard.

$FeSO_4$ ml.	0.0824 N $KMnO_4$ ml.	Mar. 1, 1933 Normality $FeSO_4$	$FeSO_4$ ml.	$K_2Cr_2O_7$ g.	April 12, 1933 Normality $FeSO_4$
25.00	21.48	0.07080	52.76	0.2000	0.0706
25.00	21.48	0.07080	43.33	0.1500	0.0706
25.00	21.50	0.7086			
25.00	21.49	0.07083			
Average		0.0708	Average		0.0706

Conclusions

The preparation of large volumes of ferrous sulfate is appropriate in such cases as those in which it is used at frequent intervals as a standard reductant as well as for checking the standard factor of permanganate solutions since one standardization serves for the entire period of consumption of the solution. This fact follows proof of the stability of the ferrous sulfate when stored under hydrogen as just shown. A transfer buret such as that shown in Figure 3 can be assembled from glass tubing by one with some little skill in glass working. A small Kipp hydrogen generator as shown is more easily made and is preferable to a larger standard generator since when the apparatus to which it is attached is free from leaks, but small amounts of hydrogen are required. Calibrated transfer burets as shown in Figure 4 can be provided together with additional equipment in accordance with the prices obtainable on request.

Oxidation and Reduction Indicators Supplied From Stock

Ortho-phenanthroline monohydrate	Walden, Hammett and Chapman(44)
0.025 Molar Ortho-phenanthroline ferrous complex	Walden, Hammett and Chapman(44)
Barium diphenylamine sulfonate	Kolthoff(56)
Diphenylbenzidine	Knop(40)
Diphenylamine	Knop(40)
Erio-glaucine	Furman and Wallace(13)
Erio-green	Furman and Wallace(13)

These indicators are especially adapted to use in the case of ceric sulfate reactions and are also of general application in other oxidation reactions.