CERATE OXIDIMETRY

Second Edition 1964

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20 Year Developments, Improvements in Techniques, and Precision Innovations

$$(NH_4)_2 Ce^{++++} (NO_3)_6$$
$$(NH_4)_4 \cdot (SO_4)_4 \cdot 2H_2O$$

G.F.S. Magnetic Stirring Motor
Drawn to Scale 1 inch = 1 inch
Weight 4 ounces
Operates Powered by Air Pressure, Water Pressure or Vacuum
Hermetically Sealed Powerful Alnico Magnet
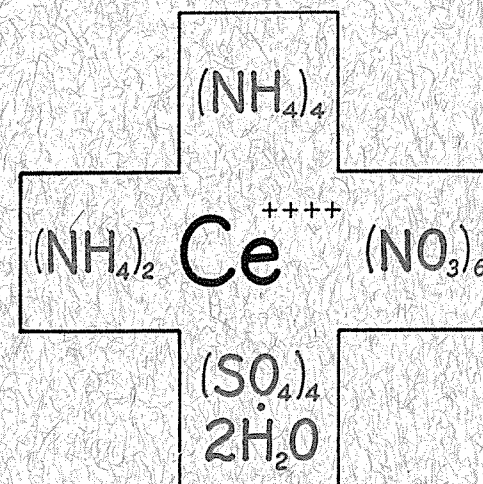Permanent Plastic Construction Throughout

FOREWORD

Cerate oxidimetry in the last 25 years has, in great measure, taken precedence over comparable permanganimetric volumetric applications in the determination of metals, non-metal, and organic compounds. Such cerate oxidation-reductions are applicable as applied to the mineral acid solutions of hydrochloric, sulfuric, nitric and perchloric acids. The range of redox potentials provided is from 1.21 volts to 1.88 volts depending upon acid types and concentrations employed. A multiplicity of super-sensitive *in situ* oxidation-reduction indicators of multiple redox potentials and high molecular extinction coefficients provide for more accurate equivalene point determination in micro — or macro volumetric operations. Ce(IV) chemicals are available having primary reference stability and purity. The major primary standard reagents including sodium oxalate, arsenious oxide and others may be employed. Standard Ce(IV) solutions of sulfatocerate in sulfuric acid solutions are permanently stable in continuous storage. Catalyst are available to overcome oxidation reaction of sluggish reaction kinetics. *Cerium(III) and cerium(IV) oxidations and reductions involve but one electron exchange.*

With all these outstanding advantages, *Cerate Oxidimetry* in modern research and routine industrial control applications takes priority over *Permanganimetry*.

CERATE OXIDIMETRY

Further Applications in the Use of Cerium in Volumetric Analysis

1942 Edition — Revised 1964

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PROFESSOR FRANCIS H. CASE, 1899 —

B.S. University of Michigan '20. M.S. Yale University '21. Ph.D. Yale University '23. National Research Fellow Harvard University '23-'25. Instructor Swarthmore College '25-'26. Research Fellow American Petroleum Institute, Johns Hopkins University '26-'27. Instructor to Professor, Temple University, Philadelphia, Pennsylvania. Specialty research organic syntheses in the field of bi-phenyls, bi-pyridines and substituted 1,10-phenanthrolines and other methine chromophore group organic chelation chemicals.

Without the pioneer and masterful synthetic research provided by Professor Case methods of the spectrophotochemical field of analysis as well as that of the use of the most important internal oxidation and reduction indicators of volumetric analysis would not now be available. The synthesis of the methine chromophore group of organic chelation reagents gives them an importance comparable to the value of any other individual or series of organic reagents now a part of the operations of analytical chemical routine and research.

PREFACE

The study of the history of chemistry for the past century and sixty years substantiates a noteworthy conclusion. Progress in all chemical advancements has been predicated upon new innovations provided by analytical research.

New analytical techniques predominantly involve the specific field of physical chemistry. X-Ray disciplines blue print molecular structures. Mass spectrometry in one of many innovations has replaced the classical atomic weight evaluation. Visual, ultraviolet and infarared spectra serve as the analyst's "finger print" of identification. Polarography clarifies many problems of reaction kinetics. All phases of chromotography add outstanding valuable analytical disciplines. The electron microscope has served to outrange the optical microscope into magnification almost beyond imaginative conception. Flame photometry* is competitive to spectroscopy in trace analytical estimations. Methods of activation analysis develop more direct and specific quantitative evaluations. Radio-active isotopes serve to clarify otherwise controversial reaction mechanisms. The ultracentrifuge classifies by molecular weight chemistry's mammoth colloidal entities. One could include other innovations.

All these developments are the conquests of analytical chemical technology.

Industry, at a score of research centers nationwide, equip control laboratories with operating personnel and maintenance experts to accompany an almost limitless financial outlay for equipment in the utilization of instrumental analytical exploitations.

These industrial research centers, aside from hundreds of thousands of dollars invested in exotic instrumental equipment also provide control laboratories which still function with elaborate facilities and multiple personnel devoting their time and talents in the application of so-called "wet chemical methods." Laboratory work benches with service utilities, fume hoods, beakers, flasks, burets, pipets and hot plates constitute the bulk of their analytical tools. The analytical balance serves as the badge of their vocation.

"Cerate Oxidimetry" involves the disciplines of wet chemical oxidation-

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* The first practical operative apparatus assembly for use in flame photometry was described by A. C. Shead (his innovation) and the present writer. The literature on the subject fails to credit this fact since the title of the published paper "The Star Trail Method" does not denote the contents of this published work as that of flame photometry. All the optics of modern flame photometry were applied and results were recorded photographically. The description of the work in question was published in the *Journal of the American Chemical Society* 52, 5295 (1930). Editorial inhibitions prevented the description of the apparatus being outlined in detail and the importance of the research was not rightfully supported. Modern developments in flame photometry are improved only in the use of only modified instrumentation. More modern devices such as optical gratings and photoelectric cell recording systems were later innovations.

PREFACE *(continued)*

reduction, volumetric stoichiometry. The new procedures cited replace formerly predominant permanganimetry processes with many noteworthy improvements. The present book is a revision of the former edition which appeared in 1942. The material extension of new applications and innovations cover progress over the past twenty years. The old has been embellished by the description of interim advances in what is new.

Over a period of 35 years the publishers of this book, widely distributed at no cost, have specialized in the origination, manufacture, and commercial distribution of a large number of new analytical reagents for use in research and routine plant control applications including instrumental adjuncts. A complete list of cerium chemicals is always available from stock as but one of our numerous companion categories similarly involved in broadening analytical technical frontiers.

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SECTION 1

INTRODUCTION

The general application of the methods of *Cerate Oxidimetry* in volumetric oxidimetry, through the pioneer studies of H. H. Willard* and N. H. Furman** opening in 1928, marks one of modern analytical chemistry's most important innovations. Originally designated *Ceric Oxidimetry,* cerium(IV) quantitative oxidation-reduction applications were thought to be unique, as distinct from permanganate oxidimetry, as being cationic in principle. Ceric sulfate, the originally concept $(Ce(SO_4)_2)$ is now recognized to be sulfatoceric acid $H_2Ce(SO_4)_3$ in sulfuric acid solution. The most important Ce(IV) analytical reagent is ammonium nitratocerate $(NH_4)Ce(NO_3)_6$ derived from nitratoceric acid $H_2Ce(NO_3)_6$ by original concept $Ce(NO_3)_4$ in nitric acid solution. Reactions employing cerium as electron donor thus involve anionic rather than cationic electron transfer distinctly contrary to the original concept.

"New developments" in chemical research are often found to involve prior documented chemical disclosures. Those responsible for their major

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* Hobart Hurd Willard, 1881 — is probably the most accomplished teacher, research director, and general originator of new disciplines in the field of analytical chemistry of the past fifty years. Nobel prize winner T. W. Richards (the second American recipient) as a result of Willard's work of 1906-1909 at Harvard in the revision of the atomic weights of lithium, silver, chlorine and oxygen, acknowledged that "his notable contribution marked the beginning of one of the most productive careers in modern analytical chemistry."

Professor Willard in an acceptance address in delivering the Henry Russell lecture at the University of Michigan acknowledging the annual achievement award for the faculty of the university, testified including the following remarks:

"Although the analytical chemist will never become famous in the eyes of the public, he is nevertheless an indispensable person in our industrial age. His services may not be sufficiently appreciated, but he is contributing in a large way to research and progress. Analytical chemistry is in itself never spectacular, but it has made possible some spectacular results and in their glamor its own contribution is usually lost sight of, even though without its help the process would not have been possible."

Professor Willard's greatest value to analytical research consists in the large number of his graduate trainees now active in either academic research and teaching or in industrial work. It is not essential to list his outstanding protegés to remind the chemical world of their contributions, lest the list would be remiss in its competitive evaluation. The list would include perhaps a score of his trainees among forty-two of his recipients of the Ph.D. degree. More than 4000 students attended his classes in 45 years of his active teaching career. The literature documentation of their accomplishments number into the thousands.

Inventive genius and the establishment of new disciplines in the field of analytical research is probably the next most outstanding contribution fostered by Professor Willard. First of these in prominence and practical utility is an extension of his Harvard graduate school exploitation of the chemistry of perchloric acid and its derivatives. A development of a practical method for the manufacture of perchloric acid employing ammonium perchlorate as raw material was introduced in 1910. The later development of the Willard and Cake method for the determination of silicon in iron and steel or in limestone and cement is now applied in millions of control analytical testing units annually in industry, world wide. Other applications in the use of perchloric acid in analyses are operative as in hundreds of individual routine analytical

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promotion find their "original ideas" previously published. This is true for the case at hand.

Probably the first published citation leading to the proposal that four valent cerium could be utilized to enrich analytical chemistry's field of oxidation-reduction reactions was made by L. Th. Lang.*

The separation of cerium from lanthanum and didymium was described by Walcott Gibbs (2) in 1864 employing lead dioxide in nitric acid as oxidant to oxidize cerium and separate it by a precipitation process as an insoluble basic nitrate. G. von Knorre also described (3) the determination of cerium as oxalate or oxide.

Andre Jos (4) employed hydrogen peroxide in the determination of cerium in nitric acid solutions of ammonium nitratocerate $(NH_4)_2Ce(NO_3)_6$ employing a visual end point to define complete reduction. Oxygen was the reduction product of H_2O_2 and two moles of Ce(IV) were reduced by each mole of peroxide. Andre Jos also pointed out that thorium if present does not interfere and that "one can employ cerium(IV) sulfate or nitrate in a procedures applied by industry. Perchlorate chemistry has involved increased consumption from that of a few pounds annually of a supposedly hazardous chemical curiosity in 1920 to consumption of an estimated one to two millions of pounds annually serving analytical chemical routine. The manufacture of solid rocket fuels is now essentially the chemistry of perchlorate oxygen donors, principally ammonium perchlorate.

Other disciplines of analytical chemistry associated with Professor Willard as entrepreneur are those of iodate and periodate chemicals, cerium chemicals as a modern development in volumetric oxidation-reduction procedures in analysis, the basic principles of the disciplines involving homogeneous precipitation techniques in analysis, outstanding electrochemical innovations in analytical instrumentation and the analytical application of phenyl-arsonium and related products.

The real evaluation of a master pioneer in analytical developments has for his major accomplishment in research the origination of new concepts that command the indulgence of associated analysts who extend the basic principles to an ever broadening and productive motivation. In such pioneering innovations Professor Willard has no peer.

Professor Willard's published work in the application of Ce(IV) in replacement of cerate oxidimetry for permanganimetry are hereinafter cited.

** N. Howell Furman 1892 — (Ph.D. Princeton, 1917, D.Sc. Boston University, 1950, past President of the American Chemical Society and Russell Wellman Moore, Professor, Princeton University, 1942-46), is noted for his many newly developed techniques in analytic chemistry both wet chemical and instrumental innovations and for his contributions simultaneously with those of Professor Willard in the field of Ce(IV) applications originating in 1928 and the following years. Professor Furman is co-author of a standard work with Professor Willard in Quantitative Analysis (4th Ed. 1956) and with I. M. Kolthoff of the book dealing with Potentiometric Titrations, and served as editor for the 1939 revised edition of Scott's Standard Methods of Chemical Analysis. Professor Furman served as OSRD consultant in the Manhattan Project of World War II (1942-46) and subsequent AEC activities.

Bibliographic references to Professor Furman's contributions simultaneously with those of Professor H. H. Willard in Ce(IV) volumetric analyses are hereinafter tabulated.

* L. Th. Lang, (1) "On dissolving ceric oxide in sulfuric acid there is produced a red-yellow solution which possesses extraordinary oxidizing power, for in the most dilute solution it instantly converts ferrous iron to ferric iron, potassium ferrocyanide to potassium ferricyanide and liberates iodine from potassium iodide. It should find use in volumetric analysis as oxidizing agent."

goodly number of cases in which the use of permanganate is inapplicable," for example in the determination of oxalic acid in oxalo-rare earth chlorides, (4) and that "one can employ the solution of Ce(IV) sulfate or nitrate in a great number of cases in which permanganate reactions are applicable."

Meyer and Aufrecht (5) described the preparation of Ce(IV) sulfate from CeO_2 or $Ce(OH)_4$ which process was originally practiced by the procedures developed by Professors Willard and Furman.

Barbieri (6) developed a method for the determination of nitrous acid employing Ce(IV) as oxidant which oxidation is not duplicated employing permanganate oxidimetry. The method employed excess Ce(IV) with iodimetric determination of excess employing thiosulfate. It was stated that hydroxylamine and hydrazine are also thus applicable in the use of the same type process.

Sommer and Pincas (7) described the oxidation and determination of hydrazoic acid employing Ce(IV) oxidimetry.

Benrath and Ruland (8) employing solutions of Ce(IV) prepared as described by Meyer and Aufrecht (5) and standardized by the method of von Knorres (3) developed Ce(IV) methods in the determination of a number of organic compositions. Their work followed the experimental observation that Ce(IV) sulfate in concentrated sulfuric acid oxidized (qualitatively) toluol, naphthalene, and anthracene to benzaldehyde, naphthaquinone and anthraquinone. The determination of tartaric, oxalic, malonic and citric acids, hydroxylamine, sulfite, thiosulfate and hypophosphite were described. The oxidation of formic acid was stated to be very slowly effective by Ce(IV) when exposed for a number of days to sunlight. More complete studies of the determinations involved in the Benruth and Ruland (8) work were carried out with extensions by Willard and Young (10) also employing sulfuric acid solutions to give empirical stoichiometry and by Smith and Duke employing (11) perchloratoceric acid in perchloric acid solution to give stoichiometric reaction equivalents.

Jerome Martin described the determination of hydrazoic acid (9) using excess Ce(IV) and iodimetric evaluation of the excess. The systematic introductory research in cerium(IV) volumetric oxidation-reduction reactions consisted in twenty-one papers, thirteen by H. H. Willard and Philena Young (10) and eight papers by N. H. Furman, three of which were the joint authorships with associated authors. (12, 13, 14, 15) With one exception all of these pioneer developments were burdened by the requisite use of potentiometric equivalence point determination. With few exceptions sulfuric acid solutions were employed. All these procedures were erroneously designated "ceric oxidimetry." All but one (15) required potentiometric equivalence point determinations.

Three new innovations have served to enhance establishment of Ce(IV)

in volumetric analysis as superior to permanganimetry in competitive adoption of the cerium procedures as preference techniques. These are the (1) the development of internal redox indicators of far greater sensitivity in brilliance of color production when compared to the permanganate self indicating equilibrium point determination and with far greater versatility in selective potential transition points. The general application of Ce(IV) reactions in perchloric acid solution represents the number two advance together with the establishment of the status of these reactions as "cerate oxidimetry" in substitution for the early concept of "ceric oxidimetry." The new concept involved the realization that conditions could be established whereby electrode potentials became applicable, by use of hydrochloric, sulfuric, nitric and perchloric acid solutions of Ce(IV), covering the potential range 1.21, 1.44, 1.61, and 1.71 volts at standard state. By employing perchloric acid solutions in 1 to 8 Formal concentrations the potential range for practical reaction conditions mounts to 1.85 volts. Improvement number three involves the need for commercial availability of Ce(IV) analytical reagents to free the early handicap of dependency upon ceric oxide as the predominant raw material for use in preparation of standard solutions. Soon the use of ammonium nitratocerate $(NH_4)_2Ce(NO_3)_6$ for the purification of cerium(IV) rare earth oxides solved this problem. With this advancement in preparational techniques pure Ce(IV) reagents presented no problem and the establishment of ammonium nitratocerate as a primary standard was a prime development differentiating cerate oxidimetry from permanganimetry as a procedural redox volumetric preference. The G. Frederick Smith Chemical Company were the original commercial distributors of a substantial number of required reagents including perchloric acid.

The need for suitable oxidation-reduction indicators applicable to Ce(IV) oxidimetry was clearly indicated by the work of Willard and by Furman and associates. (10-15) It is an anachronism of historical reality that a suitable system had been developed as early as 1898 through the pioneer studies by F. Blau (16) in the studies of the chemistry of bi-pyridine and later that of 1,10-phenanthroline. All the required chemistry of these methine chromophore group chemicals were disclosed by F. Blau. There only remained the re-discovery by Walden, Hammett and Chapman (17) of the Blau innovations and to apply them to the field of cerate oxidimetry. The use of the complex 1,10-phenanthroline-ferrous ion as redox indicator was followed by the synthesis of the 5-nitro analogue (18). Their visual, deep red to faint blue color transitions, at 1.06 and 1.25 volts played a major role in placing cerate oxidimetry in a position of preferential acceptance by comparison with permanganimetry.

It was soon made clear that the commercial preparation and sale of new Ce(IV) reagent chemicals together with the marketing of the accompany-

ing redox indicators was uniquely requisite leading to the general analytical acceptance of cerate oxidimetry. The publishers of the present book revision on the subject were first to supply the indicators and reagents involved (19).

The first applications of the newly designated "cerate oxidimetry" were developed by the research promotions having their origin at the University of Illinois. The preparation of ammonium nitratocerate as applied to the synthesis of sulfatocerate, and perchloratocerate reagents free from other rare earth associates following metathetic reactions as well as by the procedures of electrochemical oxidation, were developed (20). The determination of electrode potentials in mineral acid solutions (21) of HCl, H_2SO_4, HNO_3 and $HClO_4$ were evaluated. The preparation of ammonium nitratocerate as a primary standard (22) effectively influenced standardization techniques. The innovations provided by employing Ce(IV) in perchloric acid which extended reaction kinetics and provided practical procedures in oxidations at potentials higher than 1.71 volts were described. This eliminated empiricism in the oxidation of a wide range of organic materials (23) as a substitute for permanganimetry's Stamm reactions in strong alkali media. The determination of iron, arsenic and oxalic acid (24) on a micro-volumetric scale was provided for by employing perchloratoceric acid oxidations in perchloric acid solution. The disclosure that electrochemical oxidations of Ce(III) to Ce(IV) without the use of a partition (20) cell was made which was an innovation not previously thought to be an applicable technique.

By an additional 25 years of intense research activity (1928-1963), the great measure of which involved research at the University of Illinois, cerate oxidimetry has largely eliminated dependence upon the more complicated procedures of permanganimetry which it most closely duplicates. The determination of glycerol in the manufacture of explosives and in the control laboratories of the soap industry as well as the many routine applications of cerate oxidimetry in the manufacture of iron and steel and ferrous alloys are but a few of the triumphs of Ce(IV) in solving the problems of wet chemical operations in a wide field of important analytical operations.

With the wide range of available redox potentials (1.21 to 1.85 volts) provided by the cerate oxidations, the titrations involve many variations in the applicable internal redox indicators to be preferentially employed. Pioneer studies by Doctor F. P. Richter (25) resulted in the synthesis of a number of substituted 1,10-phenanthrolines whose ferrous sulfate complexes proved to have predictable redox potentials. These disclosures gave the first demonstration that the methine chromophore group organic chelation reagents could provide predictable property modulations depending upon specific substitutions in selective structural positions. The first clue indicating such possibility was provided by the synthesis of 5-nitro 1,10-phenanthroline by Walden Hammett and Edmonds (18). Following the many years of

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masterful synthetic studies contributed by Professor Francis Case* of Temple University in Philadelphia *(26)* there have been created approximately 150 of the various substituted methine chromophore group organic reagents. One phase of the study as redox indicators in the form of their ferrous complexes resulted from structural property prognosis. Thus redox indicators *(21)* have resulted a series of increasing magnitude of color transitions over the range, step by step of 0.85 volts to better than 1.3 volts in progressive increments of 0.01 to 0.02 volt magnitude. Their utility not only provides a wide range of redox magnitudes but their color intensity is often from 5 to 10 fold greater in value than that of the molecular extinction coefficient of the permanganate anion at approximately 2500. The Francis Case developed reagents were put to practical analytical utility through the studies conducted at the University of Illinois by the author and at Iowa State University under the direction of Professor Harvey Diehl and their graduate students.

Cerate oxidimetry thus was freed from dependence upon potentiometric equivalence point evaluation of Ce(IV) volumetric methods devised in 1928 through 1930 by professors Willard and Furman.

Many of the procedures reviewed in the first edition of *"Cerate Oxidimetry"* by the present author have now been displaced or beneficially modified as disclosed in this second edition. Support in the project resulting in over 36 years research has been augmented by many analytical research experts not herein individually cited. This help is gratefully acknowledged.

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SECTION 2

COMMERCIAL CERATE CHEMICAL MANUFACTURE

HYDRATED CERIC OXIDE AS RAW MATERIAL IN SYNTHESIS OF CERIUM ANALYTICAL REAGEANTS

Hydrous ceric oxide is prepared commercially from monosite sand after removal of thorium. The cerous oxalate obtained after removal of thorium as phosphate is ignited to oxide. The demand for 98-100% ceric oxide is found in its use as a grinding abrasive in the preparation of lens types and for the polishing of television picture tubes for which iron oxide rouge was formerly employed. In the synthesis of cerium reagent chemicals, such high temperature ignited cerous oxalate is not desirable. By low temperature firing of cerous oxalate the resulting product is hydrous ceric oxide. In this form the product is soluble in mineral acids.

Hydrous ceric oxide prepared as a second industrial chemical following the recovery of thorium in monosite sand because of isomorphism may not be entirely free from unisolated thorium. In the preparation of thorium free cerium chemicals the raw material may be cerium fluo-carbonate or bastnesite. Hydrous ceric oxide commercially available as obtained from bastnesite provides a source of cerium chemicals free from thorium.

All analytical cerium reagents are best prepared employing hydrous ceric oxide following low temperature firing of cerous oxalate. The purification of this product to free it from other rare earth products consists in its solution in concentrated nitric acid and the conversion of cerium to ammonium nitratocerate, $(NH_4)_2Ce(NO_3)_6$.

THE PREPARATION OF AMMONIUM NITRATOCERATE

Low temperatures fired cerous oxalate, accompanied by air oxidation to form hydrous ceric oxide and other rare earth oxides (and testing 40-45% ceric oxide), is dissolved in excess concentrated nitric acid. The solution thus obtained is filtered under reduced pressure using glass cloth filtering media. The filtered material is diluted with an equal volume of water, evaluated for cerium(IV) content, and the theoretical amount of ammonium nitrate added. This solution is then concentrated by boiling to precipitate out the orange colored crystals of $(NH_4)_2Ce(NO_3)_6$ which are sparingly soluble in strong nitric acid. The product thus obtained is separated employing centrifugal filtration and dried free of nitric acid at approximately 90°C. Results of this procedure are given in Table 1. Technical grades of ammonium nitratocerate should assay 99% purity or better.

The tests for purity of ammonium nitratocerate on a qualitative basis consist in the determination of complete solubility in saturated aqueous solution. This test demonstrates a limiting drying temperature of not over

85°C has been employed above which temperature the product contains water insoluble hydrolytic products. The most prevalent impurity to be guarded against is iron. If the nitratocerate has been prepared from thorium-free hydrous ceric oxide the test for thorium need not be applied. The most important test is that for cerium content.

Dissolve 5.5 g of $(NH_4)_2Ce(NO_3)_6$ in the least requisite water volume in a 400-ml beaker at ordinary temperature. The solution thus prepared should be sparkling clear, red in color, and entirely free from insoluble hydrolytic products. This qualitative test indicates a product properly prepared and dried at a temperature not above 85°C.

Iron impurity is the only heavy metal expected. Apply the iron test to the saturated solution of the sample tested for complete solution in water just outlined. Add dropwise with stirring a 30-percent solution of hydrogen peroxide until the red-orange solution is nearly colorless. Complete the reduction of Ce(IV) to Ce(III) by the dropwise addition of 3% hydrogen peroxide and dilute to 200-ml volume. Neutralize the resulting colorless solution by the dropwise addition of ammonium hydroxide until congo red indicator paper is changed in color from blue to red. Add a few milliliters of dilute hydroxylamine hydrochloride to reduce any iron present. Add 5 ml of a saturated solution of 1,10-phenanthroline to complex any trace of iron present and produce the characteristic red phenanthroline ferrous chelation complex. Dilute the solution to 250 ml in a graduated flask and compare the color, if any, thus produced with a blank determination duplicating the test conditions but without addition of the ammonium nitratocerate. One or two parts per million of iron in the reagent can be detected with certainty in a qualitative sense provided the reagents employed are themselves free from iron. The most likely reagent thus employed which is frequently contaminated with iron is hydroxylamine hydrochloride. Reagent solutions of this reductant free from iron are commercially available.

The determination of cerium in ammonium nitratocerate must follow a strictly quantitative test procedure and the procedures involved will be given in the discussion to follow. A rough qualitative test consists in the ignition of a 1- to 5-gram sample in a covered porcelain crucible at low temperature during thermal decomposition, followed by high temperature ignition to give anhydrous ceric oxide. The theoretical weight of ceric oxide should, by approximation, be obtained.

THE PREPARATION OF PRIMARY STANDARD PURITY AMMONIUM NITRATOCERATE

Potassium dichromate as oxidant has the advantage that solutions for volumetric oxidation reduction reactions can be prepared employing dichromate of primary standard purity. The early undesirable condition that chromium(VI) to chromium(III) redox reactions were not, as compared

TABLE 1

PREPARATION OF HIGH-GRADE HEXANITRATO AMMONIUM CERATE FROM LOW-GRADE THORIUM-FREE OXIDES

Impure (46%) Oxides Taken	Hexanitrato Ammonium Cerate Obtained						Total Yield Obtained		Theoretical Yield	Total Recovery
	1st Crop	Purity	2nd Crop	Purity	3rd Crop	Purity		Purity		
Grams	Grams	%	Grams	%	Grams	%	Grams	%	Grams	%
1968	1576	99.40	475	98.82	390	90.1	2432	97.7	2540	93.5
3280	2435	99.43	—		—		—			

to permanganate redox reactions, self-indicating has been eliminated through the use of newly developed *in situ* oxidation-reduction indicators such as the diphenylamines, 1,10-ferrous phenanthrolines, phenanthranilic acid, and other internal redox indicators. The known water solubility and stability of standard solutions of primary standard purity potassium dichromate, unfortunately, is accompanied by the low oxidation potential provided by its reactions in acid solution. These under no conditions except in 12 molar phosphoric acid exceed 1.3 volts in magnitude. No primary standard purity source of supply of potassium permanganate is possible, and unlike with potassium dichromate, solutions of permanganate are not stable under storage.

The combined desirable properties of permanganate oxidimetry besides its self-indicating advantage and high available oxidation potential (1.52 volts in 1 formal acid solution), and applications in basic solution (the Stamm reactions), served for many years, along with iodimetric volumetric reactions, as universal methods in quantitative volumetric redox analytical procedures.

During approximately the last 30 years, cerate oxidimetry has finally taken precedence over most procedures of dichromate, permanganate and iodimetric oxidimetry due to the many practical advantages it provides. Solutions of sulfatoceric acid in sulfuric acid are stable in storage indefinitely, provide redox potentials of 1.44 volts in 1 formal sulfuric acid, and are free from complicating reaction conditions because of their exclusive single electron reaction exchange. The availability of redox potential internal indicators of far greater sensitivity (up to tenfold greater sensitivity) than that of the self-indicating properties of permanganate redox reactions is an important advantage. The development of cerate oxidimetry to include the perchloratocerate ion in perchloric acid medium with applicable redox potentials of 1.71 to 1.85 volts provides for oxidation reactions of much higher potentials than those provided by permanganimetry. Such reactions provide for the stoichiometric oxidation of organic compositions equal in applicability to those of the Stamm reactions employing alkaline permanganate but still applying to perchloric acid solutions. Furthermore, the standardized solutions of the perchloratocerate ion in perchloric acid solution are more stable in extended periods of shelf life than are replaced permanganate solutions.

The most important advance made in cerate oxidimetry may be justifiably said to be the advent of ammonium nitratocerate as a primary standard of purity reagent. Such development was indicated as a possibility first by the present author with V. R. Sullivan and Gerald Frank *(1)*. The final exhaustive proof of the availability of $(NH_4)_2Ce(NO_3)_6$ as a primary standard in oxidimetry *(2)* was documented by the present author in collaboration with W. H. Fly.* Through its availability in established purity, the cerium content is made readily available for the preparation of high purity companion reagents as well as in the preparation of sulfatocerates and other ceric and cerous reagents of outstanding purity.

PURIFICATION OF TECHNICAL GRADES OF AMMONIUM NITRATOCERATE

The preparation of chemically pure ammonium nitratocerate has been described and two alternate procedures have been devised. Technical grade $(NH_4)_2Ce(NO_3)_6$, 98-100% in purity, prepared as previously outlined, may be dissolved and recrystallized from concentrated HNO_3 as previously indicated. The second alternate procedure is recrystallization from dilute nitric acid (1 to 4, v/v, concentrated HNO_3 Sp.Gr. 1.42 diluted with water). A third alternative involves crystallization from a saturated aqueous solution of the technical grade product following concentration at the boiling point and filtration with centrifugal extraction separation. The third of these two alternatives was applied to 50-pound samples of technical nitratocerate and pure finished product resulted. This third alternative is preferable since drying at 85°C does not evolve nitric acid as a complication. This recrystallization from aqueous solution has not previously been documented.

HEAT STABILITY OF PURIFIED AMMONIUM NITRATOCERATE

To establish the maximum temperature at which ammonium nitratocerate can be dried to eliminate adsorbed water (or nitric acid) stability tests at 79, 87, and 99°C were made and the data are given in Table 2.

In the original description of ammonium nitratocerate as a "proposed" primary standard reagent, a drying temperature of 110°C was specified. The data of Table 2 thus corrects this error. At 99°C there is a small but progressively cumulative loss in weight. The highest permissible drying temperature was found to be 87°C. Sample 1 of Table 2 was dried as taken from the centrifugal extractor. Samples 2 and 3 were dried at 79°C preliminary to the drying experiments of Table 2. The samples in the analytical determination of Ce(IV) content were dried for an additional 4 to 6 hours at 80-85°C followed by storage in desiccators over anhydrous magnesium perchlorate.

CHEMICAL ANALYSES IN DETERMINATION OF PURITY OF AMMONIUM NITRATOCERATE

Method A. Weighed samples of ammonium hexanitratocerate were dissolved in perchloric acid and titrated, using a solution of accurately known concentration of sodium oxalate dissolved in perchloric acid. For these

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* Present address The Miller Brewing Co. of Milwaukee, Wisconsin.

TABLE 2

STABILITY OF AMMONIUM HEXANITRATO CERATE
AT MODERATE DRYING TEMPERATURES

Sample Number	Sample Wt. Grams	Temperature °C	Time Hours	Total Wt. Loss Mg.	Weight Loss %
1	3.1973	79	2	10.5	0.033
			4	None	"
			6	None	"
			8	None	"
			10	None	"
			24	None	"
2	1.6093	87	2	0.5	0.031
			4	1.0	0.062
			6	None	"
			8	None	"
			10	None	"
			24	1.2	0.074
3	1.4259	99	2	0.2	0.014
			4	0.7	0.042
			6	1.2	0.084
			8	2.1	0.147
			12	3.0	0.210
			28	3.3	0.252

titrations nitroferroin (5-nitro-1,10-phenanthroline ferrous sulfate) served as indicator.

Method B. Weighed samples of the same salt were dissolved under the same conditions and titrated, using a solution of accurately known concentration of arsenious acid made from known weights of Bureau of Standards arsenious oxide, also in perchloric acid solution. For this titration a drop of 0.01 M osmic acid in 0.1 N sulfuric acid solution was employed as catalyst. Nitroferroin again served as indicator.

Method C. Weighed samples of the same material were dissolved in a small amount of water and added to a twofold excess of dilute ammonium hydroxide in the apparatus shown in Figure 1. The ceric hydroxide thus quantitatively precipitated was filtered and washed with five or six portions of water to remove ammonium nitrate. Finally, the ceric hydroxide was dissolved in hot 2 F sulfuric acid and the contents of the reaction vessel were withdrawn into a 300-ml filter flask. The reaction flask and filter disk were thoroughly washed with additions of sulfuric acid and the sulfatoceric acid thus obtained was titrated using standard arsenite prepared as for Method B, with osmic acid as catalyst but with ferroin in place of nitroferroin as indicator. [There are two sulfatoceric acids known to exist, having the formulae $H_2Ce(SO_4)_3$ and $H_4Ce(SO_4)_4$. The ammonium salt of formula $(NH_4)_2Ce(SO_4)_3$ may be precipitated from solutions of the former by the addition of ammonium sulfate to solutions of the acid which have only sufficient free sulfuric acid present to prevent hydrolysis. The latter
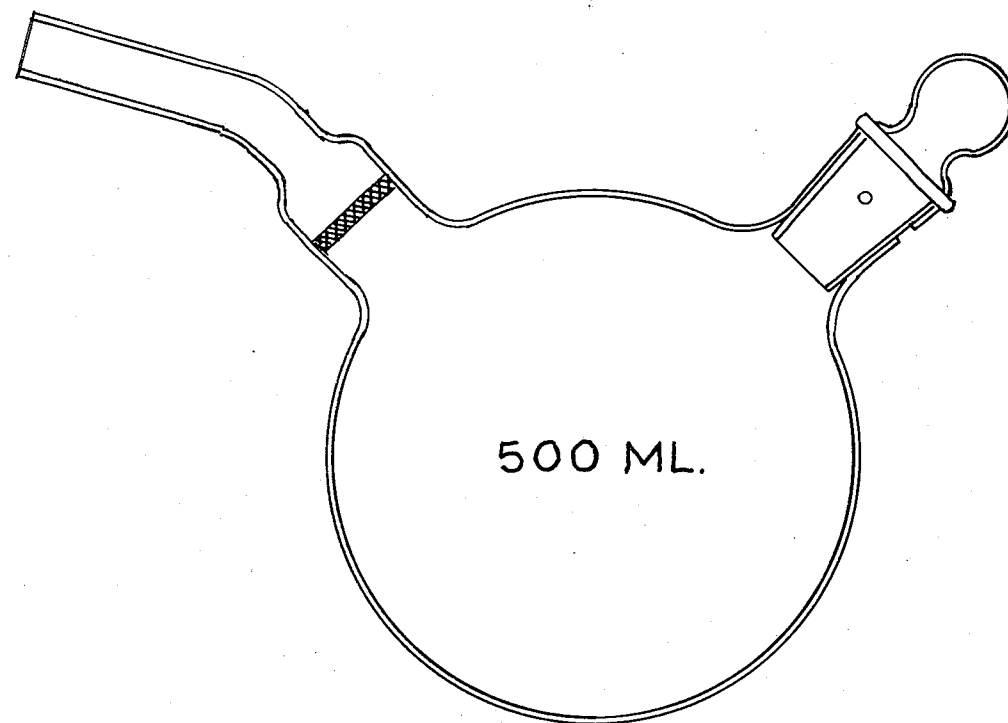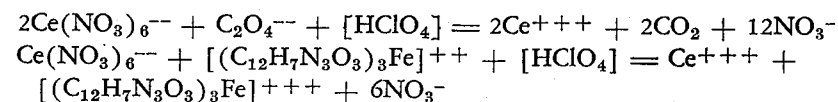
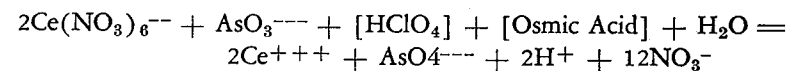14

Figure 1. Apparatus for Precipitation and Filtration

sulfatoceric acid, when present with higher concentrations of sulfuric acid, upon similar treatment forms $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$. This tetra-ammonium sulfatocerate is often described as a double salt, $2(NH_4)_2SO_4 \cdot Ce(SO_4)_2 \cdot 2H_2O$, and is known as Coffelt's salt.

The reactions involved are as follows:

Method A

$$2Ce(NO_3)_6{}^{--} + C_2O_4{}^{--} + [HClO_4] = 2Ce^{+++} + 2CO_2 + 12NO_3{}^-$$
$$Ce(NO_3)_6{}^{--} + [(C_{12}H_7N_3O_3)_3Fe]^{++} + [HClO_4] = Ce^{+++} + [(C_{12}H_7N_3O_3)_3Fe]^{+++} + 6NO_3{}^-$$

Method B

$$2Ce(NO_3)_6{}^{--} + AsO_3{}^{---} + [HClO_4] + [Osmic\ Acid] + H_2O = 2Ce^{+++} + AsO4{}^{---} + 2H^+ + 12NO_3{}^-$$

(Indicator reaction the same as for Method A)

Method C

$$Ce(NO_3)_6{}^{--} + 4NH_4OH = Ce(OH)_4 + 4NH_4{}^+ + 6NO_3{}^-$$
$$Ce(OH)_4 + 4H_2SO_4 = [Ce(SO_4)_4]^{----} + 4H_2O + 4H^+$$

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$$2Ce(SO_4)_4{}^{----} + AsO_3{}^{---} + H_2O + [H_2SO_4] + [Osmic\ Acid] =$$
$$2Ce^{+++} + AsO4^{----} + 2H^+ + 8SO_4{}^{--}$$
$$Ce(SO_4)_4{}^{----} + [(C_{12}H_8N_2)_3Fe]^{++} + [H_2SO_4] =$$
$$Ce^{+++} + [(C_{12}H_8N_2)_3Fe]^{+++} + 4SO_4{}^{--}$$
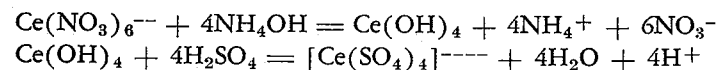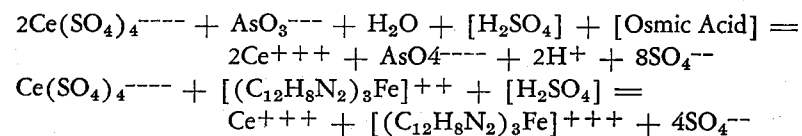
PREPARATION OF PRIMARY STANDARD ARSENITE AND OXALATE SOLUTIONS

Weighed quantities of sodium oxalate (National Bureau of Standards No. 40e) were dissolved in 2 F perchloric acid, transferred to a weighed 300- or 600-ml glass-stoppered flask, and diluted to approximately 300 to 600 ml, employing 2 F perchloric acid. For weighings under 100 grams, a Troemner No. 10 balance was employed together with a calibrated set of standard weights. The solution weights were taken using an August Sauter balance of 10-kg capacity (with a sensitivity of 10 mg) balance. Buoyancy corrections were applied in all weighings. The standard solutions thus prepared were used to titrate weighed portions of the nitratocerate; in all titrations weight burets of design previously described were employed. Weight buret readings were determined after applying buoyancy corrections using the Troemmer balance.

Sodium oxalate or arsenious oxide (equivalent weights roughly 67 and 49.5, respectively), because of their low values, make preferable the titration of weighed samples of ammonium hexanitratocerate by oxalate or arsenite to the reverse titration. By use of 0.05 to 0.06 N strength of titrating solution a 40-gram sample reacts with 1.1 to 1.3 grams of ammonium hexanitratocerate. Such samples, individually weighed, afford better accuracy than the weighing of 0.2 to 0.25 gram of arsenious oxide or sodium oxalate which would be required for individual titrations by the reverse procedure. An added advantage, following the procedure as chosen, consists in the fact that solutions of ammonium nitratocerate acidified using perchloric acid change titer detectably in 72 to 96 hours, whereas the solutions of arsenite or oxalate containing perchloric or sulfuric acid are stable indefinitely. The potentiometric titrational characteristics of these reactions have been described.

Solutions of predetermined strength in arsenious oxide were prepared from National Bureau of Standards primary standard sample 83a with acidification using either 2 F perchloric acid or 1 F sulfuric acid as solvent. The weighed portions were placed in 250-ml beakers and dissolved in a small volume of water by the addition of sufficient pellet sodium hydroxide to form sodium arsenite. These samples were then acidified with acids of the proper strength and transferred to 500- or 1000-ml glass-stoppered flasks and the solutions were weighed as previously described.

The data governing the preparation of the arsenite and oxalate solutions are given in Table 3.

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TABLE 3

PREPARATION OF ARSENITE AND OXALATE SOLUTIONS FOR EVALUATING PURITY OF AMMONIUM HEXANITRATOCERATE

Solution No.	Type	$Na_2C_2O_4$ or As_2O_3 Taken Grams	Solution Weight Grams	Acid Used	Weight of Salt G./g.	Calcd. Value of $(NH_4)_2Ce(NO_3)_6$ G./g.
1	Arsenite	3.0019(5)	1016.72(9)	2 F HClO₄	0.0028274	0.081345
2	Arsenite	3.0103(0)	1055.50(6)	1 F H₂SO₄	0.0028520	0.081611
3	Oxalate	3.2335(0)	548.37(6)	2 F HClO₄	0.0060606	0.049450
4	Arsenite	2.2845(0)	516.82(1)	2 F HClO₄	0.0044245	0.049068
5	Oxalate	1.5409(5)	278.58(4)	2 F HClO₄	0.0055813	0.045259
6	Arsenite	2.2818(5)	601.34(1)	1 F H₂SO₄	0.0038112	0.045251

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DETERMINATION OF PURITY OF AMMONIUM HEXANITRATOCERATE SAMPLE 1

Sample 1 of ammonium hexanitratocerate was analyzed by solution in perchloric acid and titration, using standard of reference arsenious oxide and sodium oxalate as two individual and distinctive procedures. The third, and radically altered, procedure followed the scheme of the precipitation of Ce(IV) from excess ammonia solution, filtration, washing, solution in sulfuric acid, and final titration by a sulfuric acid solution of sodium arsenite prepared from primary standard arsenious oxide. Standard solutions 1, 2, and 3 (prepared as shown in Table 3) were employed for these analyses. The results of the first two procedures agree to a very close tolerance (by the two directly applied analyses). The results of the indirect ceric hydroxide isolation, solution, and titration [an indirect procedure involving isolation of Ce(IV)] agree satisfactorily with the direct titrations and serve to "make assurance doubly sure." This indirect evaluation of the oxidation equivalent of the hexanitratocerate proves conclusively that its total oxidation value lies in its cerium content. In addition, the procedure as described is shown to be a reliable scheme for the preparation of solutions of sulfatoceric acid [$H_4Ce(SO_4)_4$] of predetermined titer without the ammonium nitrate and nitric acid which would be present if such solutions were to be prepared by direct solution of ammonium hexanitratocerate in sulfuric acid and dilutions to a fixed volume. The data are given in Table 4. Buoyancy corrections were calculated using the determined value of 2.61 as the specific gravity of ammonium hexanitratocerate at 25°C.

By examination of Table 4 it is observed that the maximum average deviation in results among the three methods is 2 parts in 10,000. The average analysis in 14 determinations indicates that the purity of this sample of hexanitratocerate is 99.99%. The indirect procedure of analysis, following isolation of this salt's cerium content, shows results 0.01% lower — namely, 99.98%. This lower value may be attributed to the introduction of additional manipulative processes of a less direct nature, following which the values were determined. The results given in Table 4 are consecutive analyses with no omission in any given system of analyses. The recommended purity given with the Bureau of Standards certificates of 99.99% for standard 83a arsenious oxide and 99.96% for sodium oxalate sample 40e were applied to the calculations of Table 4. Solution densities for buoyancy correction were calculated from weight data and the specific gravity of the acids used in their preparation.

The procedures described in the analysis of sample 1 of ammonium hexanitratocerate were repeated in the case of sample 2 with results shown in Table 5.

By examination of Table 5, the same conclusions may be drawn as those

TABLE 4

DETERMINATION OF PURITY OF AMMONIUM HEXANITRATOCERATE SAMPLE 1 (EMPLOYING As_2O_3 AND $Na_2C_2O_4$ AS PRIMARY STANDARDS)

$(NH_4)_2Ce(NO_3)_6$ Sample Weight Grams	Reference Solution (Table 3)	Weight of Standard Solution Required Grams	$(NH_4)_2Ce(NO_3)_6$ Indicated Grams	Error of Recovery Mg.	Calcd. Salt Purity %
1.3024(3)	1	41.546	1.3022(4)	—0.19	99.97(9)
1.3039(8)	1	41.597(5)	1.3038(7)	—0.11	99.98(4)
1.3055(3)	1	41.651	1.3055(4)	+0.01	100.00
1.3043(8)	1	41.609	1.3042(2)	—0.16	99.98(3)
				Av.	99.985
1.0066(8)	3	20.297(5)	1.0065(5)	—0.13	99.98(7)
1.0076(8)	3	20.328(5)	1.0080 8	+0.40	100.03(7)
1.0050(7)	3	20.266(5)	1.0050(2)	—0.05	99.99(5)
1.0270(0)	3	20.713(5)	1.0271(7)	+0.17	100.01(6)
1.0093(8)	3	20.351	1.0092(1)	—0.17	99.98(3)
1.0051(7)	3	20.267(5)	1.0050(6)	—0.11	99.98(9)
				Av.	100.00(1)
1.3016(1)	2	41.164	1.3012(4)	—0.37	99.97(5)
1.3016(7)	2	41.229	1.3032(9)	—0.22	99.98(8)
1.3035(1)	2	41.262	1.304(4)	—0.47	99.96(6)
1.3048(1)	2	41.252	1.3040(1)	—0.50	99.97(1)
				Av.	99.97(5)

Av. of 14 individual analyses, 99.98(9)% purity

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observed with regard to Table 4. The most probable value for the purity of ammonium nitratocerate sample 2 is 99.98%.

ERRORS IN CONVERSION OF AMMONIUM HEXANITRATOCERATE TO PERCHLORATOCERIC ACID AND CERIC HYDROXIDES TO SULFATOCERIC ACID

Solutions of ammonium hexanitatocerate in 1 F perchloric acid have an oxidation potential of 1.71 volts; they are not permanently stable and very gradually diminish in oxidation value with time of storage. If stored at ice box temperatures and in dark bottles, solutions (even of 0.001 N concentrations) need be restandardized only at 72 to 96-hour intervals. For the preparation of 0.05 to 0.1 N solutions of ammonium hexanitratocerate in perchloric acid for use in macrovolumetric determinations, restandardization is required only after 72 hours' storage. Storage in dark bottles in a cool place is recommended.

In making perchloric acid solutions of ammonium hexanitratocerate, great care should be taken to avoid the presence of organic matter. The importance of pure water and thoroughly clean containers cannot be overemphasized. Cellulose, sugars, alcohols, and many other organic materials are readily and quantitatively oxidized by the cerate ion in perchloric acid solution. The use of too much stopcock grease in burets may introduce errors. The presence of carbonaceous dusts causes perchloratocerate solutions to change titer. Contact with platinum in the form of sponge or platinum black causes comparatively rapid reduction of such solutions. These are all penalties associated with an oxidation medium of exceptionally high oxidation potential.

Special directions must be followed in the preparation of solutions of ammonium hexanitratocerate in perchloric acid.

To prepare such a solution of 0.1 N strength, 54.826 grams (corrected weight of the pure salt) are placed in a 1000-ml beaker and 83.8 ml of 72% perchloric acid are added. The salt is not soluble in perchloric acid of this strength, but should be stirred with it for 2 minutes. A 100-ml portion of water is added and the stirring is continued for 2 minutes. The addition of 100 ml of water is repeated a third, fourth, and fifth time with intermediate stirring for 2-minute intervals. By this necessary procedure all the ammonium hexanitratocerate will be in solution at 500- to 600-ml volume and may be transferred to a 1000-ml graduated flask and diluted to volume. The ammonium hexanitratocerate would dissolve completely to form a crystal-clear solution if it were dissolved in the perchloric acid first diluted and added to the nitratocerate. Such a solution after 24 hours would be partially precipitated, owing to the presence of complex nitratoperchloratocerates which are sparingly soluble. If the salt crystals are added to 72% perchloric acid the $Ce(NO_3)_6^{--}$ complex ion is sufficiently completely con-

TABLE 5
DETERMINATION OF PURITY OF AMMONIUM HEXANITRATOCERATE SAMPLE 2
(EMPLOYING AS₂O₃ AND NA₂C₂O₄ AS PRIMARY STANDARDS)

$(NH_4)_2Ce(NO_3)_6$ Sample Weight Grams	Reference Solution (Table 3)	Weight of Standard Solution Required Grams	$(NH_4)_2Ce(NO_3)_6$ Indicated Grams	Error of Recovery Mg.	Calcd. Salt Purity %
1.0039(3)	4	20.345(5)	1.0038(5)	—0.08	99.99(2)
1.0022(3)	4	20.307	1.0019(6)	—0.27	99.97(3)
1.0076(8)	4	20.397	1.0063(8)	—0.40	99.96(0)
1.0021(3)	4	20.311	1.0021(3)	±0.00	100.00
1.0063(8)	4	20.395	1.0062(8)	—0.01	99.99
1.0074(3)	4	20.406(5)	1.0068(6)	—0.50	99.97(9)
					Av. 99.97(7)
1.0022(1)	5	22.140	1.0020(2)	—0.19	99.98(1)
1.0045(3)	5	22.189	1.0042(5)	—0.28	99.97(1)
1.0204(5)	5	22.541	1.0201(8)	—0.27	99.97(4)
1.0133(3)	5	22.387	1.0132(1)	—0.12	99.98(8)
					Av. 99.97(9)
1.094(1)	6	26.251(5)	1.1091(5)	—0.26	99.97(6)
1.0795(3)	6	25.539	1.0790(4)	—0.49	99.95(5)
1.0857(7)	6	25.711(5)	1.0863(4)	—0.43	99.96(1)
1.0496(6)	6	24.841(5)	1.0495(1)	—0.15	99.99(1)
1.0379(6)	6	24.561(5)	1.0377(4)	—0.22	99.97(8)
1.0846(1)	6	25.662	1.0842(3)	—0.38	99.96(5)
					Av. 99.96(9)

Av. of 16 individual analyses, 99.97(7)%

verted to the $Ce(ClO_4)_6{}^{--}$ ion to prevent the formation of insoluble material.

The substitution of sulfuric acid for perchloric acid requires that a duplicate solution procedure be applied with slow addition of the first 100-ml of water over a 5-minute period with stirring (56 ml of 95% sulfuric required in place of 83.8 ml of 72% perchloric acid). Mixed nitratosulfatocerates are more insoluble than the mixed nitratoperchloratocerates and would precipitate copiously upon standing were this procedure not followed.

Solutions of sulfatoceric acid, $H_4Ce(SO_4)_4$, and perchloratoceric acid, $H_2Ce(ClO_4)_6$, prepared by the process described above, contain ammonium and nitrate ions. The solutions are of known normality and for most applications serve admirably. If ammonium and nitrate ions are undesirable, solutions of perchloratoceric acid are best prepared by the electro-oxidation of Ce(III) in perchloric acid. For the preparation of sulfatoceric acid the method described above in connection with the determination of the purity of ammonium hexanitratocerate is employed. The apparatus in Figure 1 serves conveniently for the precipitation of ceric hydroxide, with removal of the ammonium and nitrate ions, solution of the ceric hydroxide in warm 2 F to 4 F sulfuric acid, and final dilution to the predetermined volume. An Ace sintered-glass filtering crucible with porosity E may be used to filter and wash ceric hydroxide. Filter paper or a platinum Munroe filtering crucible must be avoided. If filter paper is used some of the sulfatoceric acid is invariably reduced; results may be 1 to 2% low. Low results are also caused by contact between hot sulfatoceric acid and platinum sponge if a Munroe crucible is employed.

DECOMPOSITION OF PERCHLORATOCERIC ACID SOLUTIONS IN CONTACT WITH PLATINUM SPONGE

A solution of approximately 0.1 N perchloratoceric acid was prepared from ammonium hexanitratocerate and perchloric acid, and was stored in contact with platinum sponge formed by the ignition of 1 gram of chloroplatinic acid. The perchloratoceric acid solution was stirred continuously at ordinary temperatures and analyzed at stated intervals. The original normality was 0.1020. After 2 hours it was 0.0996, after 5 hours 0.0980, after 22 hours 0.0925, and after 96 hours 0.0775 N. This is a drop of almost 25% in oxidation value. Sulfatocerate solutions are not as extensively affected, but the loss is readily noted when hot solutions are filtered using a platinum Munroe filtering crucible. Graphitic carbon is known to exert a similar catalytic reducing effect.

STABILITY OF CRYSTALLINE AMMONIUM NITRATOCERATE WITH LONG PERIODS OF STORAGE

Ammonium nitratocerate consists of oxidizable cations, $2NH_4{}^+$, and a complex anion, $Ce(NO_3)_6{}^{--}$, which is known to be a powerful oxidizing

material. Solutions of hexanitratoceric acid, $H_2Ce(NO_3)_6$, in nitric acid are known to be unstable to a minute but measurable extent. This instability is brought about by the decomposition of water with the evolution of oxygen through the intermediate liberation of free radical hydroxyl groups. In order to study the shelf life of crystalline ammonium nitratocerate, after completion of the present work and preparation of the manuscript it was thought appropriate to delay 2 years to permit a shelf life test period and subsequent additional analyses. The procedure duplicated that previously described and employed the same corrections and the same drying temperature and previously analyzed samples.

Sample reagent 1 with 2 years and over "shelf existence" was reanalyzed with the results shown in Table 6.

Table 6 shows that the new primary standard, $(NH_4)_2Ce(NO_3)_6$, does not measurably alter in value as an oxidant with extended periods of storage.

TABLE 6

ANALYSIS OF SAMPLE 1 AFTER MORE THAN 2 YEARS' STORAGE UNDER ORDINARY CONDITIONS

[Test of stability and retention of oxidation value with long-term storage. As_2O_3 solution, 0.027415 gram per gram, equivalent to 0.303935 gram of $(NH_4)_2Ce(NO_3)_6$ per gram of solution]

Sample No.	As_2O_4 Soln. Grams	$(NH_4)_2Ce(NO_3)_6$		Purity %
		Taken Grams	Found Grams	
1	10.3884(6)	3.1578(4)	3.1573(5)	99.986
2	8.5872(4)	2.6101(0)	2.6099(6)	99.994
3	8.1556(2)	2.4788(4)	2.4787(8)	99.997
4	8.3569(5)	2.5402(5)	2.5399(7)	99.989
5	7.8023(9)	2.3719(6)	2.3714(2)	99.977
6	8.9750(8)	2.7281(2)	2.7278(9)	99.990
			Av.	99.989

THE PROBLEM OF THE SEPARATION OF SMALL AMOUNTS OF THORIUM NITRATE IN PURIFICATION OF AMMONIUM NITRATOCERATE

It has been established that hydrous ceric oxide containing appreciable amounts of thorium when purified by the process previously applied, tenaciously retains small amounts of thorium as impurity. The most effective alternative in the preparation of primary standard ammonium nitratocerate is to employ hydrated ceric oxide prepared from thorium-free raw material with bastnesite as the mineral source. Spectrographic analyses of such materials as those exhaustively analyzed as previously described (2) by two specialists, have provided contradictory results. One expert found the absence of thorium and the other found evidence of 0.05 percent of thorium in some cases. The latter finding does not seem to be possible in accordance

with the test analyses previously outlined. There remains the need for the study of this problem starting with thorium-free hydrated ceric oxide to which has been added known amounts of thorium oxide. By successive recrystallizations of $(NH_4)_2Ce(NO_3)_6$ thus prepared, analysis will establish the progressive elimination of thorium, giving a series of diminishing returns, until complete removal of thorium can be established. Chemical analyses can then be accompanied by spectrographic tests. By such procedure this troublesome speculation involving chemical versus physical testing may possibly be rationalized. It is confidently predicted that the purification of raw material hydrated ceric oxide containing minor amounts of thorium can be accomplished by conversion to and recrystallization as ammonium nitratocerate.

A ROUTINE ANALYTICAL TESTING PROCEDURE FOR PURITY OF AMMONIUM NITRATOCERATE OF PRIMARY STANDARD QUALITY

The following procedures (3) have been devised and documented by the author to provide means to accurately test preparations of $(NH_4)_2Ce(NO_3)_6$ to be used as primary standard reference reagent, rapidly and with requisite precision. The method was applied to material recrystallized from hot saturated aqueous solution and dried to constant weight at 85°C.

Reagents

Perchloric acid: Formal, sp. gr. 1.055 at 25°/4°.

Sodium Oxalate: U.S. Bureau of Standards, primary standard.

Nitro-ferroin indicator solution: 0.001825 N; 1 ml is equivalent to 0.0010 g of ammonium nitratocerate.

Ammonium nitratocerate solution: 1 mg of nitratocerate in 1 ml of 1 F perchloric acid (0.001825 N nitratocerate).

Ammonium nitratocerate to be tested for purity: Dried to constant weight at 85° (Mol. Wt. 548.25₈).

Aparatus

400-ml beakers: Freed from the least trace of adsorbed organic matter by rinsing with hot perchloric acid containing ammonium nitratocerate, followed by rinsing with distilled water.

Transfer pipette: 1.0-ml capacity.

Calibrated 1.0-ml pipette: marked in 0.1-ml graduations.

Procedure

Weigh accurately 2.1938 g of ammonium nitratocerate. Transfer the weighed sample to a 400-ml beaker. Dissolve the sample in 125-130 ml of 1 F perchloric acid. The solution will be light yellow. This weight of sample is equivalent to 40 ml of 0.1000 N reagent for test (with a 0.0008-g vacuum weighing correction applied).

Weigh accurately 0.2680 g of standard reference sodium oxalate. Transfer the weighed sample to a 400-ml beaker. Dissolve the oxalate in 125-130

ml of 1 F perchloric acid. This weight is equivalent to 40 ml of 0.1000 N reagent solution (any vacuum weighing correction is negligible).

With thorough stirring (preferably by a magnetic device with accompanying beaker rotor) transfer the cerate solution to the oxalate solution, slowly, over an interval of 15-20 sec. The interaction is instantaneous at ambient temperature.

Now add 1 ml of indicator. With nitratocerate of 100% purity, the indicator will give a pink solution because of its own color. If the nitratocerate is somewhat less than 100% pure, the color of the solution at this point will be produced by the indicator in the presence of a minute excess of unoxidized oxalate.

Using the calibrated 1-ml pipette, now add the volume of 0.001825 N nitratocerate solution just necessary to decolorize the indicator. If 1.0 ml only of this nitratocerate solution is required, the standard of reference oxidant being tested is 100.00% pure. Each 0.1 ml of the titrant over 1.0 ml corresponds to 0.0001 g of additional nitratocerate which must be added, to be exactly equivalent to the weight of sodium oxalate oxidized. By subtracting 1.0 ml from the required addition of back-titrant, and multiplying the result by 0.0010 g/ml, the correction weight of ammonium nitratocerate is found. This value subtracted from 2.1930, and the result divided by 2.1930 will give the purity of the test sample under standardization.

PRECAUTIONS

Do not dry ammonium nitratocerate above 85°.

The reaction beakers must be completely devoid of adsorbed organic material on their inner walls. The redox potential of the

$$Ce(IV) \longleftrightarrow Ce(III)$$
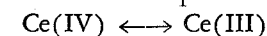
system in 1 F perchloric acid, as previously stated, is 1.71 V. Almost all forms of organic matter are rapidly oxidized, exhibiting high equivalency factors.

The indicator is added in minimal amounts because of low solubility in perchloric acid solution (less than sufficient to form a 0.001 N solution).

The redox color change at the equivalence point is not permanent. In bright daylight, or on exposure to direct sunlight, it is quite rapidly reduced from the ferric to the ferrous form with return of the red color (4-5 min).

For each ml of 0.1000 N solution, 54.4825 mg of $(NH_4)_2Ce(NO_4)_2$ are required.

Literature Cited

(1) G. Frederick Smith, V. R. Sullivan, and Gerald Frank, "Hexanitrato Ammonium Cerate as a Proposed Reference Standard in Oxidimetry." *Ind. Eng. Chem.* Anal. Ed., 449 (1936).
(2) G. Frederick Smith and Walter H. Fly, "Ammonium Hexanitrato Cerate as a Primary Standard in Oxidimetry." *Anal. Chem.*, 21, 1233 (1949).
(3) G. Frederick Smith, "An Improved Preparation of Ammonium Hexanitratocerate and Analytical Testing Procedure to Prove Primary Reference Standard Purity." *Talanta*, 10, 709 (1961).

SECTION 3

ELECTROCHEMICAL OXIDATION OF CERIUM(III) IN HCl, H_2SO_4, HNO_3 AND $HClO_4$ SOLUTION DETERMINATION OF ELECTRODE POTENTIALS

The precise oxidation potential of the Ce(III) to Ce(IV) system in sulfuric acid solution at standard state has been determined by Kuntz (1). The precise value for nitric acid solutions was determined by Noyes and Garner (2). The accurate determination of the oxidation potential in perchloric acid solution has been made by Schumb, Sherril and Sweester (3).

The electro-oxidation of cerous solutions was originally thought to require a partition cell as was employed by Hengstenberger (4). The use of a diaphragm electrolytic oxidation cell was shown to be unnecessary by Smith, Frank and Kott (5). For oxidation of cerous chloride in hydrochloric acid a diaphragm cell is requisite.

Solutions of cerous chloride, sulfate nitrate, and perchlorate were electro-oxidized to the corresponding H_2CeCl_6, $H_2Ce(SO_4)_3$, $H_2Ce(NO_3)_6$ and $H_2Ce(ClO_4)_6$ to give complete conversion to Ce(IV). Acid concentrations of 1 to 8 formal strength were applied (HCl solutions of H_2CeCl_6 only 1 normal acid were prepared).

The single electrode potential in each case was determined by reducing a known volume of solution by the addition of a few drops of 100 volume hydrogen peroxide, determining the exact point of complete reduction potentiometrically. The proper volume of the same Ce(IV) solution was then added to produce a ratio of 1 to 1 reduced and oxidized cerium in the various solutions of known free acid content. In the hydrochloric acid and sulfuric acid solutions, the saturated calomel electrode was used as reference with platinum as the other electrode. In the nitric and perchloric acid solutions, a saturated sodium nitrate or sodium perchlorate salt bridge was interposed between the calomel electrode and the cell liquid to establish the 1 to 1 ratio of oxidized and reduced cerium, and the salt bridge was removed for reading the adjusted solution potential. This was done to prevent error from diffusion of chloride into the cell which is easily oxidized in the case of the nitric and perchloric acid solution of tetravalent cerium. The final reading in direct contact with the saturated calomel cell was taken because of the unknown liquid junction potential from the salt bridge. Details of the potentiometer circuit are omitted, since an accuracy of greater than 0.01 volt is not claimed. The concentration of Ce(IV-Ce(III) employed was 0.025 normal.

The single electrode potentials found are given in Table 7.

The data of Table 7 indicate that the electrode potentials vary to a marked degree in solutions at standard state. The single electrode potential in 1 normal acid is lowest in value for hydrochloric acid solutions and increases materially for the sulfuric, nitric and perchloric acid solutions. Following the assumption that the Ce(IV) (or "ceric ion" of the earlier concept of "Ceric Oxidimetry") this fact stands out clearly as an anomaly. According to the assumption of a simple cericcerous solution the single electrode potential should not be materially affected by change in mineral acid identity or concentration.

TABLE 7
Single Electrode Potential Values, $Ce(IV)+e = Ce(III)$ in Various Concentrations of HCl, H_2SO_4, HNO_3, and $HClO_4$*

N. Acid Concentration	Electrode Potentials with Reference to the Normal Hydrogen Electrode			
	$HClO_4$	HNO_3	H_2SO_4	HCl
1	1.70	1.61	1.44	1.28
2	1.71	1.62	1.44	--------
4	1.75	1.61	1.43	--------
6	1.82	--------	--------	--------
8	1.87	1.56	1.42	--------

* The values found for normal acid concentration were the duplicate of those cited by references (1), (2), and (3) at the end of this section.

acid identity or concentration. Both sulfuric and nitric acids at increased concentration lower the potential in the range 4 to 8 normal. The most marked change, that in perchloric acid solution, results in substantial increase in value.
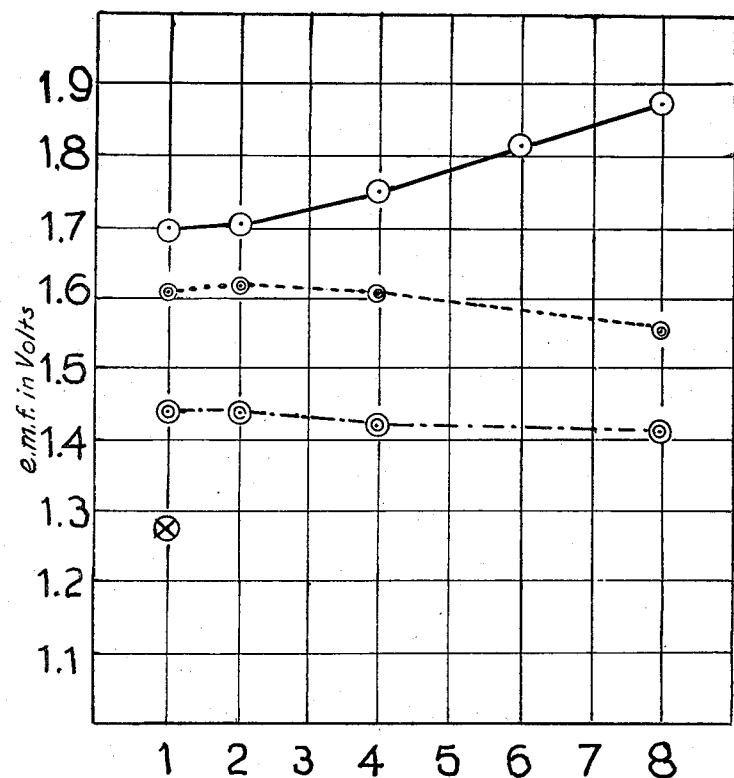
The data of Table 7 is given graphically in Figure 2.

Figure 2. Acid Formality. (Top) Perchloric Acid. (Top but One) Nitric Acid. (Top but Two) Sulfuric Acid. (Bottom) Hydrochloric Acid

POTENTIOMETRIC TITRATION OF FERROUS IRON BY Ce(IV) IN NORMAL HCl, H₂SO₄, HNO₃ AND HClO₄ SOLUTION

The results from the potentiometric titration of ferrous iron in normal HCl, H_2SO_4, HNO_3 and $HClO_4$ by the corresponding H_2CeCl_6, $H_2Ce(SO_4)_3$, $H_2Ce(NO_3)_6$ and $H_2Ce(ClO_4)_6$ oxidants, also in the same acid media and concentration is shown graphically in Figure 3.

By examination of Figure 3 it will be observed that the potential indicated for the condition of equal concentrations of Ce(III) and Ce(IV) at the end of the titrations corresponds closely to that to be predicted by the data of Table 7.

Potentiometric titrations of ferrous perchlorate in various concentrations of perchloric acid (1 to 8 normal) by Ce(IV) in solutions of the same acid normality is given graphically in Figure 4.
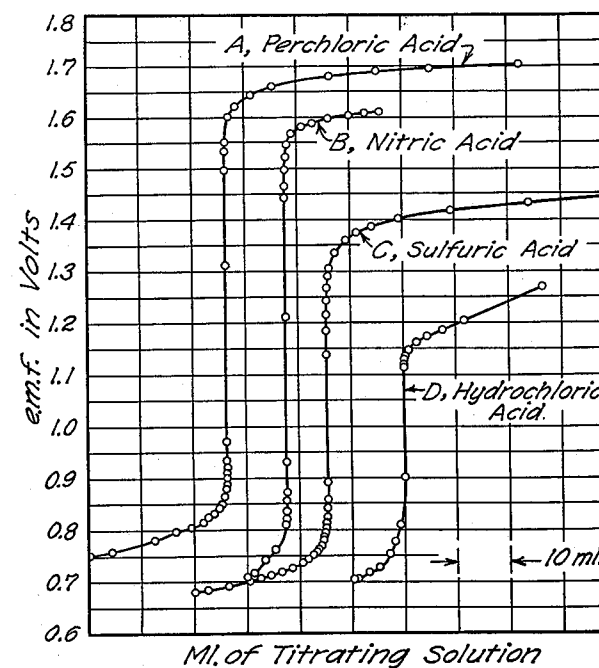
Figure 3. The Potentiometric Titration of Ferrous Iron in Normal HClO₄, H₂SO₄, HNO₃, and HCl
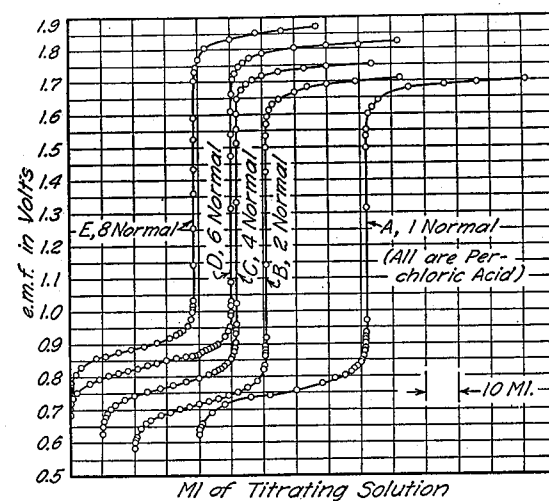

Figure 4. Titration of Ferrous Perchlorate at 1 to 8 N Perchloric Acid Strength

By use of 8 normal perchloric acid and oxidation of solutions containing both ferrous and vanadyl ions with perchloratoceric acid in 8 formal $HClO_4$ the differential determination of both iron and vanadium may be accomplished. The data are shown graphically for this potentiometric titration in Figure 5.
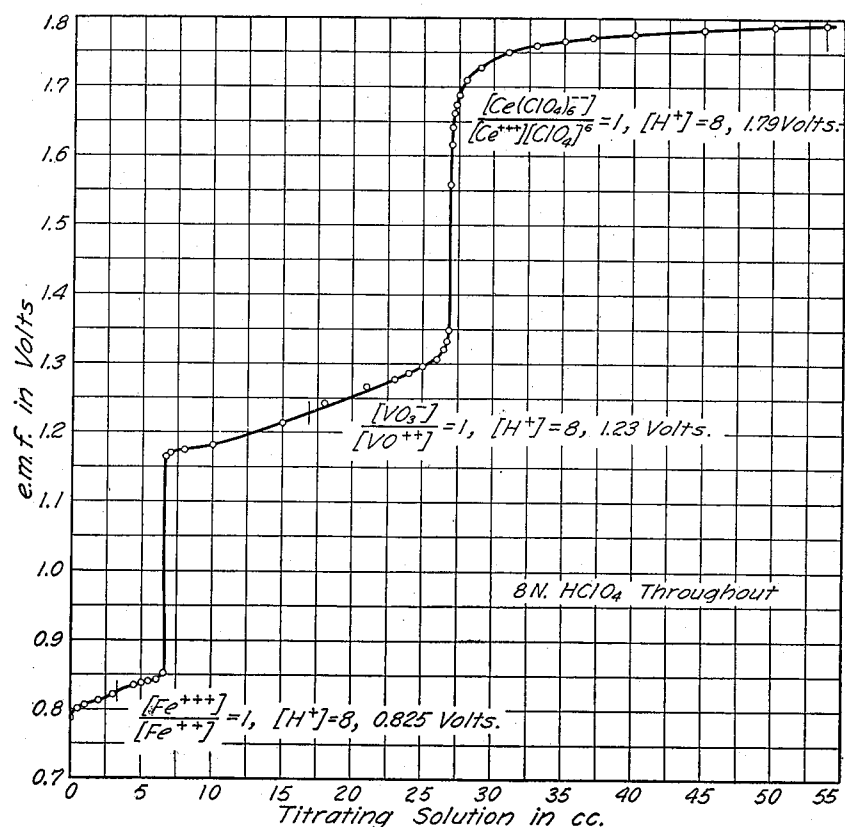

Figure 5. The Potentiometric Titration of Fe(II) and VO_2^- by $H_2Ce(ClO_4)_6$ in 1 Normal $HClO_4$

The apparatus assembly employed *(5)* in the electro-oxidation of cerous sulfate, nitrate, and perchlorate consisted in a four-liter beaker employing a small stirring motor and glass shaft with fan blades of glass at its lower extremity, (stirring magnetically would be preferable). Three liters of electrolyte can be conveniently oxidized. A six-volt auto storage battery and heavy duty rheostat with an ammeter and voltmeter supplied the energy and monitored reaction conditions.

ELECTRODES

Two types of anodes were employed, plain surface sheet platinum (Type A) and cylindrical platinum gauze (Type B). The former were 10.2 cm square, the lower half of foil 0.127 mm thick, and the upper half of sheet 0.25 mm thick. Welded to the top of each such anode was a lead-in band 12.7 mm wide, 50 mm long, and 0.75 mm thick. Two electrodes were bent to form half cylinders and mounted side by side to form a complete cylinder 10.2 cm tall and 6.0 cm in diameter. Each electrode weighed approximately 57 grams and had 207 sq. cm. of contact surface.

Type B anodes were 76 mm in diameter and 152 mm tall, made of wire 0.21 mm in diameter, 18 meshes per centimeter. Two leading wires 90 mm long and 2.5 mm in diameter were welded to two of the four vertical ribs. Each such anode weighed approximately 142 grams and had a surface area calculated to be 935 sq cm.

Three types of platinum cathodes were employed. Type C were 152-mm lengths of wire, 1 mm in diameter, giving an area of 4.75 sq cm. Type D were 152-mm lengths of platinum foil, 0.127 mm thick and 8 mm wide, having an area of 12 sq cm. Type E were the same as type A anodes.

PREPARATION OF SOLUTIONS

Ceric oxide free from thorium and containing approximately 40 per cent CeO_2 was converted to hexanitrato ammonium cerate, $(NH_4)_2Ce(NO_3)_6$, by the process described by Smith, Sullivan, and Frank *(5)* except that the final crystallization was omitted. This resulted in the preparation of a starting material of 98 to 99.5 per cent purity, the remainder consisting of rare earths of the cerium group except thorium. A gram molecule of the complex nitrate was dissolved in dilute nitric acid and reduced, using a slight excess of 100-volume hydrogen peroxide. Hydrochloric acid was then added, as well as nitric acid, followed by gentle boiling until ammonium salts were decomposed. Finally the mixture was evaporated with excess nitric acid to give cerous nitrate containing but small amounts of excess nitric acid. For the oxidation of cerous nitrate, $Ce(NO_3)_3$, to nitrato ceric acid, $H_2Ce(NO_3)_6$, a definite amount of nitric acid was added with dilution to the proper volume.

Cerous perchlorate was prepared from known amounts of cerous nitrate, obtained as described above. After the addition of known amounts of 72 per cent perchloric acid and evaporation to strong fumes to remove nitric acid, the resulting product was ready for dilution to volume and electrolytic oxidation.

Cerous sulfate octahydrate, $Ce_2(SO_4)_3 \cdot 8H_2O$, was prepared from cerous nitrate obtained as described above. An excess of sulfuric acid was added to a hot solution of cerous nitrate in water and the resulting product was

filtered, using a fritted-glass filtering funnel. The product thus obtained was washed with hot water and dried at 110°C. Weighed quantities of this product were suspended in sulfuric acid of known strength and were oxidized electrolytically.

Cerous sulfate solutions were also made by dissolving anhydrous ceric sulfate in a known amount of sulfuric acid which had been diluted to approximately the desired volume, and adding 100-volume hydrogen peroxide to reduce the cerium, followed by dilution to the proper volume for electrolytic oxidation.

If ammonium salts are not objectionable, a procedure comparable to that last given may be employed in the preparation of cerous nitrate-ammonium nitrate-nitric acid solutions for electrolysis.

ANALYSIS OF SOLUTIONS

The solutions during electrolysis were sampled at frequent intervals, generally every 15 minutes. A 5-ml sample was withdrawn with a pipet, transferred to a 250-ml beaker, and diluted to 100 ml with 1 to 10 sulfuric acid. These samples were titrated, using 0.1 N ferrous sulfate with ferroin as indicator. The total concentration of cerium present was determined following complete oxidation by ammonium persulfate, using the method of Willard and Young. The total volume thus withdrawn from the cell (50 to 100 ml) was small in comparison to the total volume present (2000 to 3000 ml). Half the volume of sampling solution was deducted from the total starting volume of solution oxidized in the calculation of the theoretical coulombs required.

Literature Cited

(1) Kuntz
     J. Am. Chem. Soc., **53**, 98 (1931.
(2) A. A. Noyes and Garner
     J. Am. Chem. Soc., **58**, 1265 (1936).
(3) Schumb, Sherrill and Sweester
     J. Am. Chem. Soc., **59**, 2360 (1937.
(4) Hengstenberger, "Electrolytic Oxidation of Cerous Salts and Chlorination Experiments in Contact with Cerous Chloride," Munich, Germany, J. Fuller, 1914.
(5) G. Frederick Smith, Gerald Frank and A. E. Kott, "Electrolytic Oxidation of Cerium without Use of a Diaphragm Cell," *Ind. Eng. Chem.*, Anal. Ed., **12**, 268 (1940).

SECTION 4

PREPARATION OF CERIUM(IV) VOLUMETRIC SOLUTIONS AND THEIR STANDARDIZATION

The first general application of cerium(IV) as a titrant in oxidations involved the preparation of its solutions in sulfuric acid. The first available reagent thus employed was ceric oxide. This CeO_2 was generally available as obtained following the separation of thorium oxide from naturally occurring monasite ore and contained notable amounts of other rare earth companion oxides as impurities. It was originally established that such rare earth associated oxides were not objectionable. However, such available CeO_2 was not easily soluble even by hot concentrated sulfuric acid first generally employed. Solutions of this oxide in sulfuric acid which were clear orange yellow in color, upon dilution with water and aging for a few hours accumulated insoluble residues and required filtration. It was early established that the resulting sulfuric acid solutions were stable as such even after their use at their boiling point in the presence of other rare earth sulfates, and for permanent storage at ordinary temperatures.

Thus cerium(IV) solutions in sulfuric acid served as improved procedural oxidation titrants when compared with dichromate or permanganate for use in comparable oxidation-reduction applications. The potentials available were greater than those in the use of dichromate and only smaller, by little, than those of permanganimetry. Like dichromate titrations, there was need for indicators to define reaction equilibria and originally potentiometric titrations were exclusively applied. The stability of sulfuric acid solutions both at ordinary temperatures and in hot solution reactions with available potentials approximately duplicating those of permanganate proved to be sufficiently attractive to command consideration even with the accompanying advantage provided by self-indicating permanganate in competitive manipulations. The need for potentiometric titrations in applied cerium(IV) oxidations was ultimately overcome by the general use of newly developed redox indicators superior in sensitivity to the self-indicator properties in permanganimetry without the handicap of obvious instability of standard permanganate solutions. Ultimately new cerium(IV) reagents and reaction conditions have been established at potentials greatly in excess of those available by comparable dichromate or permanganate reactions and the advent of the new procedures thus made available, soon became preferable to and have been found more general in adoption during and after approximately thirty years of analytical research.

To supplant the use of ceric oxide in the preparation of cerium(IV) solutions in sulfuric acid the use of acid soluble ammonium sulfatocerate, $(NH_4)_2Ce(SO_4)_3 \cdot 2H_2O$, was formerly employed. This was a marked

improvement but still involved the presence of the ammonium ion in standard solutions which was possibly undesirable and of no advantage. At present the use of acid soluble ceric hydroxide, $Ce(OH)_4$, may be employed in the preparation of standard solutions of sulfatoceric acid, $H_2Ce(SO_4)_3$, and the procedure involved will now be described. Unlike permanganate oxidimetry, cerium(IV) reactions involve but one electron exchange Ce(IV) to Ce(III) as compared with possible electron exchanges of seven to six, or to four or to two, in permanganate oxidimetry in acid solution, or seven or six to four, in alkaline solution as that in the well known Stamm reaction. While cerium oxidimetry is confined to acid solutions there are a great many reactions employing Ce(IV) in acid media which are much more attractive than the permanganate Stamm reactions in strong alkaline solutions for which they substitute with marked improvement of reaction conditions in the realization of stoichiometric oxidations of organic compounds.

PREPARATION OF CERIC HYDROXIDE

Add a saturated solution of ammonium nitratocerate,

$$(NH_4)_2Ce(NO_3)_6,$$
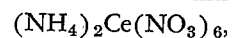
in water to an excess of reagent ammonia, Sp.Gr. 0.90 diluted with an equal volume of water, and stir vigorously. Ceric hydroxide, $Ce(OH)_4$, is quantitatively precipitated in readily filterable form. Filter the precipitate and wash it free of ammonia and ammonium nitrate. Air dry the precipitate, requiring two to three weeks. Do not carry the dehydration lower than that which corresponds to the formula $Ce(OH)_4$ preferably leaving 2 to 3 percent unremoved moisture. Grind the horny product thus obtained to pass a 100-mesh sieve. Remember that only saturated solutions of

$$(NH_4)_2Ce(NO_3)_6$$
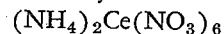
in water do not hydrolize to insoluble complex products since such solutions have a pH of unity.

PREPARATION OF SULFATOCERIC ACID IN SULFURIC ACID

Place 10.4 g of $Ce(OH)_4$ in a dry 800-ml beaker. Add 50 ml of reagent sulfuric acid. Stir well best with a magnetic stirring rotor to make sure that all $Ce(OH)_4$ has been wetted by the acid. Now with continued vigorous stirring add 150 ml of water. This can be done with no trouble in 5 to 10 seconds. In 30 to 60 seconds the solution will be clear and redish orange in color. The solution will be at or near 100°C due to the heat of dilution of the excess sulfuric acid. The fast addition of water as specified will provide the necessary elevation in temperature. If the $Ce(OH)_4$ is all of at least subdivided particle size to pass a 100-mesh sieve this amount of heat is enough to give a clear solution. If a few particles of $Ce(OH)_4$ remain undissolved at the apex of the funnel of the swirling solution, applied external heat and stirring will, in a few short moments, cause it to pass into

solution. Without this additional heating and stirring one might erroneously reason that a trace of $Ce(OH)_4$ was insoluble or that possibly some insoluble silica had been a contaminant. Keep well in mind that sulfatoceric acid thus prepared is stable in hot solutions. The color of the solution is much darker when hot than when cool.

Dilute to 650-750 ml with water, transfer to a 1000-ml graduated flask and dilute to the mark. An approximately 0.05 normal solution of Ce(IV) which is 0.75 formal in sulfuric acid is thus obtained. For example one solution thus prepared was found to be 0.0485 normal. The solutions do not form any insoluble product upon long continued storage and their standard factor does not change.

It is to be remembered that the dried $Ce(OH)_4$ is a well known abrasive now employed as in lens grinding, a preferable substitute for rouge. It is therefore extremely difficult to grind to pass a 100-mesh sieve. The product is available commercially and one pound will prepare more than 40 liters of approximately 0.05 normal solution at a cost of 20 cents per liter. Since one standardization for a given solution suffices for any solution thus prepared over long periods of time the extra cost of $Ce(OH)_4$ as compared to permanganate, which must be restandardized every few days in its storage life, is really rewarding.

This procedure has been documented by publication *(1)* over the authorship of H. Diehl and G. Frederick Smith.

STANDARD SOLUTIONS OF SULFATOCERIC ACID IN SULFURIC ACID AND PERCHLORATOCERIC ACID IN PERCHLORIC ACID EMPLOYING AMMONIUM NITRATOCERATE AS PRIMARY STANDARD

With primary standard ammonium nitratocerate as raw material procedures are available for the preparation of Ce(IV) solutions in sulfuric acid as well as perchloric acid without necessary standardization by comparison with other primary standard reducing agents.

One twentieth molecular weight of primary standard $(NH_4)_2Ce(NO_3)_6$ (548.28 Mol. Wt.) corrected for buoyancy of weighing in air (Sp.Gr. 2.61) is dissolved in water to give a saturated solution. This is quantitatively transferred with vigorous stirring to the filter flask shown in Figure 1, page 15, to which has been added 35 ml of concentrated ammonium hydroxide diluted with water to 400-500 ml.

The precipitated ceric hydroxide is then filtered employing the special precipitation apparatus, Figure 1, and washed with water applying reduced pressure until free from excess NH_4OH and NH_4NO_3.

The precipitated $Ce(OH)_4$ of the filtration apparatus is dissolved by the addition hot dilute sulfuric acid. Add 38 ml of concentrated reagent sulfuric to 115 ml of water for use in dissolving the precipitated $Ce(OH)_4$. Add the greater part of the hot dilute sulfuric acid to the reaction flask to dissolve

the ceric hydroxide and filter with reduced pressure into a clean filter flask. Rinse the reaction apparatus free from cerium using the remaining sulfuric acid. Transfer the solution of $Ce(OH)_4$ in excess H_2SO_4 to a 1000-ml graduated flask and dilute to volume. The resulting solution is 0.5000 N $Ce(IV)$ as $H_2Ce(SO_4)_3$ in 0.5 N excess sulfuric acid.

The same procedure may be employed using beakers and sintered glass Buchner type filtering funnel with reduced pressure filtration. The filtered ceric hydroxide is then dissolved off the filter in hot dilute (1 + 3 v/v) concentrated sulfuric acid diluted by water. This procedure has been employed by Smith and Fly as previously cited (page 14).

Since freshly precipitated ceric hydroxide is soluble in perchloric acid, the same procedure for the preparation of sulfatoceric acid in sulfuric acid may be applied to the preparation of 0.05 normal perchloratoceric acid $H_2Ce(ClO_4)_6$ in normal perchloric acid. In this procedure the freshly prepared ceric hydroxide is dissolved in 115.5 ml of 70 percent perchloric acid diluted by the addition of 115 ml of water and heated to 50°C. It is to be remembered that the solution of perchloratoceric acid in perchloric acid is not constant in titer upon storage. However, it loses strength at a slower pace than corresponding 0.05 normal permanganate solution upon storage. Store solutions in the dark preferably at refrigerator temperature of approximately 40°F. This slow decomposition of perchloratoceric acid solutions in perchloric acid is the penalty the analyst pays in return for the attainment of oxidation potentials in the range 1.71 to 1.85 volts provided. This subject is further covered in the following material.

ADDITIONAL PREPARATIONAL PROCEDURES AND STANDARDIZATION OF PERCHLORATOCERIC ACID IN PERCHLORIC ACID SOLUTION
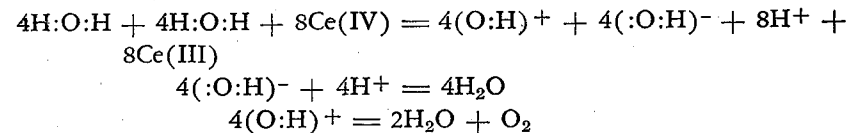
Solutions of perchloratoceric acid in various strengths of perchloric acid (2) have found many important uses in a wide field of analytical applications. The present section division describes a convenient method for their preparation and a procedure for their precise standardization. The possible objection of the presence of nitrates has been eliminated.

HALF-CELL REACTION POTENTIALS OF PERCHLORATOCERIC ACID SOLUTIONS IN PERCHLORIC ACID

The oxidation potentials of the cerium(IV)-cerium(III) couple in the half cell

$$Ce(IV) + e^- = Ce(III) \text{ (acidified with perchloric acid)}$$
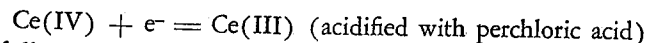
are the following: 1 F = 1.71, 2 F = 1.73, 4 F = 1.78, 6 F = 1.83, and 8 F = 1.87 volts. At these unusually high voltage values the following reactions illustrate the mechanism of oxidation involved and explain the very slow, but detectable, instability of perchloratoceric acid with water as the second reacting component.

$$4H:O:H + 4H:O:H + 8Ce(IV) = 4(O:H)^+ + 4(:O:H)^- + 8H^+ + 8Ce(III)$$
$$4(:O:H)^- + 4H^+ = 4H_2O$$
$$4(O:H)^+ = 2H_2O + O_2$$

These reactions normally involve a modest rate, but they may be catalyzed by the presence of platinum. At room temperature, if 500 mg of platinum sponge is stirred in contact with 250 ml of a 0.2 N solution of perchloratoceric acid in 2 F perchloric acid (oxidation potential 1.73 volts) for 60 minutes, over 50% of the cerium(IV) is reduced to cerium(III). Even with the same amount of platinum in the form of sheet or wire, with much reduced surface area, the decomposition is appreciable. Graphite in the form of rods (such as the electrodes employed for spectrographic emission operations) can duplicate platinum sponge in the accelerated reduction of cerium(IV) in perchloric acid solution.

The values of oxidation potential provided by perchloric acid solutions of cerium(IV) are high enough to be compared with such high values as those of sodium persulfate, ozone, and the bismuthate ion, which are not employed in quantitative operations involving standard solutions of these oxidants. Solutions of cerium(IV) in perchloric acid are as stable as or more stable than corresponding solutions of the permanganate ion employed as oxidant, at a much lower oxidation potential rating. Standard solutions of cerium(IV) in perchloric acid retain their original oxidation values better when kept at 40° F. in the absence of light — for example, by refrigerator storage — than when storage is at ordinary temperatures and in diffuse daylight. In the latter case restandardization at 72-hour intervals is requisite for the most precise applications.

PERCHLORATOCERIC ACID APPLICATIONS IN ANALYSIS

An important application of perchloratoceric acid is in qualitative organic analysis in the identification of hydroxy groups and has been described by Shriner and Fuson based upon the original description of the process by Duke and Smith. See Sections 6 and 7 of the first edition (1942) of the present book. The determination of glycerol, following its oxidation to formic acid by perchloratoceric acid, as well as the perchloratoceric acid determination of many other organic compounds has been described by Smith and Duke (8). The micro determination of calcium in blood has been described by Salamon, Gabrio, and Smith, (9) and of oxalic acid, iron, and arsenic by Smith and Fritz (10). In all these applications the reactions were found to be stoichiometric. Nitro-1,10-phenanthroline-ferrous sulfate is employed as indicator because of its high oxidation potential.

AMMONIUM NITRATOCERATE AS STARTING MATERIAL IN PREPARATION OF PERCHLORATOCERIC ACID

Ammonium nitratocerate is commercially available both as reagent grade (98.0 to 99.5% pure) and as a primary standard for use in oxidimetry (purity 99.98 to 100.00%). It is soluble in water if the solution is maintained saturated (pH approximately 1). Such solutions of ammonium nitratocerate are instantly reduced by hydrogen peroxide to ammonium nitrate, cerium(III) nitrate, and nitric acid. With an excess of concentrated hydrochloric acid these reaction products produce, on boiling, a solution of cerium(III) chloride in hydrochloric acid medium. By boiling with excess perchloric acid, the conversion to cerium(III) perchlorate is readily accomplished. The last stage in the preparation of an approximately 1.0 F solution of cerium(IV), in an approximately 1.0 F solution of perchloric acid, involves electro-oxidation. For this purpose there are applied a platinum anode and a platinum cathode. No partition cell is required. The solution thus prepared may then be readily (by appropriate dilution with perchloric acid and water) altered to give any desired strength of oxidizing reactant at any selected acid concentration. One pound of the starting material, hexanitrato-ammonium cerate, is equivalent to somewhat more than 115 grams of cerium. Over 16,400 ml of an approximately 0.05 N solution of cerium(IV) are thus provided for.

Apparatus. The manipulations outlined above are best carried out using the digestion apparatus, shown in Figure 6, which eliminates the required use of a forced-draft fume hood and can be employed on any laboratory work bench beside a sink drain, supplied with pressure tap water and a good metal aspirator pump. The use of a 500-ml 96% silica glass flask is highly recommended for carrying out the digestion reactions.

The apparatus assembly shown in Figure 6 consists of a 1000-ml reduced pressure filtering flask to which is attached a modified 500- or 800-ml Kjeldahl digestion flask serving as a fume eradicator. The aspirator flask may be filled with 800 ml of strong sodium hydroxide for the absorption of evolved acid fumes, and the aspirator pump should provide a liberal exhaust of air at the neck of the reaction flask to prevent escape of acid fumes from the digesting solution in the reaction flask. The electric hot plate should be provided with a variable heat control regulating device for convenience in controlling boiling rates.

In the assembled apparatus for the electro-oxidation of cerium(III) to cerium(IV), an electromagnetic stirring device serves as a support for a 400-ml reaction beaker containing the cerium(III) solution. A platinum gauze anode, approximately 50 by 75 mm is suspended in the center of the beaker and is elevated 5 mm above the bottom of the beaker to provide room for the stirring rotor. A 100-mm length of 0.5-mm platinum wire is
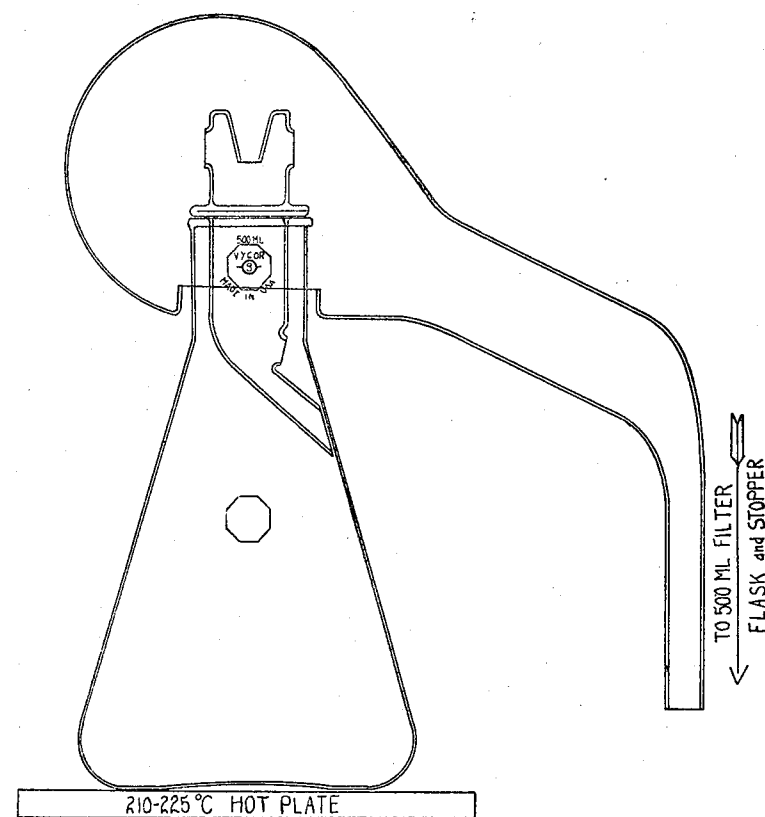
Figure 6. Laboratory Digestion and Fume Eradicator Reaction Vessel, Reflux Still Head, and Fume Extration Chamber

suspended along the inner side of the reaction beaker to serve as cathode. A 6-volt dry cell serves to supply the electric energy. This assembled apparatus requires no attention. Three 1.5-volt dry batteries are of sufficient capacity and potential to oxidize the cerium from 200 grams of hexanitrato-ammonium cerate.

Procedure. Place 220 grams of hexanitratoammonium cerate in a 500-ml Erlenmeyer flask and dissolve in 120 ml of water at 60°C. Add 25 ml of 100-volume (30%) hydrogen peroxide in small portions to reduce cerium(IV) to cerium(III) and produce a colorless solution. Place the flask and contents on the hot plate and heat to boiling (Figure 6). Add 500 ml of concentrated hydrochloric acid (specific gravity 1.19) in 25-ml portions with intermediate boiling. Maintain the original reaction volume by the stepwise addition of hydrochloric acid until all 500 ml has been added. At the end allow the solution to concentrate to approximately 200 ml.

Add a few pieces of carborundum boiling chips and 240 ml of 70% perchloric acid. (If the solution turns red and produces chlorine fumes, all nitric acid has not been removed). Boil briskly until copious fumes of perchloric acid are evolved, all hydrochloric acid has been displaced, and the cerium(III) chloride has been converted completely to cerium(III) perchlorate. The solution when hot will have a light yellow color but when cool should be colorless.

Transfer the cold solution, diluted to 500 ml, to the oxidation beaker. Connect the electrodes to the proper battery poles and start the stirrer rotating. The apparatus requires no further attention, and the oxidation is complete in 20 to 24 hours. The final solution, when finally diluted to 600 ml, will be approximately 1 F cerium(IV) in 1 F perchloric acid and will be orange in color. Store in a glass-stoppered bottle in the icebox until ready for dilution with 1 F perchloric acid to the strength of solution desired.

SODIUM OXALATE AS PRIMARY STANDARD FOR STANDARDIZATION OF PERCHLORATOCERIC ACID

National Bureau of Standards sodium oxalate (sample 40c or of equivalent purity) is employed after drying at 110° C. If an approximately 0.1 N solution of cerium(IV) is to be evaluated, weigh samples of 0.2 to 0.3 gram, correct to 0.1 mg, and transfer them to 400-ml beakers. Dissolve the sodium oxalate in 150 ml of 1 F perchloric acid. Titrate the oxalate employing the unknown cerium(IV) solution until most of the colored cerium(IV) has been reduced. Add a drop of 0.025 M nitroferroin (5-nitro-1,10-phenanthroline ferrous sulfate) and complete the reaction to the disappearance of the pink color. The reaction is carried out at ordinary temperatures. Electromagnetic stirring is recommended. When first added, the indicator will precipitate as the iron(II) perchlorate complex, but this precipitate dissolves after a few seconds' stirring. There is little warning of the approach of the equivalence point and for this reason a titration thief is employed to advantage.

Solutions of perchloratoceric acid [1 F in cerium(IV) and 6 F in perchloric acid] are commercially available.

METHODS IN THE STANDARDIZATION OF SULFATOCERIC ACID IN SULFURIC ACID SOLUTION

Pure iron may be employed as primary standard. This procedure (3) has been recommended in various quantitative books for student training courses. Pure iron titration samples are dissolved in hydrochloric acid, reduced by use of stannous chloride the excess of which is removed by addition of mercuric chloride. Phosphoric acid is then added and the reduced iron titrated by the unknown strength sulfatoceric acid solution to be evaluated. Sodium diphenylamine sulfonate is employed as redox indicator.

Procedure. Weigh 0.25-0.30 g samples of electrolytic iron and transfer

to 400 ml beakers. Add 5 ml of water and 10 ml of concentrated hydrochloric acid. Warm the solution until the iron has dissolved. Heat the solution to boiling and add 0.5 N stannous chloride dropwise from a pipet swirling the solution and keeping it hot. Continue the dropwise addition of stannous chloride until all ferric chloride is reduced and one drop of the reducing agent causes the color to change from yellow to colorless or pale green. Then add one drop excess stannous chloride. Add immediately 5 ml of reagent hydrochloric acid, rinse down the sides of the beaker and dilute the solution with cold water to 250 ml volume. Add at once 5 ml of reagent mercuric chloride to oxidize the slight excess of stannous chloride. A slight white precipitate of mercurous chloride is formed after one or two minutes. A heavy precipitate should not form and if so the reduction with stannous chloride has not been carefully done which will cause 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 the after described indicator. Titrate with the unknown strength of approximately 0.1 N sulfato-ceric acid. During the titration of the ferrous salt with the sulfato-cerate the solution is practically colorless so that the equivalence 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. For this reason the titration should be carried out more slowly towards the end. For each 0.05584 g of pure iron taken, 10 ml of exactly 0.1 N sulfato-ceric acid would be required. Otherwise, (Wt. Fe/0.05584) (1/Vol. $H_4Ce(SO_4)_4$) $=$ Normality of cerate solution.

Mohr's salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, may be employed as a substitute for pure iron as reference standard.

Procedure. Prepare a 0.1000 N solution of ferrous ammonium sulfate by dissolving 39.214 g of Mohr's salt in 200-300 ml of water to which is added 20 ml of dilute sulfuric acid. Transfer this solution quantitatively to a 1000 ml graduated flask and dilute to the mark after adjusting to the calibration temperature.

Transfer a 25.00 ml. portion of the approximately tenth normal solution of sulfato-ceric acid solution to be standardized into a 250-ml beaker using a calibrated transfer pipet. Dilute this solution by the addition of 25 ml of water and add 2-3 ml of dilute sulfuric acid. Titrate with standard 0.1000 N ferrous sulfate until the cerate color is almost bleached out and add 0.5 ml of erio-glaucine indicator. The color of the solution is now red. Continue the addition of the ferrous solution dropwise with thorough stirring until the red solution turns a permanent yellow or yellowish green color with the first drop excess of standard ferrous sulfate solution. No indicator correction is required.

The use of standard of reference purity sodium oxalate in the evaluation of solutions of sulfatoceric acid is complicated by the need to work in hot solution. This complication has led to methods devised by Willard and Young (6) employing HCl solutions with iodine monochloride as catalyst and employing ferroin as redox indicator. A similar procedure *(6)* employed arsenious oxide as standard of reference. Both these methods are now seldom employed.

THE STANDARDIZATION OF SULFATOCERIC ACID IN SOLUTION USING ARSENIC TRIOXIDE AS PRIMARY STANDARD AND OSMIC ACID AS CATALYST

As shown by Gleu (7) a solution of arsenious acid in sulfuric acid is practically completely unoxidized by a large excess of sulfato-ceric acid in any satisfactory period of time. Furthermore a solution of the oxidized form of orthophenanthroline ferrous sulfate (ferriin) is not reduced by an excess of arsenite ion in sulfuric acid solution. Both these reactions are instantaneous if a trace of osmic acid 1-2 drops of 0.01 OsO_4 in 0.1 M H_2SO_4 is added. These observations lead to the establishment of conditions under which sulfatoceric acid solution in sulfuric acid may be standardized using arsenious oxide as standard of reference.

Reagents Employed. 1. A solution of 0.01 M osmium tetroxide (OsO_4) is prepared by dissolving enough of the crystals in 0.1 N H_2SO_4 (0.25 g of OsO_4 dissolved in 100 ml of 0.1 N H_2SO_4). 2. A sample of Bureau of Standards arsenious oxide (As_2O_3) weighing 3.0740 g is placed in a 400 ml beaker and dissolved by the addition of 10 ml of water and a slight excess of sodium hydroxide pellets. Add a few pellets of NaOH until all arsenious oxide is dissolved. This will result with the addition of the first slight excess of alkali. Acidify this solution with a slight excess of sulfuric acid and transfer quantitatively to a 1000-ml calibrate volumetric flask and dilute to the mark after adjusting to temperature. This process results in the preparation of an exactly 0.1 N solution of arsenious acid 3. The solution of sulfatoceric acid to be standardized is prepared in 0.5 to 1.0 M H_2SO_4 from

$$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$$
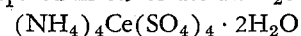
or better by the process of diluting 200 ml of 0.5 sulfatoceric acid in 0.5 M H_2SO_4 by the addition of 800 ml of 0.5 M H_2SO_4. 4. A solution of 0.025 M ferroin as indicator. (This may be purchased commercially all prepared).

Procedure of Standardization. An accurately measured portion of 25.00 ml of the exactly 0.1 N sodium arsenite solution is placed in a 400 ml beaker using a transfer pipet. Dilute to 80 ml with water and add 20 ml of 6 N sulfuric acid (1 vol. H_2SO_4 Sp. Gr. 1.84 diluted by 3 vol. of water) and one drop of ferroin indicator and 3 drops of the 0.01 M osmium tetroxide as catalyst. Titrate this solution at room temperature by the sulfatoceric acid to be standardized. As the equivalence point is approached add the titrating

solution dropwise and with a few seconds between drops with constant stirring. The reaction is complete when the addition of the last drop brings about a sharp elimination of the red tint of the solution from the oxidation of ferroin to ferriin. The calculation of the standard factor for the cerate solution follows the inverse ratio of the volume of 0.1 N arsenite taken to the volume of sulfato-cerate solution required.

In the above reaction hydrochloric acid must be absent practically completely since the osmium tetroxide does not catalyze the oxidation of arsenite in the presence of hydrochloric acid.

TABLE 1

STANDARDIZATION OF 0.01 N SOLUTIONS OF SULFATO-CERIC ACID USING ARSENIOUS OXIDE AND SODIUM OXALATE AS STANDARDS OF REFERENCE

Time of Standing Weeks	Against As₂O₃ Indicator Method	Against Sodium Oxalate Potentiometric	Indicator
Solution A, 0.5 M in H₂SO₄			
0	—	0.01017	0.01020
	—	0.01019	0.01020
	—	0.01020	—
7.5	0.01017	—	0.01017
	0.01017	—	0.01014
12	0.01017	—	0.01016
	0.01017	—	0.01014
Solution B, 0.25 M in H₂SO₄			
0	—	0.01117	0.01116
	—	0.01118	0.01117
	—	0.01019	0.01116
3	0.01114	—	0.01116
	0.01117	—	0.01117
7.5	0.01117	—	0.01113
	0.01117	—	0.01112
12	0.01115	—	0.01111
	0.01115	—	0.01111

The Standardization of Perchloratocerate Solutions in Perchloric Acid. Solutions of the perchlorato- and nitratocerate ions in perchloric and nitric acid solution, respectively, have been shown to have the oxidation potentials of 1.71 and 1.61 volts at standard state. These potentials might logically be expected to be high enough to cause their reactions with the oxalate and arsenite ions to be more rapid at ordinary temperatures than is the case with sulfatocerate solutions in the presence of sulfuric or hydrochloric acid. This

was found to be the case by Smith and Getz. In the latter reaction osmium tetroxide must be present as catalyst.

To define the electrochemical properties of the reactions, the oxidation of sodium oxalate and sodium arsenite using perchloratocerate ions was carried out potentiometrically, using N perchloric acid solutions of the $C_2O_4^{--}$ and AsO_3^{---} ions at room temperature. The same potentiometric assembly of apparatus was employed as that previously described. Nitro-ferroin was added as indicator to compare the visual and potentiometric end-point phenomena. The results are shown graphically in Figure 7.
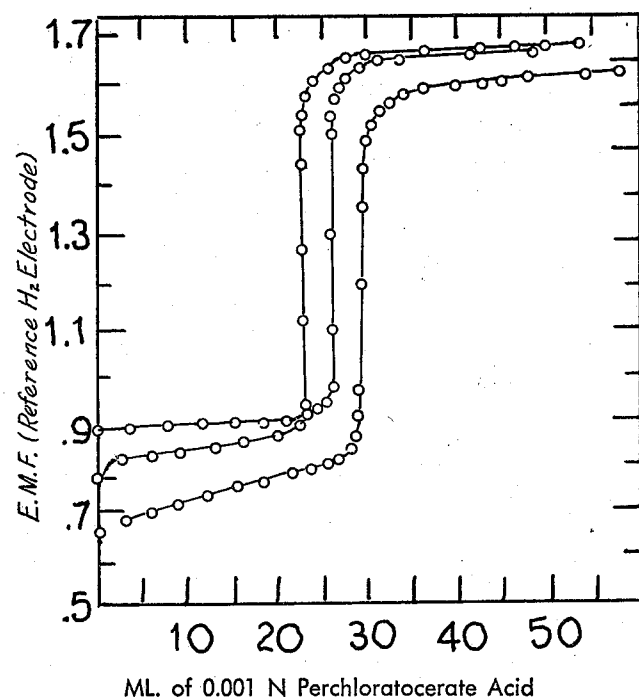

Figure 7. Potentiometric Titration of Ferrous Iron (Lower), Arsenious Acid (Middle), and Oxalic Acid (Top) in 2 F Perchloric Acid Solution

The equivalence-point "break" in potential is 650 mv in the case of the oxalate titration and 600 mv in the case of the arsenite oxidation. Nitro-ferroin as indicator has its transition interval at an average potential of 1.25 volts, which corresponds to a value 0.11 volt higher than would be the case if ferroin were used. There is a noticeable advantage in the use of the former, since with ferroin a momentary preferential oxidation of the indicator occurs and a second or two is required for the pink color to return.

Data employing various methods of standardization of nitrato- and per-

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TABLE 2

Various Procedures in Standardization of Ce(IV) in Perchloric and Nitric Acid Solutions Employing Sodium Oxalate, Arsenious Oxide and Iron as Reference Standards

Solution Number	Na$_2$C$_2$O$_4$ Factor N	No. of Deter'ns.	Fe Factor N	No. of Deter'ns.	As$_2$O$_3$ Factor N	No. of Deter'ns.	Cerate Ion Present	Acid Used	Average Value
1	0.05624	5	0.05624	3	0.05627	4	Ce(ClO$_4$)$_6$$^{--}$ =	N HClO$_4$	0.05625
2	0.05642	6	0.05649	3	0.05663	5	"	3 N HClO$_4$	0.05651
3	0.05439	7	0.05438	4	0.05442	4	"	8 N HClO$_4$	0.05440
4	0.09700	7	0.09704	3	0.09746*	6	"	4 N HClO$_4$	0.09702
5	0.05333	4	0.05332	3	0.05344	4	"	N HNO$_3$	0.05336
6	0.05147	6	0.05146	4	0.05147	5	"	3 N HNO$_3$	0.05147
7	0.04274	5	0.04265	4	0.04267	5	Ce(NO$_3$)$_6$$^{--}$ =	N HClO$_4$	0.04269
8	0.08313	4	—		0.08267	3		N HClO$_4$	0.08220

*Omitted from the average value.

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chloratocerate solutions using three reference standards, Na_2C_2O, As_2O_3 and Fe, are given in Table 2.

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THE METHINE CHROMOPHORE GROUP FERROIN OXIDATION-REDUCTION INDICATORS AND RELATED COMPLEX CHELATION TYPES

The early volumetric oxidation-reduction analytical reactions, introduced in the pioneer studies of Professor Willard and Furman and associates, were all (with one exception) *(1)* followed potentiometrically. The first *in situ* indicators for Ce(IV) oxidations were of the non-reversible type erioglaucine and eriogreen *(1)*. The use of N-phenanthranilic acid (redox potential 1.08 volts) which can be employed in Ce(IV) oxidimetry was introduced by Syrokomsky and Stiepen (2). An important characteristic of N-phenan-thranilic acid is its unaltered oxidation potential (1.08 volts) with alteration of solution pH even at high sulfuric acid concentrations.

The first of the methine chromophore group ferroin redox indicator described was that of the 1,10-phenanthrolinium ferrous ion of Waldon, Hammett, and Chapman, *(3)* (redox potential 1.06 volts). This was followed by the introduction of the 5-nitro-1,10-phenanthrolinium ferrous ion *(4)* (redox potential 1.25 volts).

The study of the relationship of the nature and position of newly developed substituted methine chromophore group ferrous phenanthrolinium complex ions as redox indicators and the determination of their altered values and the influence of pH environment in altering their redox potentials was begun by the studies of Smith and Richter *(5)*. The oxidation-reduction potential of a series of methyl substituted 1,10-phenanthrolines has been determined by Brandt and Smith (6). The special use of the 5,6-dimethyl-1,10-phenanthrolinium ferrous ion as redox indicator preferably employed in dichromate oxidimetry was described by Smith and Brandt *(7)*. The determination of formal oxidation potentials of the methine chromophore group phenanthroline ferrous ions which are low in solubility as sulfates or chlorides or perchlorates was described by Smith and Banick *(8)*.

The use of 2,2'-bypyridine ferrous cation as redox indicator was described by Cagle and Smith *(9)*.

FACTORS INVOLVED IN DEVELOPMENT OF THE METHINE CHROMOPHORE GROUP OXIDATION-REDUCTION INDICATORS

The most important property of the ferroin and related types of organic chelation reagents as redox indicators is their remarkable stability in acid solutions and high molecular extinction coefficients. The presence of excess oxidizing agent does not decompose the indicator and the equilibrium of the oxidation-reduction color change may be reversed without restriction or diminution in color intensity. By comparison with the molecular extinction

coefficient of the permanganate anion (2400 approximately) the molecular extinction coefficient of the methine chromophore group ferroin type redox indicators have values of 8000 to 15000, in most cases 11000 to 15000.

An equally important property of these redox indicators is their range of oxidation potentials at the color transition points as a function with modifications due to substitution of methyl, phenyl-, nitro-, bromo-, chloro- or hydroxyl groups among other types. The range covered in redox potential evaluation covers values from 0.85 to 1.41 volts with small increments of 0.01 to 0.02 volt variation up to the value 1.25 volts and higher.

A distinct advantage results from the condition that the reduced form of these indicators carries the high molecular extinction values at 500-600 $m\mu$ wave length absorption at sharply defined selected wave lengths while the same values for the oxidized form of the indicators is of low molecular extinction. As a result the methine chromophore redox indicators are essentially single color reactives in general deep red or purple in reduced form and almost colorless after oxidation.

As a result of the high values in molecular extinction coefficients so little indicator concentration for clear-cut equilibrium point transitions (a single electron exchange), readily detected by color transition, is required that an indicator correction is avoided for oxidant demand involved. Only micro-volumetric titrations involve indicator corrections. In addition solutions of the reduced form of the indicators are stable for years in storage under ordinary shelf-life conditions. The stability of the oxidized form in many cases, while less in permanency under the influence of exposure to sunlight or diffused daylight, is still sufficient to not interfere materially under actual working conditions.

An important variable in the practical application of the methine chromophore group redox indicators is that their transition potentials are sharply pH dependent. This fact, in reality, is a marked advantage. For example in volumetric oxidation procedures employing dichromate as oxidant the oxidation potential of the $Cr(VI) \rightarrow Cr(III)$ electrode system is also sharply pH dependent. In formal sulfuric acid solutions this conversion (a three electron exchange) is at approximately 1.0 volt. For titrations employing $Cr(VI)$ as oxidant at pH of 1.0 volt a methine chromophore group indicator must be selected to have a transition potential of considerably less than 1.0 volt. This contingency is discussed in detail by Brandt and Smith (6).

The study of conditions involved in the selection of the proper redox indicator for a given volumetric oxidation-reduction reaction for any routine analytical control procedure should be first studied by application of a potentiometric end point evaluation. Following such treatment, the most appropriate methine chromophore group redox indicator applicable can be readily selected from the long series of systems hereinafter designated.

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A wide range of transition potentials for the redox indicators selected for cerate oxidimetry is essential because of the wide range of potentials (1.28 to 1.85 volts), realized in Ce(IV) redox operations if potentiometric end point determinations are preferentially avoided.

Since these redox indicators involve only one electron exchange and the molecular extinction coefficient of the reduced form is roughly tenfold higher than that of the oxidized form visual end point observation of the color transition occurs at a potential 0.06 volts higher than for the potentiometric equivalence point determination.

pH DEPENDENCE OF THE METHINE CHROMOPHORE GROUP REDOX INDICATORS

To indicate the pH dependence of redox potentials of this group of redox indicators data are graphically recorded in Figure 8 for four individual redox indicators (8). The redox transition potentials for a long list of
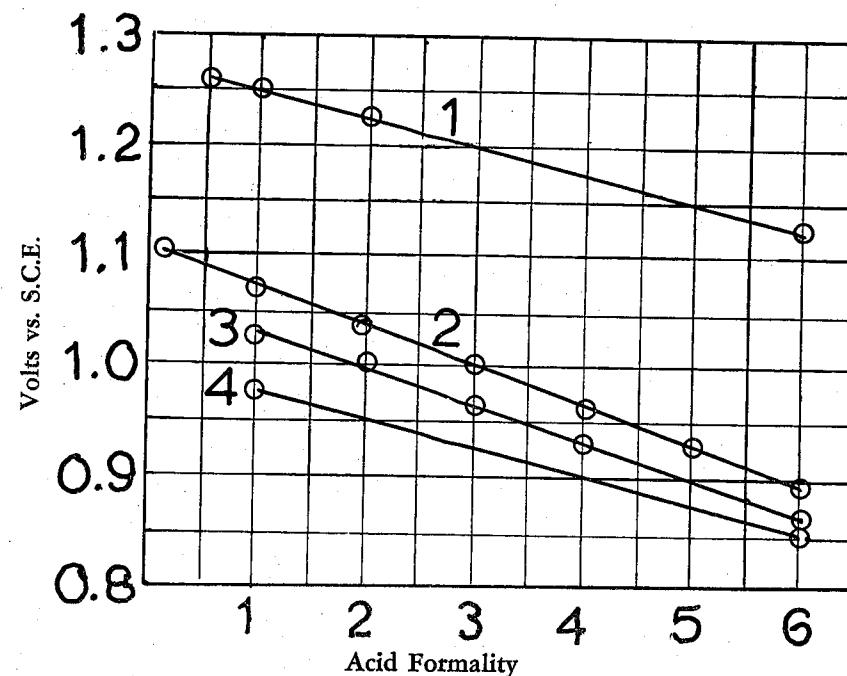

Figure 8. Sulphuric Acid Formality
  (1) 5-Nitro-1:10-phenanthroline-Fe^2 ion.
  (2) 1:10-Phenanthroline-Fe^2 ion.
  (3) 5-Methyl-1:10-Phenanthroline-Fe^2 ion.
  (4) 2:2'-Dipyridyl-Fe^2 ion.

methine chromophore group redox indicators is tabulated in the following material.

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THE REDOX TRANSITION POTENTIAL OF THE METHINE CHROMOPHORE GROUP REAGENTS

Three procedures are applicable in the determination of the redox potential of the methine chromophore group redox indicators. The most general and precise measure involves the oxidation of a reference element such as ferrous iron followed by the simultaneous oxidation of an equal quantity of the indicator contained in the same solution at a given concentration of acid. The titration thus involved is authenticated by the correctness of the single electrode potential found for the ferrous to ferric oxidation and for the determination of the oxidation potential obtained at the conclusion of the titration for the electrode potential of the oxidant and its corresponding reductant. If these two reference points are found to be correct for the acidity of the reaction applied the determination of the second transition oxidation of the redox indicator is obviously a very closely defined value.

In certain cases in which the stability of the reduced and oxidized forms of the redox indicator is not satisfactorily high to permit of the use of the first and most generally applicable procedure a second method involves a so-called pouring technique. A solution of the reduced form of the indicator at a definite concentration and established acid concentration is first prepared. A solution of the oxidant to be employed is then made at the same acid concentration but which is exactly twice the oxidizing concentration of the solution to be oxidized. These two solutions are then mixed and the potential of the transition of the indicator from the reduced to the oxidized form is rapidly observed. This potential in such required manipulation has been found to be of satisfactory accuracy although possible not as precise as by the use of the first and most general procedure described above.

The third procedure for measurement is that of the use of potentiopoised solutions as described by Smith and Banick (8). This procedure is requisite when applied to redox methine chromophore indicators of low solubility, not sufficient for application of method one without employing micro-techniques. This procedure is also of value when applied to the determination of redox potentials at the decolorization point of internal redox indicators of the non-reversible type such as those of the type of bordeau or amaranth, naphthol blue-black and others (10, 11). Determination of the values in question for non-reversing internal redox indicators have not as yet been explored employing the use of potentiopoised solutions and procedures published in previously cited reference (8).

TABULATED REDOX POTENTIALS OF METHINE CHROMOPHORE GROUP INDICATORS

The determination of the redox potential of 5 methine chromophore group indicators studied by Smith and Richter (5) are given in Table 1.

The oxidation potential of 24 single and multiple methyl substituted

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TABLE 1

PHYSICAL CONSTANT OF PHENANTHROLINES AND THEIR SUBSTITUTION PRODUCTS

Compound	M. P. (Anhydrous) °C.	Common Name of Ferrous Sulfate Complex	Mol Wt.	Amount Required for 1000 Ml. of 0.01M Fe++ Complex Grams	Formal Oxidation, E. M. F. Volts*
5-Nitro-1,10-phenanthroline	202	Nitro-ferroin	225.20	6.7560	1.25
5-Nitro-6-methyl-, 1,10-phenanthroline	269	Nitromethylferroin	239.23	7.1768	1.22
5-Bromo-1,10-phenanthroline monohydrate	119	Bromo-ferroin	277.11	8.3134	1.12
5-Chloro-1,10-phenanthroline monohydrate	123	Chloro-ferroin	232.66	6.9800	1.12
1,10-Phenanthroline monohydrate	117	Ferroin	198.22	5.9464	1.06
5-Methyl-1,10-phenanthroline monohydrate	114	Methyl-ferroin	212.24	6.3673	1.02

*Formal potential, when oxidized and reduced forms are equal, in sulfuric acid solutions of one molecular weight per liter (without reference to their possible incomplete ionization, hydrolysis, formation of complexes, etc.) and at 25°C.

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1,10-phenanthrolines is given in Table 2 from the data *(6)* of Smith and Brandt.

The redox potential of the ruthenous-ruthenic bipyridine complex cation in 0.1 to 16 F hydrogen ion concentration is given in Table 3.

TABLE 2

EFFECT OF METHYL GROUP SUBSTITUTION ON PHYSICAL CONSTANTS OF FERROUS COMPLEXES OF 1, 10-PHENANTHROLINE DERIVATIVES

Methyl Substituted Derivative	Absorption, Mu		Molecular Extinction Coefficient	Redox Potentials, Volts		
	Found	Calcd.		In 0.1 F Acid		In 1.0 F acid, found
				Found	Calcd.	
1, 10-Phenanthroline	510	--	11,100	1.10	--	1.06
3	502	--	11,500	1.07	--	1.03
4	511	--	13,500	--	--	--
5	515	--	12,200	1.06	--	--
3, 4	505	504	13,700	0.97	0.96	0.93
3, 5	506	507	12,500	--	1.03	--
3, 6	506	507	12,200	--	1.03	--
3, 7	502	504	12,600	--	0.96	--
3, 8	496	496	11,500	1.03	1.04	--
4, 5	516	516	12,700	0.95	0.95	--
4, 6	516	516	12,700	0.95	0.95	--
4, 7	512	512	14,000	0.88	0.88	0.87
5, 6	520	520	12,600	1.00	1.02	0.97
3, 4, 6	510	508	12,400	0.92	0.92	--
3, 4, 7	504	504	14,000	0.88	0.85	--
3, 4, 8	497	495	13,000	--	0.93	--
3, 5, 6	512	512	11,800	--	0.99	--
3, 5, 7	507	509	12,500	0.93	0.92	0.89
3, 5, 8	500	499	11,900	0.99	0.99	--
3, 6, 7	510	508	13,600	--	0.92	--
4, 5, 7	517	517	14,500	--	0.84	--
3, 4, 6, 7	510	510	14,000	0.84	0.81	--
3, 4, 6, 8	504	501	11,600	0.89	0.89	--
3, 4, 7, 8	500	496	13,800	0.85	0.82	--
3, 4, 6, 8	504	504	11,600	0.93	0.96	--

TABLE 3

Oxidation Potential of Ruthenous-Ruthenic Bipyridine Complex Cation in 0.1 F to 16 F Hydrogen Ion Concentrations

Hydrogen ion formality	0.1	1.0	4.0	8.0	12.0	16.0
Oxidation potential, volts	1.27	1.25	1.21	1.16	1.07	0.98

From examination of the data of Table 2, it is found that the wave length of maximum absorption varies from 496 mμ in the case of the ferrous complex of 3,8-dimethyl-1,10-phenanthroline, to 520 mμ for the 5,6-dimethylferroin in steps of 1 to 3 mμ. From the data for ferroin and its 3-, 4-, and 5-methyl derivatives, the basis of the predicted or calculated values shown in column three is obtained. The 4,7 positions raise the wave length of maximum absorption 1 mμ, the 5,6 positions raise the value 5 mμ, and the 3,8 positions lower it 8mμ. The values calculated in column three duplicate the experimentally determined values tabulated in column two exactly in ten cases, and the variation is in no case greater than 2 mμ, except for two cases of 4 mμ with two of the tetra-substituted products.

As a color-producing reagent for use in the quantitative determination of iron, the first popularly applied ferroin reaction was that of bipyridine. Here the molecular extinction coefficient is 8650 and the wave length of maximum absorption is 522 mμ. It was proposed to use 2,2′,2″-terpyridine, therefore, as a preferred reagent, because in the form of its ferrous complex, its molecular extinction coefficient is 12,500 and the wave length of maximum absorption is 552 mμ. Because 2,2′,2″-terpyridine was not commercially available, 1,10-phenanthroline soon supplanted 2,2′-bipyridine in the spectrophotometric determination of iron with the favorable value of 11,100 for its molecular extinction coefficient and 510 mμ as its wave length of maximum absorption. The available sensitivity of the ferroin reaction is thus increased further by the introduction of methyl substitutions to a molecular extinction coefficient of 14,500 for the 4,5,7-trimethylferroin.

The redox potentials of the ferroins vary over a wide range (0.84 to 1.30 volts in 0.1 F acid solution) by proper selection of the organic base. The redox potential may be lowered by increasing the hydrogen ion concentration. The lowering of the redox potential by this means brings about a diminuation of approximately 0.1 volt from 0.1 M to 8 M acid strength, and approximately 0.18 volt between 8 M and 16 M. The stability of the ferroins toward heat is limited to temperatures below 50° C. In some cases the stability is maintained at 100° C or more.

The redox potentials of the ferroins follow a predictable pattern of unusual exactitude, as seen in Table 2, columns 4 and 5. Methyl groups in the 3 or 8 position lower the value 0.03 volt, the 5 and 6 positions lower it 0.04 volt, and the 4 and 7 positions lower it by 0.11 volt. The redox potential can be varied in steps of 0.01 to 0.03 volt over the range covered (0.84 to 1.10 volts). The 4,5,7-trimethylferroin has not only the highest molecular extinction coefficient, but also one of the lowest potentials, thus indicating the possibility of use as indicator for iron titrations with dichromate. The oxidation potential of the 4,5,6,7-tetramethylferroin would be predicted to have a potential of 0.81 volt in 0.1 F acid solutions. In a similar solution,

TABLE 4

COLORIMETRIC FORMAL OXIDATION POTENTIALS OF THE Fe^{II} COMPLEXES OF PREVIOUSLY UNDETERMINED 1,10-PHENANTHROLINES

1,10-Phenanthroline derivative	H$_2$SO$_4$ formality	E$_0^1$, volts	1,10-Phenanthroline derivative	H$_2$SO$_4$ formality	E$_0^1$, volts
5-fluoro-	3.2	1.05	3, 7-dimethyl-	1.4	0.96
3-chloro-	4.4	1.11	3, 8-dibromo-	5.4	1.21
3-phenyl-	2.4	1.02	4, 7-dimethoxy-	0.1	0.85
3-ethyl-	2.1	1.00	4, 7-diethyl-	0.9	0.94
4-bromo-	2.9	1.04	4, 7-diphenoxy-	2.9	1.04
4-phenyl-	1.9	0.99	4, 7-diphenyl-	4.6	1.13
4-ethyl-	1.4	0.96	4, 6-diphenyl-	4.5	1.12
4-n-propyl-	1.4	0.96	5, 6-cyclohexeno-	1.4	0.96
3, 4-cyclopenteno-	1.4	0.96	5, 6-diethyl-	1.6	0.98
3, 4-cyclohexeno-	0.9	0.94	5, 6-dimethoxy-	2.4	1.02
3, 4-cycloocteno-	1.0	0.95	5, 6-dichloro-	4.4	1.11
(3, 4) (7, 8)-dicyclohexeno-	0.3	0.87	3, 5, 6-trimethyl-	1.0	0.95

the as yet untested 5,6-dibromoferroin would be predicted to have a potential of 1.22 volts.

The variation in properties of the methyl substituted ferroins indicates that substitutions for the 4,7 hydrogens effect the greatest change in the oxidation potential, whereas the 5,6 and 3,8 positions effect a much smaller change. The effect upon the molecular extinction coefficient is in the same order, but the trend is reversed when considering the effect upon the wave length of maximum absorption. Assuming that the same order of influence is exerted by substituents other than methyl, if a choice of new syntheses were to be made, the substiutions in the 4,7 positions would be preferred.

The variations in properties of the mon-, di-, tri-, and tetra-methyl-1,10-phenanthrolines have thus been shown to be specific and additive. These compounds represent the first type of organic analytical reagents thus far known, whose analytical application and functional group activities may be predicted on the basis of alterations in structure not involving changes in the functional group itself. The values for the molecular extinction coefficient are added in Table 2 as indicative of comparisons in depth of indicator color for equal concentration of indicator which may be in question.

The determination of redox potentials of additional methine chromophore group redox indicators determined by use of the third type of estimation employing vanadate-vanadyl potentiopoised solutions as reference standards (8) is given in tabular form in Table 4.

By the study of the large number of methine chromophore group redox indicators herein documented, it is to be kept in mind that the work of Blau followed up by that of George Walden, Jr. and associates which was augmented by the outstandingly productive syntheses of required new organic reagents by Professor Francis Case, represents a most important series of advances in the field of cerate oxidimetry.

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SECTION 6

MICRO-VOLUMETRIC DETERMINATION OF ARSENIC, IRON AND THE OXALATE ANION

The most fruitful volumetric oxidation-reduction determinations which may be employed in Cerate Oxidimetry (which are not possible employing permanganimetry processes) involve the reactions of 0.001 N perchloratoceric acid in perchloric acid solution. At perchloric acid concentrations of 1 to 8 formal the available oxidation potentials of the Ce(IV)-Ce(III) half cell are 1.71 to 1.85 volts. For this reason a 0.05 ml increment in addition of one thousandth normal oxidant under these conditions produces a large increase in potential. Such reactions under the conditions of their potentiometric equivalence determination are far too sluggish and time consuming to be practical. On the contrary the use of nitroferroin as indicator for such reactions is ideal, for perchloric acid formalities of one and two. If such reactions at 4 to 6 formal are in demand still high potential redox indicators are available.

Two handicaps apply to the micro-oxidation procedures now to be described. One of these involves the requirement that perchloratocerate solutions in perchloric acid are not permanently stable under storage as compared to complete stability of the sulfatoceric oxidants in sulfuric acid solution which have permanency with shelf life. The second imperfection of the procedures involves the requisite that all glass ware in use must be scrupulously clean and free from traces of organic matter. Such contaminations are readily oxidized by perchloratoceric acid and their oxidation equivalency is always high. This second imperfection is easily removed by treatment of the glass ware in cleansing by use of ammonium nitratocerate in hot normal perchloric acid followed by thorough pure water rinsing. This secondly cited inhibition is common to all microvolumetric procedures.

The following work of Smith and Fritz is reprinted in illustration of the applicability of perchloric acid solutions of perchloratoceric acid in microvolumetric procedures in the hope that a more enthusiastic effort by others will serve to extend such investigations. It is a practical certainty that the micro research experts could profit by an extension of effort in such direction as illustrated in Section 7 to follow in the micro determination of protein blood iodine which is one of the more important reactions of cerate oxidimetry.

The volumetric microdetermination of oxalate and the indirect determination of calcium as applied to blood plasma have been described by Salomon, Gabrio, and Smith, (loc cit) whose procedure involved the titration of very small amounts of oxalic acid in a 2 F perchloric acid solution.

The titrating reagent was a 2 F perchloric acid solution of perchloratoceric acid, and the ferrous sulfate complex of 5-nitro-1,10-phenanthroline (nitro-ferroin) served as indicator. A similar volumetric micro-determination of oxalic acid has been described by Ellis and Kirk and Tompkins, who employed the ferrous sulfate complex of 1,10-phenanthroline (ferroin) as redox indicator. As indicated by Salomon, Gabrio, and Smith, the indicator transition potential is much more favorable when nitroferroin rather than ferroin (nitroferroin 1.25 volts, ferroin 1.06 volts) is employed, and a more precise determination is practicable. Ten micrograms of oxalic acid can be determined by the newer procedure with an accuracy of ± 0.05 micrograms ($\pm 0.5\%$).

The present section shows that the same degree of accuracy results from an extension of the process to include the volumetric microtitration of iron and of arsenic. The determination of iron by the procedure described compares in accuracy with the best existing colorimetric methods for amounts of iron from 100 to 500 micrograms. Comparable accuracy is attained in the case of arsenic.

POTENTIOMETRIC TITRATION OF FERROUS IRON, OXALIC ACID, AND SODIUM ARSENITE WITH PERCHLORATOCERIC ACID

The titration of 0.001 N solutions of ferrous, oxalic, and arsenite ions in 2 F perchloric acid solutions by oxidation using 0.001 N solutions of perchloratoceric acid in the same acid medium will serve to define the reaction constants involved. The data for the constants of these three potentiometric titrations are given in Table 1 and the titrations are reproduced graphically in Figure 7, page 44.

The data of Table 1 and graphical representation in Figure 7 indicate that the vertical break in potential at the equivalence point for all three titrations covers the range 0.95 to 1.5 volts. Here the slope of the graph

TABLE 1

TITRATIN CONSTANTS FOR POTENTIOMETRIC TITRATION OF FERROUS, OXALATE, AND ARSENITE IONS

(0.001 N solution of Ce(IV) in 2 F perchloric acid as oxidant. Potential break at equivalence point = 600 millivolts)

Electrode Reaction	Molal Oxidation Potential E_0, Volts	Formal Oxidation Potential $E_0,^1$ Volts
$Fe^{+++} + e^- = Fe^{++}$	$+0.771$	$+0.75$
$2CO_2 + 2H^+ + 2e^- = H_2C_2O_4 + 2H_2O$	-0.49	$+0.88$
$H_3AsO_4 + 2H^+ + 2e^- = HAsO_2 + H_2O$	$+0.559$	$+0.84$
$Ce^{++++} + e^- = Ce^{+++}$	$+1.71$	$+1.71$

representing the vertical break is at its maximum at approximately 1.23 volts. At this point the ratio of change in potential to oxidant addition following the addition of the smallest increment of oxidant is greatest. Potentiometric determinations of oxalate, arsenite, and ferrous ions such as those shown in Figure 7, in which the reacting solutions are 0.001 N or less, are very time-consuming; equilibrium conditions are slowly attained and such conditions are not acceptable for routine work. The procedures described below are equally precise without any of the disadvantages of the potentiometric determinations.

TITRATION OF FERROUS IRON, OXALIC ACID, AND SODIUM ARSENITE BY PERCHLORATOCERIC ACID

The selection of a redox indicator for the titrations, the electrochemical characteristics for which are shown in Table 1 and Figure 7, requires that such an indicator have a transition potential of 1.23 volts. The ferrous nitrophenanthrolinium ion was selected because it has an oxidation potential of 1.23 volts in solutions which are 2 F in acid. Its color change at the transition point is from red to a faint blue.

Reagents

Arsenious Acid. Primary standard arsenious oxide (National Bureau of Standards sample 83a) was weighed accurately, transferred to a 250-ml beaker, and dissolved in approximately 10 ml of conductivity water after the addition of a few pellets of sodium hydroxide. This solution was transferred to an accurately weighed 1-liter flask with ground-glass stopper. Enough 72% perchloric acid and conductivity water to give a free acid concentration of 2 F after dilution to approximately 1000 ml were added, the flask and contents were again weighed, and the calculation was made of the weight of arsenic trioxide per gram of solution. Vacuum corrections were applied to all weighings. The solution prepared following these directions contained 0.04350 mg of arsenic trioxide per gram of solution and samples from it were weighed into titration beakers from a weight buret.

Ferric Perchlorate Solution. Iron wire (99.858% iron) was accurately weighed and dissolved in hot perchloric acid in a 250-ml beaker. The resulting solution was transferred to a weighed 1-liter glass-stoppered flask. Enough perchloric acid diluted with conductivity water to give approximately 1000 ml of final solution 2 F in perchloric acid was added and the weight of flask and contents was again determined. The solution prepared for use in the present work contained 0.05010 mg of iron per gram of solution. As in the previous case, samples of this solution were transferred into titration beakers from a weight buret.

Sodium Oxalate Solution. Bureau of Standards sodium oxalate (primary standard 40e) was employed. Concentrated 72% perchloric acid was diluted

with conductivity water to a concentration of 2 F and a volume of approximately 1000 ml. This solution was transferred to a weighed glass-stoppered flask into which had been transferred an accurately weighed sample of the pure sodium oxalate. The weight of this solution was then determined. This acidified solution of oxalic acid is stable over extended periods of time and as prepared for the present work contained 0.062187 mg of sodium oxalate per gram of solution. Sampling by use of weight burets was again applied.

Perchloric Acid, 72%. The vacuum-distilled commercial reagent manufactured by the G. Frederick Smith Chemical Company was employed.

5-Nitro-(1,10)-Phenanthroline Ferrous Sulfate (Nitroferroin). A commercial source of supply of this reagent (0.025 M solution) was diluted with water to form a 0.0005 M solution.

1,10-Phenanthroline Monohydrate. C.P. white crystalline material purchased in routine trade channels.

Osmic Acid Catalyst. Enough osmic acid was dissolved in 0.1 M sulfuric acid to make an approximately 0.01 M solution. One drop of this catalyst serves for each titration of arsenite by the perchloratocerate ion.

Perchloratoceric Acid. This reagent was supplied as a stock item from the G. Frederick Smith Chemical Company in the form of an approximately 1 N solution of $H_2Ce(ClO_4)_6$ in 6 M perchloric acid. Sufficient of this stock solution was diluted by addition of conductivity water and perchloric acid to prepare an approximately 0.001 N solution which was 2 F in perchloric acid. Such solutions when kept in the dark and preferably 40° C are sufficiently stable to use after 72 hours' storage without detectable alteration in oxidation value.

EXPERIMENTAL PROCEDURES

Standardization of Approximately 0.001 N Perchloratoceric Acid. The procedure duplicated that described by Salomon, Gabrio, and Smith in the microdetermination of calcium, except for the use of weight burets for the sampling (volume burets for titrations).

Portions of the standard oxalate solution were weighed into 30-ml beakers and 3 drops of 0.0005 M nitroferroin were added as indicator. The sample solutions were stirred with a magnetic stirrer and titrated, using additions of the 0.001 N solution of perchloratoceric acid to be standardized at room temperature. The equivalence point potential was sharply indicated by the elimination of the pink indicator color at the point of the addition of the first slight excess of the cerate solution. As all solutions to be titrated in connection with this work were of the same relative normality, and the same amount of indicator was employed in each titration, no indicator correction was necessary. An automatic filling microburet and reagent

reservoir were used in all titrations. The buret was of 10-ml capacity, intended to be read with accuracy of ±.01 ml. The results are shown in Table 2.

TABLE 2
Standardization of Approximately 0.001 N Perchloratoceric Acid

	Solution No. 1			Solution No. 2	
$Na_2C_2O_4$ taken G.	$H_2Ce(ClO_4)_6$ required Ml.	Normality found N	$Na_2C_2O_4$ taken G.	$H_2Ce(ClO_4)_6$ required Ml.	Normality found N
5.535	6.41	0.0008014	4.425	5.16	0.0007959
5.545	6.43	0.0008004	4.425	5.18	0.0007929
5.546	6.42	0.0008017	4.425	5.17	0.0007944
		Av. 0.0008011			Av. 0.0007943

Titrimetric Determination of Arsenic Following Perchloratocerate Oxidation. Weighed samples of arsenite solution were taken as described in the standardization of the cerate solution and the same technique of titration was followed (Table 3).

TABLE 3
DETERMINATION OF ARSENIC BY TITRATION WITH PERCHLORATOCERIC ACID (SOLUTION 2) IN 2 F PERCHLORIC ACID
(Nitroferroin as indicator)

Arsenite Solution G.	As_2O_3 Taken Mg.	Cerate Required Ml.	As_2O_3 Found Mg.	Error Mg.
5.550	0.2414	6.125	0.2406	—0.0008
5.550	0.2414	6.12	0.2404	—0.0010
5.540	0.2410	6.10	0.2397	—0.0013
5.540	0.2410	6.12	0.2404	—0.0006
6.184	0.2690	6.74	0.2648	—0.0042
4.103	0.1785	4.51	0.1772	—0.0013
4.238	0.1844	4.675	0.1837	—0.0007
3.720	0.1618	4.12	0.1619	+0.0001
3.518	0.1531	3.915	0.1538	+0.0007
			Av.	0.0012
			% error	0.57

Titrimetric Determination of Iron Following Perchloratocerate Oxidation. Weighed samples of the ferric perchlorate were reduced using a micro-Jones reductor, the effluent from which was received in a 30-ml beaker. This solution of known ferrous iron content was then titrated as in previous cases by use of perchloratoceric acid in 2 F perchloric acid, using nitroferroin as

indicator and employing magnetic stirring. The reduction of ferric perchlorate to ferrous perchlorate in the Jones reductor does not cause reduction of the perchlorate ion, but a blank correction of 0.10 ml of the cerate solution due to the "hydrogen peroxide" error of the reductor was applied as determined by the passage of comparable volumes of 2 F perchloric acid through the micro-Jones reductor and subsequent addition of indicator and perchloratocerate solution. The results from these titrations are given in Table 4.

TABLE 4

DETERMINATION OF IRON BY TITRATION WITH PERCHLORATOCERIC
ACID (SOLUTION 1) IN 2 F PERCHLORIC ACID

(After reduction with zinc and using nitroferroin as indicator)

$Fe(ClO_4)_3$ Solution Grams	Fe Taken Mg.	$H_2Ce(ClO_4)_6$ Required Ml.	Fe Found Mg.	Error Fe Mg.
5.545	0.2778	6.23	0.2775	—0.0003
5.545	0.2778	6.22	0.2771	—0.0007
3.921	0.1965	4.46	0.1987	+0.0022
5.553	0.2782	6.24	0.2780	—0.0002
5.848	0.2930	6.59	0.2935	+0.0005
5.077	0.2544	5.77	0.2570	+0.0016
4.412	0.2211	5.00	0.2227	+0.0016
6.259	0.3136	7.08	0.3153	+0.0017
			Av.	0.0011
			% error	0.42

Colorimetric Determination of Iron in Ferric Perchlorate Solution. For the purpose of comparing the accuracy of this type iron determination following perchloratocerate oxidation, a colorimetric determination of iron by the 1,10-phenanthroline reaction was carried out. The preparation of the solutions of iron for spectrophotometric analysis was as follows:

Samples of the standard iron solution (0.05010 mg per gram of solution) were weighed out of the weight buret into 100-ml beakers. A small excess of sulfuric acid was added and the solutions were evaporated to fumes of sulfuric acid to remove perchloric acid. The solutions thus obtained were diluted with conductivity water and the ferric iron was reduced by the addition of hydroxylamine hydrochloride. The solutions were then neutralized (Congo red paper) by the addition of dilute ammonia and the ferroin reaction was produced by the addition of 5 ml of 0.33% aqueous solution of 1,10-phenanthroline. The solutions thus obtained were transferred to 100-ml volumetric flasks and diluted to the mark with conductivity water. Spectrophotometric transmittance curves for these solutions were obtained using the G.E. recording spectrophotometer and the per cent transmittancy

was read at the point of maximum absorption wave length 512 mμ. From a previously accurately determined calibration curve the weight of iron present was determined. A blank correction to account for traces of iron in the reagents employed was applied. The results are given in Table 5.

Examination of Tables 4 and 5 shows that the colorimetric determination of iron and the volumetric determination by the perchloratocerate titrational procedure are of comparable accuracy and precision.

TABLE 5

SPECTROPHOTOMETRIC DETERMINATION OF IRON IN FERRIC
PERCHLORATE REFERENCE SOLUTION

Iron Taken Mg.	Transmittance %	Iron Found Mg.	Error Fe Mg.
0.239	33.9	0.236	—0.003
0.339	21.3	0.340	+0.001
0.149	49.7	0.151	+0.002
0.245	32.4	0.244	—0.001
0.246	32.1	0.247	+0.001
0.458	12.7	0.456	—0.002
0.249	31.3	0.251	+0.002
		Av.	0.0017
		% error	0.061

SECTION 7

CLINICAL TESTING IN DETERMINATION OF PROTEIN-BOUND IODINE

It has become increasingly routine in medical practice to call into play the clinical testing of blood serum for protein-bound iodine in treatment of cretinism, mysedema or pro- or post-thyroidectomy resulting from malfunctioning of the thyroid gland. Since the determination of protein-bound iodine in blood plasma is a micro- or semi-micro chemical process in analysis the quantitative analytical work involved was complicated and by early methods was time-consuming and involved complicated equipment not ordinarily a part of clinical routine laboratories.

Protein-bound iodine determination (o to 10 microgram magnitudes) follows the reaction of the oxidation of arsenite by sulfatoceric acid, in acid solution, as catalyzed by the presence of iodide, iodine or iodine monochloride. The progress of the oxidation of As(III) to As(V) by sulfatoceric acid as catalyzed by the presence of iodine is a function of time as observed spectrophotometrically by the reduction of Ce(IV) to Ce(III).

The early designation of iodide as catalyst in a volumetric procedure was made by Lang (1) in the reaction of permanganate in oxidation of arsenious acid. The use of a chronometric reaction technique described by Baines (2) for the determination of iodine is an additional clock reaction in the determination of iodine. Iodine as catalyst in volumetric Ce(IV) reactions has been described by Willard and Young (3).

The preliminary study of the iodide catalysis of the oxidation of As(III) to As(V) by Ce(IV) was made by Sandell and Kolthoff (4). The completion of this preliminary study was made by Sandell and Kolthoff (5). As stated by these investigators in their study, "this investigation was of a general nature, and the application of the method to specific cases was not considered. If the general method is found to be of value, it is left to others to modify the procedure to suit their needs and possibly to improve its accuracy." This has been done in the study of the determination of protein-bound iodine in the medical clinical routine analytical laboratory.

K. Gleu (6) has employed osmium tetroxide in the catalysis of the same reaction as that employed by Sandell and Kolthoff and the osmium catalyzed reaction in the oxidation of As(III) and $(C_2O_4)^{-2}$ by Ce(IV) sulfate is extremely valuable in cerate oxidimetry. For this use the Gleu reaction is of importance in the use of arsenic trioxide and sodium oxalate as primary standards in oxidimetry. The same oxidation carried out in perchloric acid solution by perchloratoceric as oxidant unlike in sulfuric acid by sulfatoceric acid as oxidant require no osmium catalyst.

The catalytic effect of the halides in the reaction of oxidation of arsenious acid by sulfatoceric acid are compared as follows:

chloride < bromide < iodide
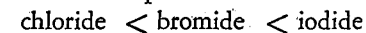
By roughly accurate evaluation the effect of bromide is less by a factor of 3×10^{-6} and the chloride less than 2×10^{-7}. Hence small amounts of chloride and bromide are of small effect and their presence does not cause complications. Fluoride, mercury salts, cyanide and silver are interferences, all other ordinary contaminating metals are without influence.

The oxidation of trivalent arsenic to pentavalent arsenic by sulfatoceric acid as oxidant in sulfuric acid solution may be written as follows:

$$AsO_3^{----} + 2Ce^{++++} + H_2O + \text{iodide as catalyst} \rightarrow$$
$$AsO_4^{---} + 2Ce^{+++} + 2H^+$$
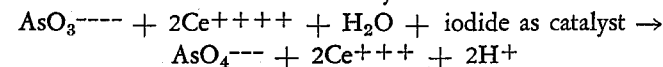
This reaction in the absence of the iodide does not apply in many hours time in sulfuric acid solutions either hot or cold if the cerium oxidant is of high purity. The presence of either a trace of iodide ion or the presence of a small amount of osmic acid (6) promotes instant fast reaction. The completion of the reaction in fact may be chronometrically evaluated as a function of the concentration of catalyst present. For amounts of iodide as catalyst which bring about complete oxidation in 1 to 30 seconds the completion of the oxidation of arsenic is measured either by having present a methine chromophore group redox indicator such as the 1,10-phenanthroline ferrous ion to give a red color when all Ce(IV) present has been reduced by excess arsenite ion or less exactly by the disappearance of the yellow color of the Ce(IV) ion alone.

In the determination of protein blood iodine a modified technique with spectrophotometric evluation of the time rate of reduction of Ce(IV) to Ce(III) is employed as will be detailed in subsequent material.

The material of the original publication of Sandell and Kolthoff (5) has been herein reprinted with much of the details concerning the influence of presence of large amounts of foreign ions omitted. In the determination of protein-bound iodine organic matter and interfering high concentration of ions other than the iodide ion being determined are absent.

THE MICRO DETERMINATION OF IODINE BY A CATALYTIC METHOD(5)

"In the determination of iodine in the general case, there will be present in the sample greater or less amounts of foreign substances which will effect the rate of the catalyzed reaction between quadrivalent cerium and trivalent arsenic, so that iodine in the unknown solution can hardly be determined by comparing the effect of such a solution on the reaction rate with that produced by a known iodide solution in pure water. The difficulty can be overcome with fair success by adding a suitable known amount of iodide to the unknown solution and comparing the catalytic activity of the solution so

obtained with the activity exhibited by the original solution, there being present the same initial amounts of ceric cerium and arsenite in both cases. That is, after the reaction time has been noted with the unknown amount of iodine and the given amounts of cerium and arsenite, let there be added the known amount of iodine and sufficient ceric salt and arsenite to replace that destroyed in the reaction and let the time required for the completion of the reaction the second time be noted. Then it is a simple matter, at least in principle, to find the unknown amount of iodine by proceeding as follows:

Let $x =$ quantity of iodine (as iodide) in the sample

$a =$ known quantity of iodine added

$v_1 =$ original volume of reaction mixture containing the sample

$v_2 =$ volume of reaction mixture after the known quantity of iodine (iodide) solution, and sufficient ceric and arsenite solutions to restore these to their original amounts have been added

$t_1 =$ reaction time with the quantity x of iodine in the volume v_1

$t_2 =$ reaction time with the quantity $a + x$ of iodine in the volume v_2

Assuming reaction time to be inversely proportional to the iodine (iodide) concentration under conditions described, the following expression should hold:

$$t_1 = kv_1/x$$
$$t_2 = kv_2/(a + x)$$

and $\qquad t_1/t_2 = v_1/v_2 \cdot (a + x)/x$

hence $\qquad x = av_1t_2/v_2t_1 - v_1t_2$

. . . . If sufficient sample is available, the difficulty due to volume change can be overcome by taking two equal portions of unknown, adding to one a known quantity of iodide, making the volumes of both portions the same, and then measuring the reaction with the same amounts of ceric and arsenic solutions in the two cases. Then the formula for calculating the unknown amount of iodine becomes

$$x = at_2/t_1 - t_2.$$

It is assumed that the catalytic activity of the iodine present is directly proportional to its concentration.

. . . . In the absence of chloride, the values for iodine are seriously low when the amount present is less than $0.25\text{-}0.5\gamma$ in consequence of the failure of the linear relationship between catalytic activity and iodine concentration at very low concentrations. If a small amount of chloride is added, the linear relation is fulfilled at concentrations of iodide as low as $1:10^9$. Therefore if chloride is not present in the sample, it is necessary to add it in small amount (ca. 10 mg of sodium chloride) when quantities of iodine of the order of a few tenths of a microgram are to be determined. The concentration of iodine in the reaction mixture should generally be less than $1:2 \times 10^7$,

for otherwise the second reaction time, t_2, becomes so small that it cannot be measured precisely. With amounts of sodium chloride of the order of 10 mg, positive and negative errors appear to be nearly equal. For amounts of iodine (as iodide) ranging from 0.05 to 1γ in the presence of 5 to 15 mg of sodium chloride, the largest error was 20 percent, and the average error was approximately 10 percent. Considering the small absolute amount of iodine and the rather large ratio of chloride to iodide (as great as 10^6 to 1), the accuracy may be regarded as satisfactory. . . . When the quantity of sodium chloride present is in the neighborhood of 100 mg, the average error is estimating amounts of iodine ranging from 0.1 to 3γ is about 15 percent; the results tend to be high."

SOLUTIONS REQUIRED AND PROCEDURE OUTLINE

Standardized 0.1000 N sodium arsenite.

Standardized 0·1000 N ammonium sulfatocerate,

$$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O.$$
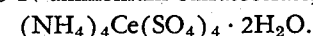
Standard Iodide Solution. 0·01308 g of pure dry KI in a liter of water.

1,10-Phenanthroline Ferrous Sulfate, 0.001 N.

"The following directions (continuing the above quatation from Sandell and Kolthoff) hold for a sample which does not contain constituents reacting with either ceric cerium or arsenite in sulfuric acid solution at room temperature. Organic matter should be absent. . . . . Iodine should be present in the form of iodide. The sample may be neutral or slightly acid; if it is alkaline it should be neutralized by hydrochloric acid (iodine free)."

"First of all, the reagents should be tested for the possible presence of traces of iodine. Mix 2 ml of sodium arsenite, 1 ml of ceric ammonium sulfate, 1 ml of 6 N sulfuric acid, and 0.1 ml of o-phenanthroline ferrous sulfate indicator, and allow the solution to stand at room temperature. The yellow color of the mixture should not be discharged within 24 hours."

If the sample is solid (soluble in aqueous solution) transfer a quantity sufficient to contain 0.05 to 3γ of iodine to a dry vial conveniently 2 x 7 cm in size. The weight of the sample should generally not exceed 0.1 g, because larger quantities may cause the formation of a precipitate in the reaction mixture when the reaction time is long. If the sample is in the form of a solution, transfer a known volume to the vials the volume of the liquid sample should be as small as possible, preferably not exceeding 1 ml, when very small amounts of iodine are to be determined, because the reaction time increases as the dilution of the reaction mixture is increased. Then add to the vial 2.00 (± 0.01 ml) of sodium arsenite solution, and shake to dissolve the sample if solid; the volume change occurring with a solid sample may be neglected. At this point, if the sample does not contain chloride, and quantities of iodine less than 0.5γ are to be determined, add 10 mg of pure (iodine free) sodium chloride. Next add 1 ml of 6 N sulfuric acid (or

more if the volume of the sample is unavoidably large) so as to make the acidity 1.5 to 2 N and 0.10 ml of o-phenanthroline ferrous sulfate solution. In another vial, preferably 2 x 4 cm in size and provided with a lip to facilitate pouring, measure out 1.00 ml of ceric ammonium sulfate solution. Immerse both vials in a constant temperature water bath (room temperature) and keep therein until the contents have assumed the temperature of the bath."

"At one stroke pour the mixture of sample and arsenite (vial 1) into the ceric solution (vial 2), starting a stop watch at the instant of mixing. Quickly pour the mixed solution into vial 1, and drain out the second vial as completely as possible into the first. Return the vial containing the reaction mixture to the water bath, and shake gently at intervals, or continuously if the yellow color of the solution fades rapidly, taking care not to heat the contents inadvertly with the hand. When the yellow color has become very pale, hold the vial over a white background in good light in order that the end point may be observed under the best conditions. Obtain the time of the appearance of the first pink tinge in the solution. It is important to shake the solution near the end point. The color change is from yellow through colorless or very pale blue to red. If the reaction velocity is great, the color stage may not be observed. When the color change is slow (very small amounts of iodine present) it may be advantageous to use a comparison solution containing the same amount of indicator as the reaction mixture, which has been converted into the pale blue oxidized form by a trace of ceric solution."

"When the reaction has been completed, add to the solution by means of a microburet sufficient standard iodide solution to furnish an amount of iodine which is estimated to be two or three times as great as that present if the latter is in the approximate range 0.5 to 2.5γ.* For quantities of iodine below 0.5γ add 1 to 2γ of the element. Allow the mixture to stand for a minute or two after the addition to insure the complete reduction of the cerium. Then measure out into a clean vial 0.5 ml (measured with accuracy of ±0.005 ml) of ceric ammonium sulfate solution, and add to the latter, all at once as before, the reacted arsenite-iodide solution, and determine the second reaction time. Calculate the quantity of iodine in the sample by making use of the formula $x = a v_1 t_2 / v_2 t_1 - v_1 t_2$ where the symbols have the meaning (previously cited)."
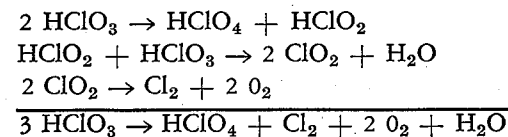
"The procedure just described is to be used when the amount of sample,

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* The quantity of iodine added should be so chosen that the second time, t_2, is not less than 20 or 30 seconds, for otherwise the error in time measurement is likely to be unduly large. It will be seen that for the best accuracy the original iodine content should not be greater than approximately 3γ, unless salts are present that appreciably decrease the reaction velocity.

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very low in iodine, is limited. When sufficient sample iv available,* it is usually better to take two equal portions of sample and arrange matters so that the final reaction volumes, v_1 and v_2, are the same. This can be done by adding the first portion, containing the quantity of iodine x, sufficient water to exceed slightly the maximum volume of iodide solution, which it is necessary to add to the second portion to furnish the amount (a). Then after t_1 has been determined on the first portion of sample, there is added to the second portion a suitable volume of iodide solution together with enough water to make the total volume the same as that of the other portion. For each portion of sample, 2 ml of arsenite and 1 ml of ceric ammonium sulfate solution are used in obtaining the reaction times. Under these conditions $x = a t_2 / t_1 t_2$. This technique eliminates any error due to change of salt concentration, and is to be preferred to that described in the preceding paragraphs."

CHLORIC ACID METHOD FOR DETERMINATION OF PROTEIN-BOUND IODINE

A rapid method for the determination of organic-bound iodine was described by Zak and Boyle (9) using chloric acid as the oxidizing digestion reagent. The iodine concentration which may be determined with analytical accuracy ranges from a fraction of a milligram to 100 mg. The method is an extension of that described by Shahrokh (10). This method involves the wet oxidation of organic matter employing a mixture of sodium chlorate, perchloric acid and disodium hydrogen phosphate. If iron is absent the phosphate may be omitted. The method of Zak and Boyle (9) may be employed with accuracy to carry out as many as 20 samples daily since very little care is needed per individual sample. No extensive preparations are required and the number of manipulations per sample has been reduced to a minimum. The final determination of iodine, following wet oxidation of the sample, is carried out employing 0.001 N thiosulfate titration of iodine liberated from the iodic acid formed in the digestion. The reactions involved in the digestion are given as follows:

$$2\ HClO_3 \rightarrow HClO_4 + HClO_2$$
$$HClO_2 + HClO_3 \rightarrow 2\ ClO_2 + H_2O$$
$$2\ ClO_2 \rightarrow Cl_2 + 2\ O_2$$
$$\overline{3\ HClO_3 \rightarrow HClO_4 + Cl_2 + 2\ O_2 + H_2O}$$

The same procedure has been employed by Zak, Willard, Myers and Boyle (11) for the determination of protein-bound iodine in blood plasma now to be reviewed.

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* Or even if the absolute amount of iodine is very small it may be advisable in certain cases (even when relatively much sulfate is present) to divide the sample into two parts and proceed as described in the paragraph above.

CHLORIC ACID METHOD FOR DETERMINATION
OF PROTEIN-BOUND IODINE

This important biological routine determination of protein-bound iodine (11) employs the previously described procedure (9) with a much-improved determination of iodine following the procedure of Sandell and Kolthoff, (5) the iodide catalytic promoted oxidation of As(III) by sulfatoceric acid as a chronometric or "clock" reaction. The sample size required for successful analysis is either 2 or 3 ml of serum, the latter being preferable. The procedure effectively reduces the manipulation to a minimum and makes possible the determination of protein-bound iodine in many more samples in a given period of time than appears to be possible using other methods.

For the wet oxidation of isolated protein, isolated from blood: "It was found that chloric acid containing a small amount of sodium chromate was the most satisfactory digesting and oxidizing agent because the acid, along with organic matter, could be subsequently volatilized without loss of iodate, to leave a few milligrams of soluble residue suitable for direct colorimetric estimation of iodine. Another departure in the method reported is the use of a 180-ml electrolytic beaker as container for precipitation of protein, centrifugal separation of the supernate, digestion of the protein residue with simultaneous release of bound iodine and oxidation to iodate, evaporation to a small volume for removal of acid and organic matter, and dilution of residue to a fixed volume in preparation for direct colorimetric estimation. The use of an open beaker for evaporation obviates the danger of explosion. Because all steps in the preparation of the sample are carried out in the same container, losses of iodine through transfer or dilution are avoided. Furthermore, the method lends itself to simultaneous determination of several samples. Possible errors from iodine contamination of C.P. reagents are cancelled out by a simultaneous blank, carried through the same procedure as the serum sample." . . . .

The determination of iodine in blood was described (12) by Chaney employing chromic-sulfuric acid wet oxidation and iodine determination following distillation of the iodine from the wet ashing residue employing the iodine catalyzed oxidation of cerium. The purpose of the protein-blood iodine determination by Zak, et al., was to utilize the same technique of iodine determination with a more applicable wet oxidation procedure which did not involve distillation or special designed laboratory apparatus.

"The estimation of iodine by measurement of its catalytic action on the ceric-arsenic system described by Sandell and Kolthoff and adopted by Chaney (12) and later by most investigators, was utilized in the submicroprocedure. The color intensity of Ce(IV) is measured in the presence of arsenic (III) under controlled conditions of time, temperature and acidity."

REAGENTS AND SUBMICROPROCEDURE

Chloric Acid Reagent. Weigh into a 3-liter beaker 500 grams of potassium chlorate. (Potassium is used in place of barium chlorate for the preparation of chloric acid, because the presence of barium in the reagent causes precipitation during the procedure that mechanically interferes with the recovery of all iodine). Add 900 ml of distilled water and heat the mixture until solution is effected. With constant stirring slowly add 375 ml of 72% perchloric acid. When the addition is complete, the solution will be light green with chlorine, owing to the decomposition of chloric acid. Potassium perchlorate will be largely present as a precipitate at this time. Cool and place the covered beaker in the freezing compartment of a refrigerator for 24 hours. Decant the supernatant liquid through a Whatman 41 H paper; it represents approximately a 28% solution of chloric acid. The potassium remaining in this reagent is approximately 0.3 gram per liter.

Sodium Chromate. Weigh out 5 grams of sodium chromate and dilute to 1 liter.

Trichloracetic Acid. Weigh out 150 grams of reagent trichloracetic acid and dilute to 1 liter.

Ceric Ammonium Sulfate (0.1 N). Transfer 200 ml of 0.5 N reagent grade ceric sulfate solution 1 M in sulfuric acid by pipet into a 1-liter volumetric flask and dilute to about 600 ml. Add 13.2 grams of ammonium sulfate, 83 ml of concentrated sulfuric acid, and 1.8 grams of sodium chloride and dilute to the mark. This solution has an acidity of approximately 3.2 N.

Arsenious Acid (0.2 N). Weigh out 9.8910 grams of arsenic trioxide and 7 grams of sodium hydroxide and dissolve in a volume of 100 ml. (The Mallinckrodt brand of arsenic trioxide was found preferable for this work because of smallest iodine contamination). Dilute to about 400 ml and neutralize to phenolphthalein with concentrated sulfuric acid. Add 42 ml of concentrated sulfuric acid and dilute to 1 liter. The final acidity is approximately 1.5 N.

Standard Iodate. Weigh out 168.5 mg of dried analytical reagent potassium iodate and make up to 1 liter. Dilute 10 ml of this stock solution to 1 liter to make a standard solution containing 1 microgram of iodine per ml.

SUB-MICRO PROCEDURE FOR PROTEIN-BOUND IODINE

Preparation of Sample. Pipet 2.0 to 3.0 ml of serium into a 180-ml electrolytic beaker. Add 25 ml of the trichloracetic acid reagent, mix well and centrifuge at 2000 r.p.m. for 10 minutes. Decant the supernatant liquid and again add 25 ml of the trichloracetic acid reagent. Stir the precipitate with a glass rod, centrifuge again for 10 minutes, and decant the supernatant, as before. Add 1.0 ml of the chromate solution, followed by

25 ml of the chloric acid digestion reagent. Add 15 to 20 glass beads and digest at the low temperature of the hot plate. Continue the evaporation of the digestion mixture until approximately 0.5 ml remains in the bottom of the beaker. One or two drops of chloric acid reagent should be added periodically (total 0.5 to 1.0 ml) during the final stages of evaporation and at any time during the procedure when the chromate appears to be reduced, as indicated by the development of a green color. If gross reduction of the chromate takes place due to rapid evaporation of the chloric acid, or if too little chloric acid is employed for the amount of protein present, iodine will be lost.

Preparation of Standards. Pipet into four 180-ml electrolytic beakers 0.0, 0.2, 0.4, and 0.6 ml, respectively, of the standard iodate solution. Add 1 ml of the chromate solution and 25 ml of the chloric acid reagent to each of the four beakers. Place on a low temperature hot plate and evaporate to approximately 0.5 ml.

Colorimetric Estimation. Remove the beakers containing the samples and standards from the hot plate, cool, and add 5.0 ml of distilled water to each. Warm slightly to hasten solution of the soluble salts, and transfer to a 10-ml volumetric flask. Rinse the beaker with 1-ml washings and dinally dilute to the mark. Insert the glass stopper and mix thoroughly by inversion.

Transfer 3.0 ml by pipet from each flask to matched photometer tubes. Add 2.0 ml of arsenic(III) solution to each tube and mix thoroughly by sharply striking the lower end of the tube while holding the top between the thumb and index finger. Place the tubes in a constant temperature bath at 30°C and allow them to stand for 20 minutes. At accurately timed intervals of 1 minute, add 1.0 ml of the standard cerium(IV) solution to each of the tubes. Mix at the time of the cerium addition by removing the tube from the bath for a few seconds and manipulating as described above. Measure in the cerium(IV) color of each tube at the end of an exact time, usually 20 to 30 minutes. (Measurements are made at the end of a 20-minute period, rather than 30-minute period, when there is much iodine in the blank). Measure in the order of cerium(IV) addition at 1-minute intervals; this may be done satisfactorily in a Klett-Summerson colorimeter, using the proper blue filter or more precisely with a spectrophotometer at 420 mμ. The time of standing depends upon the amount of iodine in the blank and must be determined experimentally. Prepare a graph, showing iodine concentration against extinction.

Results. Table 1 gives a few examples to illustrate reproducibility and recovery with this method.

TABLE 1

DETERMINATION OF PROTEIN-BOUND IODINE

Sample	Ml. Used	Iodine Added as KIO₃ γ	Iodine Found γ
Serum A	3	0.00	0.34
	3	0.00	4.37
	3	0.00	0.34
	3	0.12	0.43
	3	0.12	0.43
Serum B	2	0.00	0.28
	2	0.00	0.30
	2	0.18	0.48
Serum C	2	0.00	0.18
	2	0.00	0.16
etc.			
Serum 0	2	0.00	0.20
	2	0.18	0.37

DISCUSSION

The small amount of serum required, the rapidity of the method, and its adaptability to the simultaneous analysis of several samples are evident from the description of the technique. The accuracy is illustrated by the tabulated results.

Trichloracetic acid proved to be the most suitable agent for protein separation because it produced a precipitate that could be packed by centrifugal force into a small cohesive, rubbery mass, from which the supernate could be decanted with ease. The two treatments with trichloracetic acid sufficed to separate protein-bound from inorganic iodine, as shown by the fact that further washing with distilled water, followed by centrifuging did not alter results significantly, even when iodine had been added to the sample just before precipitation.

The prevention of iodine loss during evaporation, particularly in the stage of fuming, depends upon maintenance in the form of iodate. Iodic acid is not volatilized at the temperature employed, as shown by recovery data in Table 1. Although the presence of chloric acid will maintain iodine in the oxidized form, this acid disappears during the fuming stage, partly by decomposition to volatile products, partly by conversion to perchloric acid. Loss of iodine occurs in fuming mixtures of iodic acid and perchloric acid in the absence of chromium. Hot and concentrated perchloric acid will oxidize trivalent chromium to chromate and the presence of the latter will maintain iodine as iodate throughout the procedure. The 5-mg amounts of sodium chromate employed are adequate for keeping iodine in the oxidized form. Nevertheless, it was found advisable to add one or two drops of

chloric acid reagent when the first fumes of perchloric acid appear or whenever there is any indication of reduction of chromium to the green-colored trivalent state.

Glass beads must be present to avoid loss of sample by bumping. Toward the end of the digestion, there is a distinct crackling of the solution, which is probably due to the decomposition of chloric acid. This occurs irrespective of whether or not organic material was originally present.

The elimination of sample transfer throughout a procedure is an important consideration in any analytical method. This is particularly true in submicro techniques. The only transfer made in this process is to the volumetric flask for accurate dilution, preparatory to the removal of the aliquot for final measurement of iodine. For routine determinations, it was found that transfer to the volumetric flask for dilution could be eliminated by the experienced worker. Success of this modification depended upon the ability to carry the evaporation of each sample and standard to a uniform volume, as judged visually. Ten millimeters of distilled water were then added to each beaker from a pipet and after mixing, aliquots were taken for analysis. After some experience, it was found that this short cut could be carried out with a volume error of only ±2% in the final dilution.

Steam distillation is required in most acid oxidation methods to separate iodine from large salt concentration, but it is rendered unnecessary in this procedure by the low salt concentration in the chloric acid digest. Even though the amount of perchloric acid in the final residue may be subject to variation, this does not influence the subsequent colorimetric estimation of iodine. Approximately 15% of the chromate ion is lost during digestion and evaporation. Although the decrements in chromate were found to be fairly constant, it became necessary to determine the influence of variations in the amount of chromate on the colorimetric estimation of iodine in the cerium(IV)-arsenic(III) system. Twice the customary amounts of chromate caused no significant change in the values for iodine.

A new calibration curve must be established whenever new reagents are introduced. Blank determinations of the trichloracetic acid reagent have shown no iodine. As the procedure for samples and standards were identical in other respect, blank corrections were the same.

The reduction of iodate in the residue is accomplished by a measured excess of arsenic(III). The amounts of arsenious acid employed are large enough to provide the needed excess in the event of variable amounts of chromate or other oxidizing agents in the treated sample.

"To demonstrate the effectiveness of the reduction of iodate by the use of arsenic(III) in acid solution, amounts of iodate and excess potassium iodide in association with starch were treated with 2 ml of 2 N arsenic(III),

which was 1.5 N in sulfuric acid. Immediate discharge of the starch-iodine complex was noted."

"To two 5-ml samples of a solution of iodate (0.028 N) in 1 N acid were added 10 ml of standard arsenic(III) solution of the same normality. The mixtures were permitted to stand for 3 and 20 minutes, respectively. The mixtures were then neutralized with sodium bicarbonate and the excess arsenic(III) was titrated with standard iodine (0.0073 N). Five milliliters of the arsenic(III) alone in sodium bicarbonate buffered solution required 19.3 ml of standard iodine. The values obtained in the back titration of the excess arsenic(III) were 19.34 and 19.35 ml of standard iodine. To carry the experiment to lower values a curve based upon potassium iodide as a primary source of iodine covering the range from 0.00 to 0.74 microgram of iodine was prepared. Recovery of 0.59 micrograms of iodine as potassium iodate under the conditions of the procedure described was then made. Percentage recovery values were found to be 100.4, 100.4 and 90.6 on three separate samples. This was considered to be within the range of accuracy of the cerium(IV)-arsenic(III) end point."

"The precautions to be observed in estimating iodine by its catalytic effect on the cerium(IV)-arsenic(III) system have been brought out adequately by Sandell and Kolthoff, and others (4,5). Minute traces of mercury, silver, fluoride, or cyanide are known to check the reaction. The amounts of mercury present in the blood after a therapeutic dose of a mercurial diuretic may interfere with the determination of iodine. Osmium chloride and bromide are known to be positive catalysts in this system. It is not likely that osmium would be encountered in human serum. Chloride and bromide are removed in the digestion process."

Zak, Koen and Boyle have reported (13) favorable results obtained employing the chloric acid method of Zak, et al., in comparison results employing other procedures and by other investigators.

AMMONIUM SULFATOCERATE IODINE PURITY EVALUATION

The routine quality control to insure the absence of iodine in ammonium sulfatocerate (7) is provided by the use of the following procedure:

10 grams of $(NH_4)_2CeSO_4)_4 \cdot 2H_2O$ is dissolved in 200 ml of water containing 10 ml of reagent sulfuric acid. Stir to dissolve and dilute to 350-400 ml. Add ammonium hydroxide to precipitate ceric hydroxide $Ce(OH)_4$. Test with indicator paper to insure the solution is alkaline. Filter on a Buchner funnel, wash once with water.

Transfer the filtrate to a 500 ml stoppered Erlenmeyer flask. Neutralize the solution by addition of 18 N sulfuric acid in dropwise additions until the test solution is neutral to pH paper. Add 10 ml of dilute sulfuric acid (5 H_2O plus 1 concentrated H_2SO_4) beyond neutral point. Add 3 g of potassium iodide, swirl the solution in the stoppered flask and allow to stand

5 minutes. Add water until the Erlenmeyer flask is quite full and starch (vitex) indicator 100-200 milligrams. Titrate with 0.01 N sodium thiosulfate by use of a calibrated pipet to the disappearance of the starch blue color. The thiosulfate need not be of known strength closer than ±0.001 in normality.

The iodine content in parts per million = (ml thios) · (N thios.) (180).

The iodine content should be less than 0.5 parts per million.

DEPROTEINIZATION OF BIOLOGICAL FLUIDS INCLUDING BLOOD PLASMA

For the isolation of blood plasma proteins the method of Neuberg and Strauss (8) which has been applied in the determination of protein blood iodine by a number investigators was not made available until 1944 and has been proved to be superior to the use of trichloracetic acid for deproteinization of many biological entities and been given preference by certain investigators as hereinafter cited in the modification of the Zak, Willard, Myers and Boyle. Neuberg and Strauss *(8)* have been the source of the following quoted material.

"A 1 or 2 M perchloric acid solution (about 10 or 20%) may be employed. A solution of trichloracetic acid of the same molality was used as a comparison. Generally the biuret reaction (or the Million test) was employed to indicate the presence or absence of protein material in the filtrates. . . . .

"The precipitation can be effected at room temperature."

"The following minimum effective concentration of perchloric acid were obtained. They are expressed as the minimum percent by weight of acid in the protein-acid mixture which will give negative filtrates by the biuret test."

Protein solution	Minimum effective concentration percent
Ovalbumin (1-5%)	1.1
Caseinate (2-5%)	6.7
Casein-free milk filtrate (diluted 1:1)	3.3
Blood (beef, defibrinated) (diluted 1:10)	1.6
Yeast extracts (diluted 1:1)	6.7

A procedure by Barker, Humphrey and Soley in the determination of protein-bound iodine (14) which anti-dates that of Zak, *et al.,* employes the the same terminal measurements employed by these latter investigators. Protein separation employing either blood plasma or blood serum (with no difference in results) is deproteinated employing zinc to isolate the zinc proteinate, centrifugal separation in centrifuge tubes in which receptacles the dry ashing is at 600 ± 25°C with the protein product mixed with sodium

carbonate and the ignited ash dissolved in hydrochloric acid followed by added sulfuric acid. The use of an exclusively employed electric muffle furnace to carry out these preparational steps provided the motivation leading to the Zak, Willard, Myers and Boyle *(11)* much more simple chloric acid oxidation.

The details of the terminal part of a PBI determination following either the Barker, *et al.,* procedures of dry ashing zinc proteinate isolation of the iodine involved or following the terminal PBI determination of Zak, *et al.,* are supplied by Dr. H. E. Thompson of the Youngstown Ohio Hospital Association by private communication, 1960. For the manipulations involved in the experience of Doctor Thompson the directions of Zak, Willard, Myers and Boyle were found to be effective and were duplicated.

Doctor Viola Graham, of the research laboratory of the Tallahassee Memorial Hospital introduces the perchloric acid procedure for isolation of serum protein. The blood plasma (or serum) contained in an "Opticlear" vial (Ohio Glass Co., Gas City, Indiana) or a similar vessel, place 0.5 ml of serum. Slant the vial and very rapidly at first pour into it $HClO_4$ (50 ml 70-72% perchloric acid diluted to 1000 ml), protein precipitant from the reagent bottle leveling off at about a half inch below the shoulder of the vial. Centrifuge until precipitate is firmly packed; about 15 minutes at 2500 R.P.M. Thoroughly discard supernatant fluid: decant and invert vial on folded paper towel. The remainder of the determination follows that of Zak, *et al.,* previously outlined employing chloric acid as protein oxidant with recovery of iodine.

The catalytic action of iodine as employed in the reaction between Ce(IV) and As(III) in the microdetermination of iodine in the PBI studies of the above material is duplicated in the reaction of the nitrite-arsenite reaction described by Hart and Meyerowitz *(16).*

The importance of the clinic routine determination of protein-bound iodine in thyroid diagnostic medical interpretations is attested to by the many studies made and papers published relative to the subject. First wet ashing of isolated proteinized iodine from blood serum or plasma was developed to eliminate the early inconvenient method of electric muffles dry ashing procedure. Following the introduction of the chloric acid wet oxidation of precipitated plasma proteins employing trichloracetic acid, the late popular trend *(15)* seems to be precipitation of plasma protein employing perchloric acid in place of trichloracetic acid. It might be predicted that in future improvements, the necessary troublesome preparation and storage of the chloric acid wet oxidation of precipitated blood proteins could be improved upon without complicating the procedures now in practice. It would be possible to substitute the use of concentrated sulfuric acid to which has been added perchloric as the digestion oxidant.

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SECTION 8

Cerate Oxidimetry Bibliography

Literature citations involving the use of cerium(IV) in analytical chemistry by their number indicate the importance of such disciplines. By survey through *Chemical Abstracts* for the years since 1928 several hundred references to this subject are to be found. Not all references to Ce(IV) applications in analysis are found by this type survey since often the title of a given contributor is not indicative of the fact that cerium analytical usage is involved.

As an illustration the contribution of Byron Kratochvil and D. D. Zato entitled, "Ruthenium 2,2'-Bipyridine as Fluorescent Oxidation-Reduction Indicators," *Analytical Chemistry,* 36 527 (1964) is cited. This work is not only primarily on the subject indicated by title, but is equally valuable involving the Ce(IV) analytical chemistry described.

Space does not allow an exhaustive review except to list by author and title the more important papers on the subject since 1952. By reference to Philena Young, "Ceric Salts in Volumetric Analysis," *Ind. Eng. Chem.* Anal. Ed., 23, 1516 (1951) 164 references on the subject are cited covering the period prior to 1951.

Philena Young. "Ceric Salts in Volumetric Analysis." *Ind. Eng. Chem.* Anal. Ed. 23, 1516 (1951). A review paper with 164 references. Determinations referred to include, I, Fe, Mg, Hg(I), Mo. P, K, Na, Te, Th, Sn, Ti, U, V, Zn, As, Sb, Al, Ca, Cr, Cu, Nitrous Oxide, Plutonium Thiosulfates, Ferrocyanide, Hydrazine, Hydrazoic Acid and Organic Compositions.

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Cerate Oxidimetry Nomenclature vs. Ceric Oxidimetry

The original designation applied to the use of Ce(IV) in volumetric analysis is an expression implying that such oxidation-reduction reactions involve cerium as a cation. Originally it was this concept that led manufacturers to assume that electro oxidation of Ce(III) to Ce(IV) necessitated employing a partition cell. This concept was dispelled by the work of G. Frederick Smith, Gerald Frank and A. E. Kott, "Cerate Oxidimetry. Electrolytic Oxidation of Cerium Without the Use of a Diaphragm Cell," *Ind. Eng. Chem.* Anal. Ed., 12, 268 (1940).

The work of E. G. Jones and F. G. Sopher, J. Chem. Soc., pt 1, page 1935 (1935) on the subject, "The Nature of the Ceric Sulfates is quoted as follows on this subject: "The existence of the stable sulfate" $Ce(SO_4)_2$. Meyer and Aufrecht, Ber., 37, 140 (1904). *Z. anorg. Chem.,* 39, 261 (1904) is largely responsible for the accepted belief in an electropositive ceric ion. The normal nitrate has not been isolated but only a red hydroxynitrate, $CeOH(NO_3)_3 \cdot H_2O$, Meyer and Jacaby, Ber., 33, 2135 (1900). Moreover the cerium in the double nitrates, $M_2Ce(NO_3)_6$ was shown. *Z. anorg. Chem.,* 27, 359 (1901) to exist as an anion. Similarly, ceric chloride has not been isolated, but probably exists in solution as the complex, H_2CeCl_6, corresponding to the known series of salts M_2CeCl_6. Brauner (loc. cit), regards the complex cerous-ceric sulfate as the cerous salt of sulfatoceric acid, $H_4Ce(SO_4)_4$, and writes its formula as $Ce(III) HCe(SO_4)_4 \cdot 12H_2O$. Praseodymium, neodymium and lanthanum can replace the cerous atom and form analogous salts.

Brauner's formula for the ceroso-ceric sulfate suggests that ceric sulfate might be of analogous constitution, i. e., $Ce(IV)Ce(SO_4)_4$, the cerium existing partly as positive and partly as negative ions. Transport experiments have now been carried out which disprove this. The cerium in ceric sulfate solutions and in the double sulfates, $M_2Ce(SO_4)_3$ has been found always to exist as an anion. No evidence for any positive ceric ions in these sulfate solutions has been obtained. The ionization of the solid formula, $Ce(SO_4)_2$ must therefore be of complex character."

The over all manufacture processes in commercial production of all marketed cerium chemicals substantiate the interpretations of Jones and Soper quoted above. "Ceric Oxidimetry," the early 1928-1931 concept, has been corrected to bear the correct concept under the classification as "Cerate Oxidimetry" the title of the present work.

ELEMENTS DETERMINED BY PROCEDURES INVOLVING
OXIDATION WITH TETRAVALENT CERIUM

H   He

Li Be   B   C   N   O   F   Ne

Na Mg   Al Si P   S   Cl A

K   Ca Sc Ti V   Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr

Rb Sr Y   Zr Cb Mo   Ru Rh Pd Ag Cd In Sn Sb Te I   Xe

Cs Ba La Hf Ta W   Re Os Ir Pt Au Hg Tl Pb Bi Po   Rn

Ra Ac Th Pa U