An International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS
LONDON NEW YORK PARIS LOS ANGELES
VOLUME 7 NUMBERS 3/4 FEBRUARY 1961

IN HONOUR OF PROFESSOR HOBART H. WILLARD

EDITOR-IN-CHIEF

Professor Cecil L. Wilson; Department of Chemistry, The Queen's University, Belfast, Northern Ireland.

ASSISTANT EDITOR

Dr. M. Williams; Department of Chemistry, College of Advanced Technology, Gosta Green, Birmingham 4, England.

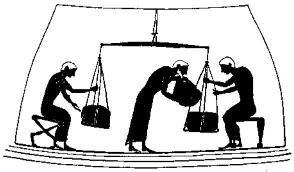
REGIONAL EDITORS

Professor L. Gordon; Department of Chemistry and Chemical Engineering, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.

Dr. R. Přibil; Czechoslovak Academy of Sciences, Chemical Institute, Laboratory of Analytical Chemistry, Praha, I, Jilská 16, Czechoslovakia.

Professor T. Takahashi; 1051 Wadahon cho, Suginami ku, Tokyo, Japan.

Professor G. Gopala Rao; Department of Chemistry, Andhra University, Waltair, S. India



ADVISORY BOARD

Professor F. E. Beamish—Toronto
Professor R. Belcher—Birmingham (Chairman of the Board)
Professor H. Bode—Hanover
Professor G. Charlot—Paris
Professor C. Cimerman—Haifa
Dr. C. E. Crouthamel—Argonne, Illinois
Professor P. Delahay—Baton Rouge, Louisiana
Professor H. Diehl—Ames, Iowa
Dr. C. Drăgulescu—Timisoara
Professor L. Erdey—Budapest
Professor F. Feigl—Rio de Janeiro
Professor H. Flaschka—Atlanta, Georgia
Professor W. Geilmann—Mainz
Dr. J. Hoste—Ghent
Mr. H. W. Kirby—Miamisburg, Ohio
Professor J. J. Lingane—Cambridge, Massachusetts
Professor F. Lucena-Conde—Salamanca
Dr. S. J. Lyle—Durham
Dr. R. J. Magee—Belfast
Professor H. Malissa—Vienna
Professor W. Wayne Meinke—Ann Arbor, Michigan
Professor J. Minczewski—Warsaw
Dr. G. H. Morrison—Bayside, New York
Professor F. Nydahl—Uppsala
Dr. Maurice Pesez—Paris
Dr. E. Rancke-Madsen—Copenhagen
Professor C. N. Reilley—Chapel Hill, N. Carolina
Dr. M. L. Salutsky—Clarksville, Maryland
Professor E. Schulek—Budapest
Professor G. Semerano—Padova
Professor G. Frederick Smith—Urbana, Illinois
Professor H. Specker—Dortmund-Aplerbeck
Professor E. H. Swift—Pasadena, California
Professor P. S. Tutundžić—Belgrade
Professor F. L. Warren—Pietermaritzburg
Professor H. Weisz—Freiburg-Breisgau
Dr. T. S. West—Birmingham
Dr. James C. White—Oak Ridge, Tennessee
Professor H. H. Willard—Ann Arbor, Michigan
Mr. F. J. Woodman—Sellafield

Publishing Offices: Headington Hill Hall, Oxford (OXFord 64881).

Published monthly - 1 Volume per year

Annual subscription (including postage): (A) for Libraries, Government Establishments and Research Institutions—£21 ($60). (B) for private individuals, who place their orders with the Publisher and who certify that the Journal is for their personal use—£5.5. ($15).

Payments must be made in advance

Copyright © 1961
Pergamon Press Ltd.

Pergamon Press are also the publishers of the following journals:

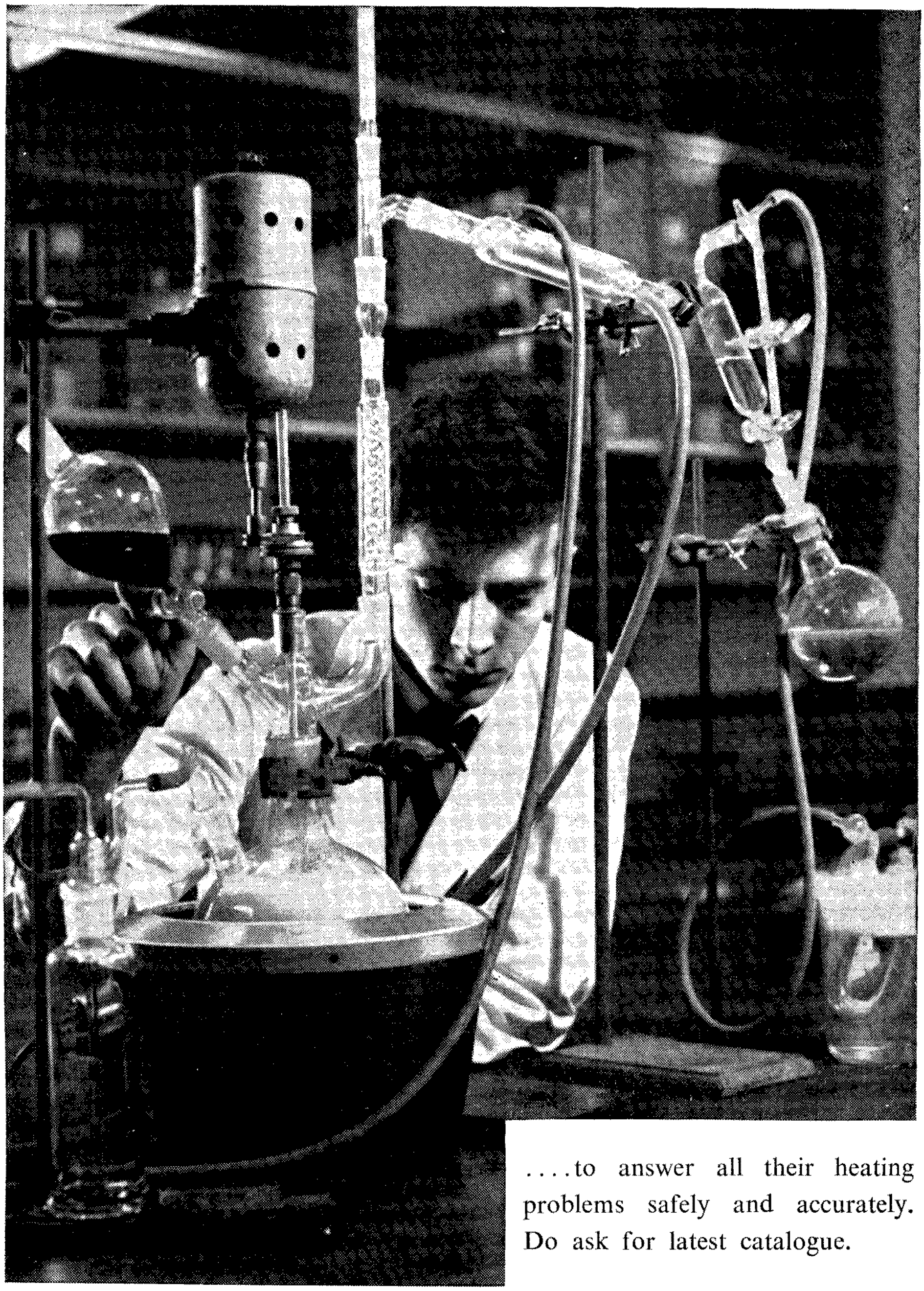
Journal of Nuclear Energy (*including* The Soviet Journal of Atomic Energy—Part A: Reactor Science; Part B: Reactor Technology)
Health Physics (*The official journal of the Health Physics Society*)
Journal of Inorganic and Nuclear Chemistry
Tetrahedron (*The International Journal of Organic Chemistry*)
International Journal of Applied Radiation and Isotopes
Biochemical Pharmacology
* Biophysics
* Journal of Microbiology, Epidemiology and Immunobiology
* Problems of Hematology and Blood Transfusion
* Problems of Virology
* Problems of Oncology
* Sechenov Physiological Journal of the U.S.S.R.
* Bulletin of the Academy of Sciences of the U.S.S.R., Geophysics Series
* Electric Technology, U.S.S.R.
* Radio Engineering
* Radio Engineering and Electronics
* Telecommunications
* Physics of Metals and Metallography
* The Abstracts Journal of Metallurgy
* Applied Mathematics and Mechanics
Chemical Engineering Science
Journal of Atmospheric and Terrestrial Physics
Planetary and Space Physics
Geochimica et Cosmochimica Acta
Bulletin Géodésique
Annals of the International Geophysical Year
Spectrochimica Acta
Acta Metallurgica
(*for the Board of Governors of Acta Metallurgica*)
Journal of the Mechanics and Physics of Solids
International Journal of the Physics and Chemistry of Solids
Deep-Sea Research
Journal of Neurochemistry
Journal of Psychosomatic Research
Journal of Insect Physiology
International Journal of Air Pollution
International Abstracts of Biological Sciences (*for Biological and Medical Abstracts Ltd.*)
Rheology Abstracts
Vacuum
Operational Research Quarterly
Annals of Occupational Hygiene
Archives of Oral Biology
Planetary and Space Science
Electrochimica Acta

**Translations of Russian Journals published on behalf of Pergamon Institute, a Division of Pergamon International Corporation*

Leaflets giving further details and subscription rates of each of these Journals are available on request.

The illustration of a Greek balance from one of the Hope Vases is reproduced here by kind permission of Cambridge University Press

22 มิ.ย. 2504



Talanta, 1961, Vol. 7, p. 133. Pergamon Press Ltd. Printed in Northern Ireland

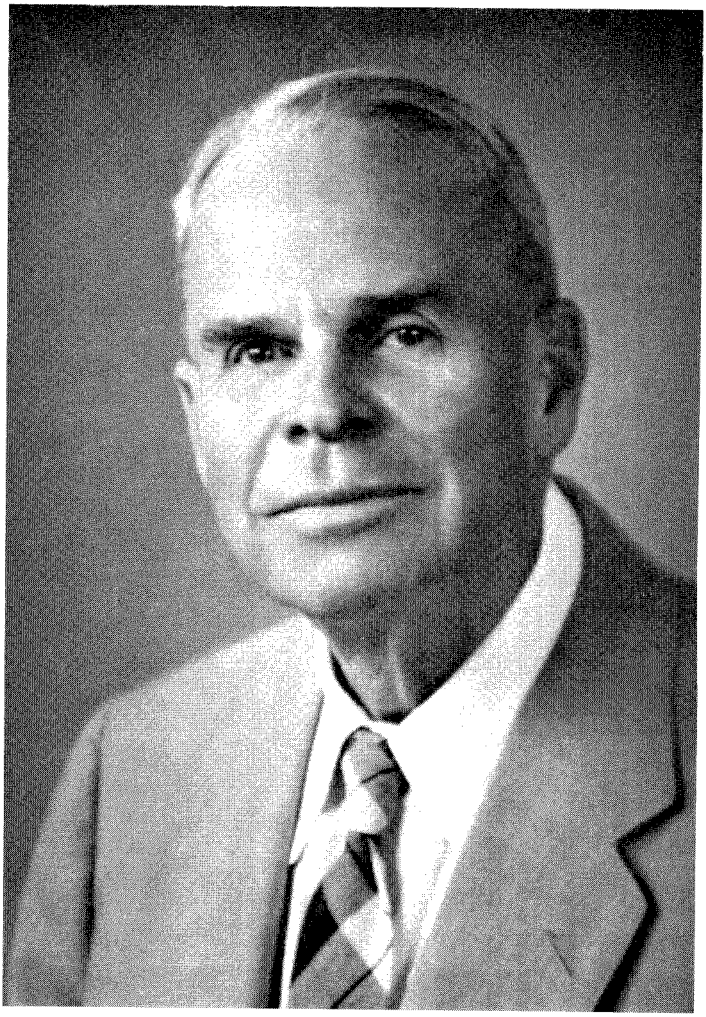
EDITOR'S FOREWORD

The editorial board and publishers of TALANTA take great pleasure in honouring the eightieth year of

Hobart H. Willard

by presenting this special issue, to which contributions have willingly been made by his former co-workers,

Gilbert H. Ayres
Albert J. Boyle
Frank L. Chan
John A. Dean
Harvey Diehl
Louis Gordon
Richard B. Hahn
Arno H. A. Heyn
Charles A. Horton
James L. Kassner
Headlee Lamprey
Elmer Leininger
Lynne L. Merritt, Jr.
G. Frederick Smith
Albert E. Taylor
Taft Y. Toribara



Hobart H. Willard

Talanta, 1961, Vol. 7, pp. 135 to 151. Pergamon Press Ltd. Printed in Northern Ireland

HOBART H. WILLARD

HARVEY DIEHL
Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

HOBART H. WILLARD, Emeritus Professor of Chemistry at the University of Michigan, will reach his eightieth birthday in June of 1961. There will thus reach the venerable age of four score, ripe in wisdom, in good health, and with unimpaired intellectual vigour, one of America's most creative chemists and outstanding teachers of chemistry.

Willard began his career in chemistry in a home laboratory and received his formal training at Michigan (A.B., 1903; A.M., 1905) and at Harvard (Ph.D., 1909). Following the Harvard period he resumed his instructorship at Michigan and rose rapidly through the various ranks to professor (1922). The Michigan tenure continued uninterrupted to 1951, the prescribed retirement age of seventy, but retirement meant simply a change in scene for he has continued research and teaching, in less vigorous but no less fruitful fashion, at the laboratories of the Atomic Energy Commission at Oak Ridge and Los Alamos and on single semester assignments at other universities, New Mexico (1951, 1952), Southern Illinois (1956, 1958), Washington State (1957), and Valparaiso (1959, 1960).

Willard's long academic career was marked by the usual activities of a university professor-chemist: a moderate teaching load at the undergraduate and graduate levels, the direction of graduate students, research, university committee work, the writing of text-books, participation in the affairs of the American Chemical Society, lecture trips, a share of industrial consulting work. All of these he carried on with extraordinary energy and with great enthusiasm. This astonishing performance was carried on, too, with a healthy interest in other fields of science and with an intense desire that his research be of service to others. It was also accompanied by a harmonious family life. And as was eminently fitting, recognition came both nationally and locally: in 1951 the Fisher Award of the American Chemical Society for outstanding contributions to analytical chemistry, in 1953 the Annual Award of the Association of Analytical Chemists of the Detroit Section of the American Chemical Society, in 1948 the Henry Russell Lectureship of the University of Michigan.

It is pleasing indeed to have one of our profession reach the age of eighty; it is doubly pleasant that he should reach this age in full mental and physical vigour. Mankind is certainly fortunate when such a long and busy life is devoted to creative work and to the education of youth.

EARLY PROFESSIONAL YEARS

Although born in Erie, Pennsylvania (June 3, 1881), Willard's boyhood was spent under exceptionally happy circumstances in the small, southern Michigan farming community of Union City.

Willard was early attracted to chemistry, and was fortunate in that a sympathetic father, a newspaper editor, procured for him texts and chemicals on business trips to

Chicago. The faculty of the University of Michigan, too, proved co-operative in forwarding to him for analysis the materials given out as unknowns in the course in qualitative analysis. As a consequence of intensive study backed by good experimental work in his home laboratory, Willard was immediately admitted to advanced course work in chemistry on his entrance into the University.

Willard's undergraduate years at Michigan were marked by the usual mixture of academic, social and fraternal activities characteristic of mid-western university life in the pre-World War I period. Willard was robust physically, alert, and popular, and it was during this period that the first of numerous stories originated which came later to surround him in Paul Bunyonesque fashion. It was during this period also that he became a vegetarian—after hearing a lecture by the physician John Harvey Kellogg. It was during these years, too, that Willard's first publication appeared, that on the silver perchlorate coulometer with Professor Carhart and Mr. Henderson.

The nature of the research that men do is often determined by, and is certainly profoundly influenced by, their early training and associations. Willard's early experience with perchloric acid determined the nature of his research efforts for some years, first on the use of perchlorates in atomic weight work and then on the uses of perchloric acid in chemical analysis. Again, chemistry at the University of Michigan bore a practical, or applied chemistry stamp. Science with practice, with the emphasis on practice, was a general characteristic of all the mid-western state colleges and was the natural face of a civilisation just emerging from a rugged, frontier economy. At Michigan this approach to science was especially marked because of the presence on the campus of chemistry professors whose interests were in applied analysis—A. B. Prescott, O. C. Johnson, and E. D. Campbell. Prescott, a pharmacologist as well as a chemist, and Johnson were the authors of *Qualitative Chemical Analysis*, a text which went through seven editions and for two generations shared honours in the United States with the texts of Fresenius and Treadwell-Hall. Campbell, although primarily a chemist, contributed greatly to metallurgy, principally along the lines of methods of chemical analysis of ferrous materials and of the effects of alloying elements on steel. The strongly practical bent of these men lent to their teaching an earthy quality which was transmitted to and flowered in Willard, for the majority of his contributions are practical solutions to the problems of analysing things as they are actually found in nature or are produced by industry.

Willard chose Harvard for his doctoral work on the advice of Moses Gomberg, then a young instructor newly back from Europe and in the midst of his epoch-making work on tervalent carbon. This, it will be recalled, was the period when all Americans, and indeed most Europeans, secured their research training in the laboratories of the German Universities. Willard's break with tradition was dictated by the emergence of the Harvard laboratory under T. W. Richards as the leading institution for atomic weight measurements.

The great stability and high oxygen content of the alkali metal perchlorates suggested to Willard that they afforded an excellent scheme for determining the silver-oxygen ratio. Richards approved this suggestion, and Willard for his Ph.D thesis (1909) measured the conversion of lithium chloride to silver chloride and of lithium chloride to lithium perchlorate and thus obtained the atomic weights of both silver and lithium. The silver value of 107·871 was superseded in later years by the value 107·880, but, remarkably enough, is closer to the very recent value, 107·8731, obtained at the National Bureau of Standards by the mass spectrographic method.

Willard's first paper, after returning to Michigan, dealt with the preparation of perchloric acid dihydrate by the oxidation of ammonium perchlorate with nitric and hydrochloric acids. All of the perchloric acid manufactured between 1924 and 1940 was made by this process, and currently it is again being used. The paper is a prophetic one, for it closes with a long paragraph pointing out the remarkable properties of perchloric acid dihydrate and suggesting a number of uses of the acid in analysis and in electrochemistry, all of which were subsequently worked out in brilliant fashion by Willard or by his student G. Frederick Smith.

Willard was once heard to remark, later in his life when he was approaching retirement, and when he was encouraging a younger man who had started on a university career, that he wished he had begun a more vigorous research programme at an earlier date. The implication that he had wasted a few years was hardly justified, for World War I drew him off to Detroit to supervise an analytical laboratory connected with aircraft production. Then too, this was a period of intense reading, for we find him acquiring complete sets of the *Zeitschrift für analytische Chemie*, *Chemical Abstracts*, the *Journal of the American Chemical Society*, and an extensive collection of German doctoral theses. Exhaustive reading, coupled with an excellent memory, made it possible for him to recall vast amounts of chemistry, and to quote authors, journals and years at will. This facility has stayed with him to an astonishing extent into his later years.

Willard's first graduate student was Lucien Greathouse, whose Ph.D. thesis dealt with the periodate method for manganese, a method which was widely adopted and is the standard procedure to this day. The work on the perchloric acid dehydration of silica, the first of three investigations with Wallace Cake, dates from this time too. These two contributions were certainly a most auspicious beginning as a research director, but more followed quickly. The other two papers with Cake deal with the use of hypobromite as a standard oxidising agent and its use in the determination of amino nitrogen and of sulphide. Another investigation, with C. C. Meloche, was on the determination of bromide in brines.

THE 1920'S

Willard's next major effort was with his student Roy K. McAlpine on the revision of the atomic weight of antimony, one of the few atomic weight values to reach the post-war period grossly in error. Willard and McAlpine measured the antimony tribromide-silver and antimony tribromide-silver bromide ratios using antimony tribromide prepared from elaborately purified metallic antimony and bromine and distilled in the absence of moisture and oxygen. The titrimetric and gravimetric methods agreed well, and gave a value of 121·773.

The four papers which appeared in 1922 with Dorothy Hall are a critical review of the gravimetric and titrimetric methods for the determination of cobalt. In these papers phenylthiohydantoic acid is introduced as a precipitating reagent for cobalt and copper.

Concurrently there was progressing, with two graduate students, two other investigations, both destined to open up large fields for analytical chemistry.

Taking note of the singular behaviour of palladium in a dichromate titration, Willard concluded that palladium might even function as a reference electrode. Actually, it behaves as an indicator electrode only slower in response and with smaller potential change than platinum. Platinum-palladium together then yield a differential titration curve. The details of this were worked out by Willard and Florence Fenwick, and the idea was extended to electrode pairs of the same metal but with polarisation deliberately produced by the passage of a small current. Two papers describing these bimetallic electrode systems were published in 1922, opening up a new and useful chapter in potentiometric titrations. The following year Willard and Fenwick published three papers detailing applications of the bimetallic electrode couples: to the determination of vanadium in alloy steel, to neutralisation reactions by a clever conversion of an oxidation-reduction system to one responsive to hydrogen ion concentration, and to the determination of sulphide by titration with silver nitrate in alkaline solution.

The other work of Willard in the early 1920's was that with G. Frederick Smith on perchlorate chemistry. The first of three papers, all published in 1922, describes the properties of magnesium perchlorate, the second the separation of sodium from lithium by precipitation of the chloride from a butyl alcohol solution of their perchlorates, and the third the solubilities of the alkali and alkaline earth perchlorates in water and in organic solvents. Magnesium perchlorate has, of course, been since used as the drying agent *par excellence* in all analytical work. The solubility work laid the basis for the perchlorate method for the separation and determination of potassium; the latter method was worked out later by Smith as an instructor at the University of Illinois (Smith, 1923, 1925; Smith and Ross, 1925) and has become the standard method for potassium.

Looking back at this period we can feel the energy Willard was deploying to his work. It must certainly have been a stimulating experience for the graduate students who came at this period, judging from the number of papers they published; four with Dorothy Hall, eight with Florence Fenwick, three with G. F. Smith and twenty-two with Philena Young.

The papers with Philena Young published between 1928 and 1934, are concerned principally with ceric sulphate as a standard oxidising agent. This subject was developed concurrently by Willard and by N. H. Furman of Princeton University. Furman's interests were largely in the theoretical aspects of the subject, Willard's almost exclusively in the applications; the two programmes thus were neatly complementary. In quick succession, then, Willard and Young published on the preparation of ceric solutions, on the determination of iron, iodide, arsenic, antimony, cerium, vanadium, chromium, thallium, organic acids, tellurium, and mercury, and later, on further studies on the preparation and stability of ceric solutions and on indicators for use in ceric titrations. The latter papers with Philena Young were done on a post-doctoral fellowship and during summers when she returned to Ann Arbor from her teaching position at Wells College, and are concerned with the determination of chromium and vanadium in alloy steels by differential oxidation and reduction. The difficulties inherent in these determinations are evident in the sequence of papers on the subject, a complete understanding of the chemistry being gradually attained and the procedures gradually elaborated to their final form. The problem was wrapped up in the 1933 paper, even for those alloys containing tungsten. The final paper (1934) is a most ingenious scheme by which both chromium and vanadium are determined on the same sample, both being oxidised to their higher valence, the excess oxidising agent removed, both reduced with excess standard ferrous sulphate, the excess ferrous sulphate then titrated in high acidity, the acidity reduced and the vanadyl titrated using the same indicator.

Reflecting again Willard's great interest in applied analysis are the three papers dealing with the determination of tervalent chromium, of boric acid, and of sulphate in chromium plating baths, done respectively with Young, Ashworth and Schneidewind. The determination of sulphate in the presence of tervalent chromium is complicated because a portion of the sulphate is often bound to the chromium so tightly that it is not precipitated as barium sulphate. Willard's solution was to add acetate, which combines more firmly with the chromium and displaces the sulphate so that it is immediately precipitated.

The 1920's closed with work by three other students. With Kassner, Willard investigated lead perchlorate, preparing the anhydrous, hydrated and basic forms and determining their compositions and solubilities. In another study with Kassner the solubilites of lead sulphate, chromate and molybdate in perchloric acid solutions and in nitric acid solutions were measured, the solubilities being significantly less in the perchloric acid solutions.

Of the three papers with Boldyreff, the first describes a simple reference electrode prepared by sealing a platinum wire into the tip of a burette, the opening of the burette dipping into the solution being titrated. This rather cute device has never been much used, probably because it is easier to control the flow from the burette by watching the drops form than by watching the meniscus. The second of the papers with Boldyreff prescribes the conditions for the reduction of mercury salts to metallic mercury by hydrazine and the collection and drying of the mercury. The third paper defines the conditions, 475° to 500°, for igniting calcium oxalate to calcium carbonate for weighing.

The oxidation of chromium to chromate by boiling perchloric acid, and the application of this to the titrimetric and gravimetric determination of chromium in chromic oxide, chromite, steel and ferrochrome, was worked out in detail with R. C. Gibson and reported in 1931.

Late in the 1920's, Willard engaged in the first of a series of major lawsuits in which he took part as a chemistry expert. This first one was a patent infringement charged by the Parker Rust Proof Company against the Ford Motor Company and involved the chemistry of the iron phosphates.

THE 1930'S

One especially interesting investigation of the early 1930's was that with R. D. Fowler on the thermal decomposition of anhydrous mixtures of metal sulphates. The idea was to effect the differential decomposition of an anhydrous mixture of metal sulphates by a careful regulation of temperature, and by later cooling and extracting the undecomposed sulphate with water to effect a separation of the metals involved. This project was well thought out and beautifully executed experimentally. Various binary mixtures of anhydrous sulphates formed by evaporation were studied. It was found that non-isomorphous sulphates, of aluminium and zinc for example, could be preferentially decomposed yielding basic sulphates or oxides, and a ready separation of the unchanged sulphate by dissolution in water was possible. Anhydrous mixed crystals of isomorphous sulphates, of nickel and cobalt for example, or of two rare earths, however, decompose into mixed crystals of basic sulphates or oxides, and a separation becomes impossible. A sufficient number of systems was studied so that the results appear to be general, and thus a separation scheme which had been bruited about for a century was laid to rest.

During the 1930's Willard renewed work on the periodates. Between 1931 and 1934 he published a series of papers with J. J. Thompson dealing with the gravimetric and titrimetric determination of mercury and of lead, based on the precipitation of mercurous paraperiodate, $Hg_5(IO_6)_2$, and of triplumbic paraperiodate, $Pb_3H_4(IO_6)_2$; and with the titrimetric determination of manganese following periodate oxidation to permanganate and removal of excess permanganate by precipitation as mercuric periodate. Another paper dealt with the detection of iodate and periodate in the presence of each other. With another student, R. R. Ralston, he perfected a procedure for the preparation of free periodic acid, a technique currently in use for the manufacture of periodic acid, unchanged in all the details as initially devised. The procedure involves two successive electrolytic oxidations, of iodine in hydrochloric acid to iodic acid at a platinum anode in a partition cell, and of the iodic acid in water solution to periodic acid at a lead dioxide anode in a partition cell. The periodic acid is finally recrystallised from concentrated nitric acid.

The periodic acid prepared by the electrolyic process often contains a little platinum, and after a year is contaminated with iodic acid brought about by the decomposition. Such decomposition is obviated in another method of preparation published by Willard in the first volume of *Inorganic Syntheses.* In it iodine is oxidised by sodium chlorate in a slightly acid solution to sodium iodate, the latter then being oxidised to the periodate by chlorine in an alkaline solution and isolated as trisodium paraperiodate, $Na_3H_2IO_6$. Barium paraperiodate, $Ba_3H_4(IO_6)_2$, is then prepared and converted to periodic acid by treatment with concentrated nitric acid, in which barium nitrate is insoluble, so that it can be filtered off. The final recrystallisation of the paraperiodic acid is made from concentrated nitric acid.

With a convenient source of periodic acid available, it became possible to consider the determination of potassium by precipitation as the periodate. This procedure was worked out with A. J. Boyle.

Two other papers with J. J. Thompson appeared during the early 1930's. One described a method for perchlorate, based on reduction with starch and sulphuric acid, the liberation of free chlorine with permanganate, and the distillation of free chlorine into standard arsenite. This scheme of distilling the free halogen was applied also to the determination of halogen in organic compounds, following decomposition of the sample with fuming sulphuric acid and persulphate. Although widely applicable, the method has never really caught on with the analytical chemist, possibly because the apparatus required appears to be too complex.

The early 1930's saw also the publication of another paper that was to become a classic in the literature of analytical chemistry, the separation of fluoride by distillation of fluosilicic acid, followed by titration with thorium nitrate using zirconium-alizarin lake as indicator. This work was done with O. B. Winter at the Michigan Agricultural Experiment Station at East Lansing. Earlier attempts to separate fluoride by distillation as anhydrous hydrofluoric acid invariably gave inconsistent results. The deliberate introduction of water (steam at 135°) causing the formation and distillation of fluosilicic acid was truly a master stroke. The method has been universally adopted, and although the titration phase has been subjected to considerable tampering by others, the distillation procedure is universally used as originally set forth. The method made possible an accurate measure of small amounts of fluoride, and the consequences of this have been manifold.

The middle 1930's saw also the publication of a number of isolated studies, each significant but not immediately related to some larger project. One was a study with R. C. Thielke of the preparation of potassium molybdocyanide and molybdicyanide. Molybdicyanide is a strong oxidising agent in alkaline solution. With a convenient source of molybdicyanide at hand, conceivably it should have been possible to apply it as a standard oxidant. Solutions of molybdicyanide are not stable, particularly when exposed to light, and this militated against any extensive development as a standard oxidising agent such as that which occurred with ceric sulphate.

With Edwin Goodspeed, Willard made a study of the separation of strontium from calcium, by precipitation of strontium nitrate from concentrated nitric acid by the addition of sufficient 100% nitric acid to bring the concentration to 80%. The separation is clean; it also separates strontium from some twenty-five other elements and although awkward it had not been superseded twenty-five years later.

The three papers with Heman Fogg on the analytical chemistry of gallium represented one of the first attempts to apply chemical methods to the determination of gallium, the spectrographic method having been the sole and traditional tool from the time of the discovery of the element. The final proposals were a colorimetric method using quinalizarin, and precipitation of the basic sulphate, a thorough study having been made of the separation from aluminium, iron, and indium and of the interference of other elements.

Two other fruitful pieces of research, done with people off the Michigan campus, produced methods of great utility. The 1,10-phenanthroline method for iron was worked out with Frances Cope Hummel of the Research Laboratory of the Children's Fund in Detroit, specifically for the determination of iron in foods, blood and fæces. The paper was published simultaneously with papers by Saywell and Cunningham (the idea was G. Frederick Smith's who suggested to these authors the wet-ashing of wine with perchloric acid followed by a measurement of the iron as the phenanthroline compound) and by Fortune and Mellon who made a thorough study of the spectrophotometry and interferences of the process. The honour for introducing this popular method was thus shared by three groups. The other work was that with John Center of the Oliver Iron Mining Company of Hibbing, Minnesota, and had to do with the determination of phosphorus in iron ore by measuring the colour of the complex vanadophosphomolybdate.

The three papers with George M. Smith, published in 1939, and dealing with tetraphenylarsonium chloride, uncovered some rather astonishing bits of chemistry. The compound was first prepared by Professor F. F. Blicke of the College of Pharmacy at Michigan, and it is fortunate that he directed Willard's attention to it. Tetraphenylarsonium chloride forms insoluble salts with perchlorate, permanganate, periodate and perrhenate. Moreover, it can be accurately titrated potentiometrically with iodine in the presence of iodide. George M. Smith worked out the details of this titration, and showed also that the chloro-complexes of mercury, tin, vanadium and zinc form insoluble compounds with tetraphenylarsonium chloride, and that a titration of the excess reagent permitted the determination of these metals.

One of the students who worked with Willard in the closing years of the 1930's was

Lynne L. Merritt, Jr., whose thesis work dealt with the use of ozone to effect the oxidation of elements to their higher valence states for later titration with a standard reducing agent. The published paper carries a description of a neat apparatus for generating ozone, and describes the action of ozone on a variety of elements. It contains also detailed directions for the determination of manganese in steel and in ores, for the determination of vanadium in steel, and for the determination of iodide. In the last method, iodine is oxidised to periodate, the excess ozone is removed with a stream of carbon dioxide, and the periodate is determined colorimetrically.

During the 1930's Willard was engaged in a succession of patent infringement suits related to chromium plating. The suits centred around the presence of sulphate in the bath, and the chromic oxide to sulphate ratio. Willard's success in these patent affairs can be judged from the number of cases that he was called in on, and from the fact that the side calling him always won. One suit in particular made chemico-legal history of a sort by going all the way to the Supreme Court. The case was concerned with a patent covering a welding rod coating consisting of an alkaline earth silicate and calcium fluoride, which had been circumvented by the substitution of manganese silicate for magnesium silicate. Willard's thesis was that manganese was essentially an alkaline earth and he marshalled sufficient evidence to convince the Courts. Legally now in the United States, it appears, manganese is an alkaline earth (339 U.S. 605).

Willard had great interest in apparatus as far as it was useful as a tool. Thus, he followed closely and with great interest the development of the polarograph and of the glass electrode, experimenting constantly with them himself. He published two papers on the design of instruments, one with Hager (1936) on an electronic titrimeter, and another with Ayres (1940) on a photoelectric colorimeter. In view of the competence and tremendous success of the people who did enter the instrument design business, it is fortunate for chemistry that Willard remained on the side-lines of this field and devoted his superb talents to purely chemical problems. He entered his last decade at Michigan, then, with a brilliant record of achievements in analytical chemistry, an unlimited number of ideas for further exploitation, and his mind firmly focussed on problems he could handle best.

THE CLOSING DECADE AT MICHIGAN

The war broke as Willard entered his last ten years at Michigan. Numerous, non-creative duties intervened, the number of graduate students dropped and the activities of those who remained were directed into matters of military interest, so that often the work presented as thesis material was non-classified and often only a minor phase of some larger effort. The renewed interest in inorganic chemistry which accompanied the advent of atomic energy made Willard's vast knowledge of inorganic and analytical chemistry of particular value, and fortunately it was effectively employed.

Of the work published during the war years, the three papers with Taft Toribara deal with some "off-beat" and intriguing chemistry of tin. In the first paper, a study of the tin oxalate-potassium oxalate system was made and potassium oxalatostannate, $K_6Sn(C_2O_4)_7{\cdot}4H_2O$, was isolated. In the second, the chemistry involved in the action of hydrogen sulphide on tin in oxalic acid solution was straightened out, and in particular the conditions for stability of dipotassium dioxalatothiometastannate, $K_2SnS(C_2O_4)_2{\cdot}2H_2O$, established. In the third paper the information gathered in the first two were utilised in a titrimetric method for tin. The tin is converted to potassium oxalatostannate at pH 2·5, potassium sulphide is added, forming dipotassium dioxalatodistannate, the hydrogen sulphide is then swept from the solution by a current of carbon dioxide, and finally the sulphur in the compound is titrated with iodine. The tin does not change valence during the entire operation. The method was checked on standard samples, and all in all is a pretty bit of work.

The work with Zuehlke on germanium also was done in the early 1940's and as with tin was again a question of straightening out the nature of the sulphur compounds, thiogermanic acid and its salts. The titrimetric method finally recommended is based on the quantitative formation of potassium thiogermanate in an acetate-buffered solution by treatment with potassium sulphide, removal of the excess hydrogen sulphide by carbon dioxide, and titration of sulphur with iodine. Willard and Zuehlke also found that 5,6-benzoquinoline formed an insoluble derivative with trioxalatogermanic acid and could be used for the gravimetric determination of germanium.

In a paper with Arno Heyn the determination of bromide in brines by hypochlorite oxidation to bromate and subsequent indirect iodometric titration was examined critically, and the procedure was placed on a firm basis.

Willard's great interest in oxidation-reduction reactions led him to an examination of titrations with strong oxidising agents in alkaline solution. The 1947 paper with Manalo has an excellent general survey of this field, and in the experimental work describes fifteen diphenylamine derivatives which can be used as indicators in titrations with ferricyanide, hypobromite and sodium vanadate. Their use was checked in titrations of a large number of inorganic and organic substances. In the course of the work it was necessary to measure the formal potentials of certain couples in alkaline solutions. Values for the ferricyanide-ferrocyanide, hypobromite-bromide, arsenate-arsenite and vanadate-vanadyl couples in solutions $1M$ to $15M$ in sodium hydroxide were reported in a later paper.

Two studies of colorimetric methods were published in the late 1940's, on cobalt with dithio-oxamide, with Mosher and Boyle of Wayne University. Both are rather short papers but are thorough studies of the conditions and interferences.

Tetraphenylarsonium chloride, introduced by Willard and G. M. Smith in 1939, developed such an extensive use in the succeeding decade that it prompted an investigation of the corresponding phosphonium and stibonium compounds. New procedures were developed for synthesising these compounds (Willard, Perkins and Blicke, 1948) and the compounds were then subjected to an intensive study. The properties of both are similar to those of the arsonium compound in that they form insoluble, crystalline salts with permanganate, perrhenate, pertechnetate, perchlorate, periodate, fluoroborate and certain complex metal chlorides. They can also be titrated iodometrically in the presence of potassium iodide. And, quite astonishingly, the salts are all extractable into chloroform; the tetraphenylphosphonium permanganate, for example, is completely insoluble and completely extractable.

At intervals throughout his career Willard made studies of the applications of organic compounds as analytical reagents for the metals, but the field of organic chemistry and its subdivisions of ultimate analysis and functional group analysis apparently held little attraction for him. Perhaps he felt like Berzelius a hundred years earlier, when he wrote to Wöhler that organic chemistry was an impenetrable forest into which one could only enter with trepidation. Almost his sole excursion into the field was the work with Wooten on the colorimetric and iodometric determination of resorcinol and other phenols. Wooten brought the problem with him from the Reichhold Chemicals, Inc. and the methods he and Willard devised proved highly useful to an important segment of the chemical industry.

One of Willard's last graduate students was Charles Horton, with whom he developed methods for the determination of traces of fluoride. An examination of a large number of organic compounds as possible indicators in the titration of fluoride with thorium yielded several good ones, particularly purpurin sulphonate, Alizarin Red S, Eriochromcyanin R and Chrom Azurol S. Two fluorescent indicators were found too, morin and quercetin, and the best conditions were worked out for a fluorometric titration. Fluoride in microgram amounts can be titrated with thorium using the fluorometric end-point, and the final method was adapted to the determination of fluoride following alkaline decomposition of an organic fluorine compound, or following the Willard and Winter distillation. Among the older methods of determining fluoride a favourite approach has been to measure the bleaching effect of fluoride on coloured compounds of titanium and zirconium. In the latter part of the work with Horton aluminium was used in the same way, the excess aluminium, that not bound to fluoride, being determined by extraction of the oxinate into chloroform for fluorometric measurement, or being measured fluorometrically with morin in 50% alcohol. As with all of Willard's investigations these are thorough studies leaving not the smallest detail unattended.

John Dean was also among the last of Willard's Ph.D. men. He and Willard devised an ingenious polarographic method for aluminium based on the change in half-wave potential of a dihydroxyazo dye on complexing with aluminium. Pontachrome Violet SW proved a suitable dye and the method was found sensitive to 5 μg. of aluminium in 50 ml. The effects of pH, time of standing, temperature and diverse ions were all thoroughly studied, and the method was checked by the analysis of NBS samples of a variety of materials.

Willard's last decade at Michigan closed suitably with his reception of the Fisher Award. In his Fisher Award address, published in *Analytical Chemistry* of December 1951, Willard might have reviewed some phases of his own work or have presented resumes of his individual contributions such as has been attempted here. Instead, he chose to acknowledge his indebtedness to his many fine students and co-workers for their contributions to their joint efforts, and then to survey the development of analytical chemistry during his lifetime. The acknowledgements are done in graceful fashion and he pays particular tribute to his former student G. Frederick Smith for the brilliant way that he carried on in research in analytical chemistry after leaving Michigan, and especially for the tremendous service he has rendered the profession by making newly discovered reagents commercially available. The address is entitled *From Buret and Balance to Spectrometer and Titrimeter*. It is a splendid review of analytical chemistry in the first half of the twentieth century. Willard's grasp and appreciation of every facet of the subject stands out starkly. In particular, his understanding of the role of physical methods and of instruments is revealed, and quite understandably he closes with the admonishment to use them when helpful but not to neglect the chemical side of the subject.

Willard's papers in the post-Michigan years reflect his activities after retirement. For the most part they represent problems he helped to solve in connection with his consulting activities at the laboratories of the Atomic Energy Commission or of the various universities where he took short-term teaching positions.

One especially interesting paper in this group is that on the determination of protein-bound iodine. This was done with Albert Boyle, one of his earlier Ph.D. men who had later earned the M.D. degree and entered medical research at Wayne University. Following precipitation of the protein in serum with trichloroacetic acid, the remaining protein is destroyed and iodide is oxidised to iodate by digestion with chloric acid in the presence of a little chromate. The chloric acid and organic matter are then removed by evaporation to small volume, and the iodine is measured by its catalytic action on the ceric-arsenite system. The method is a brilliant application of analytical chemistry to a tough biochemical problem, and judging from the sale of the iodine-free cerium salt needed it is very widely used. The use of 28% free chloric acid makes such experts in the business of destroying organic matter as G. Frederick Smith blanch, but apparently the procedure as finally described is safe. There are two sentences in the paper, though, which can hardly fail to produce a chuckle in the reader: "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."

One piece of work, done at the University of New Mexico with Martin and Feltham, is a colorimetric method for vanadium based on dissolving in acetone the precipitate of vanadate with cupferron. Vanadium can be separated from copper by cupferron precipitation if ethylenediaminetetra-acetate is added to tie up the copper. Utilised together these processes make possible the determination of vanadium in the presence of copper.

Willard's vast knowledge of the analytical chemistry of the rarer elements has been put to great use at the laboratories of the Atomic Energy Commission. We may never have a real measure of his value to the programme of the Commission but can get a glimpse of it from the paper with Mosen and Gardner on the determination of thorium in uranium alloys published in 1958. The procedure involves precipitating the thorium as the fluoride using lanthanum as a carrier, concluding by a titration of the thorium with ethylenediaminetetra-acetate.

In the post-Michigan period, also, Willard published two papers with Van Lente and Van Atta of Southern Illinois University. One deals with student experiments with a flame photometer, and the other describes apparatus for coulometric titrations using the silver coulometer for the measurement of the current passed.

PRECIPITATION FROM HOMOGENEOUS SOLUTION

In this review of Willard's scientific work we have so far ignored one important work done during the 1930's, that with Tang on the precipitation of aluminium as the basic sulphate. This was purposely done to permit discussion of the entire subject of precipitation from homogeneous solution as a unit, for it constitutes one of Willard's major contributions. Although the idea was conceived in the 1920's, and the early work was published in 1930's (Tang 1937, Fogg 1937), it really bore fruit in the 1940's. The precipitation of the hydroxide of a metal by the addition of a base usually does not produce a separation of one metal from another even though the pH of the solution may be such that a separation should appear possible. Thus, aluminium, which is precipitated completely at pH 4·5, cannot be separated from nickel, even though the latter by itself is not precipitated from a solution of pH 6. A local concentration of alkali exists where the drop of the precipitating solution agent, ammonia or sodium hydroxide, strikes the solution and locally the pH is sufficiently high to precipitate both the aluminium and the nickel. The nickel precipitate is enclosed by the aluminium hydroxide, and although the pH of the main body of the solution is sufficiently low to hold the nickel in solution, it is carried along with the aluminium hydroxide. Willard reasoned that if the hydroxyl ion could be generated by a chemical reaction taking place throughout the solution, local concentration effects would be avoided, and a purer precipitate should result. This proved to be the case, although a secondary, "anion" effect was found. The slow decomposition of urea in a boiling solution proved to be a convenient way to generate ammonia internally, and the separation of aluminium from a number of elements proved to be remarkably clean. The precipitate is a basic salt rather than a hydroxide, and the nature of the anion determines the character of the precipitate. Thus, the aluminium precipitated from a sulphate or succinate solution is crystalline, more dense, and more readily filtered than one precipitated from a chloride solution. The same technique, that is, raising the pH by the decomposition of urea, was applied to the precipitation of calcium oxalate (Chan, thesis 1933). In a single precipitation of this kind calcium can be separated as cleanly from magnesium as by a double precipitation in the normal fashion with ammonia.

Following the work on aluminium and calcium, similar work was done with gallium by Willard and Fogg. Just as with aluminium, the precipitate from a sulphate solution produced by the hydrolysis of urea led to a dense, readily filterable precipitate which provided a clean separation of gallium from zinc, manganese and calcium.

The next application of precipitation from homogeneous solution was with Harry Freund, on the precipitation of zirconyl acid ethylphosphate by hydrolysis of triethylphosphate. The product was obtained as a dense, granular, easily filterable precipitate, in contrast to the gelatinous zirconium phosphate obtained by direct precipitation. The process was then applied to the separation of hafnium from zirconium by fractional precipitation.

Later, with Hahn (1949), several other hydrolytic procedures for the precipitation of zirconium from acid solution were tried, and a detailed study was made of the separations from other metals made possible by hydrolysis of trimethyl phosphate from solutions 3·6*N* in hydrochloric acid. Although the composition of the precipitate was somewhat variable, ignition at 950° yielded zirconium pyrophosphate for weighing, and the process effected the separation of zirconium from a large number of metals.

One especially fine application of the precipitation from homogeneous solution was that by Gordon, 1948, to the determination of thorium in monazite sand. The method begins with a perchloric acid attack of the mineral, which dissolves the monazite but leaves the quartz, rutile and ilmenite. Thorium and the rare earths are then precipitated as the oxalates, the oxalate being generated by the decomposition of methyl oxalate in a hot, acid solution. In contrast to the usual gelatinous precipitate, the oxalates so precipitated are crystalline. A re-precipitation is made to remove the trace of phosphate carried down. Oxalate and filter paper are then decomposed with nitric and perchloric acids, and after reduction of the quadrivalent cerium with iodide, the thorium is precipitated at pH 5·5 to 5·9 as the formate by the decomposition of urea. A re-precipitation is then made. Some interesting side-lights appeared in this work. The basic thorium formate clings tenaciously to the walls of the beaker, and the last of the thorium can be removed only by refluxing hydrochloric acid in the beaker for a few minutes; the thorium so recovered is then precipitated by ammonia. Basic thorium formate carries down any trace of silica present, and the precipitate must be given a hydrofluoric acid-sulphuric acid treatment before the final ignition to the oxide. The paper with Gordon is an exceptionally thorough one, with all of the minor aspects worked out in detail, and even with a study made of the errors in the older iodate method. A modification of the procedure was published somewhat later by Gordon, Vanselow and Willard, in which the thorium formate-urea precipitation was replaced by precipitation with tetrachlorophthalic acid. This again is a precipitation from homogeneous solution, and effects the separation of thorium from the rare earths.

In another study with Gordon, tin was precipitated as a basic stannic sulphate at pH 1·3 by boiling with urea. The precipitate formed was extremely dense, but unfortunately adhered to the walls of the beaker tenaciously, so tenaciously indeed that it could be stripped off as a film. Manganese, nickel and iron were adsorbed so strongly that the procedure was not recommended for the determination of tin.

Still another study was that with John Sheldon on the precipitation from homogeneous solution of iron as the basic formate with urea. A dense, readily filtered precipitate was obtained, which provided an excellent separation from bivalent metals and provided an excellent separation of iron preparatory to the determination of other metals in the filtrate.

Even nickel dimethylglyoxime, a notoriously bad precipitate to filter, yielded to precipitation from homogeneous solution. In the work with Bickerdike (1952) sufficient dimethylglyoxime in 1-propanol was added to the nickel solution which was at an acidity which would prevent precipitation. The precipitation was then brought about by the decomposition of urea on boiling. The large crystals which formed filtered readily, and large amounts of nickel could be handled readily.

The precipitation of cerium from homogeneous solution presented a more difficult problem. Ceric iodate was the obvious choice for the chemical form for precipitation, but of the two routes, internal generation of iodic acid or internal oxidation of cerous to ceric in the presence of iodate, only the latter worked. Either persulphate or bromate could be used as the oxidising agent, but attention had to be paid to the concentration of nitric acid present. The determination was concluded by ignition to ceric oxide. The procedure separates cerium from lanthanum and the rare earths, and from a large number of other metals. This work was done with Willard's last Ph.D. student, Sylvia T'sai Yu.

The subject of precipitation from homogeneous solution was reviewed by Willard (1950). The technique was extended by others, notably by Louis Gordon, and by 1959 had expanded sufficiently to be the subject of a monograph by Louis Gordon, Murrell L. Salutsky and Hobart H. Willard, *Precipitation from Homogeneous Solutions.*

WILLARD AS A TEACHER

The long line of chemistry students, graduate and undergraduate, who received their training in quantitative analysis under Willard at Michigan were subjected to an exceptionally rigorous course, as up-to-date as the very latest chemical journal, backed by an enormous collection of well-prepared and carefully analysed samples, brilliantly and enthusiastically taught, but graded with no sympathy whatever for human frailty or the fumbling that often accompanies learning. Presumably the presence of anyone in a quantitative analysis course denoted a professional interest in chemistry; quantitative analysis was the bread-and-butter course, the very foundation of any professional career in chemistry, and it had better be learned thoroughly; and not just in the class room but at the workbench; and not by just going through the routine but by actually securing the correct result; or by repetition until the correct result was obtained.

The undergraduate and graduate courses were conducted as recitation only, with extensive reading assignments and oral quizzes which were deadly frightening to the novice and embarrassing to the unprepared, but stimulating to the diligent and even a great deal of fun to those with wit or with an appropriate bit from the recent chemical literature.

For a long period Willard refused to write a text, contending that the subject was changing so rapidly that no text-book could be kept reasonably up-to-date. Rather he relied on mimeographed material bound anew each semester, and with new material inserted in the most unlikely places. That excellent teaching could be accomplished with such disorganised text material was understandable only to those who experienced it. At one time there was even sold on the Ann Arbor campus an index to the Manual on Advanced Quantitative Analysis prepared by one frustrated student. Following unsuccessful approaches to Willard by various publishers, one house finally prevailed upon him by the process of locating a co-author. By a brilliant stroke, E. J. Crane of Van Nostrand brought Willard and Professor N. Howell Furman together. The Willard and Furman text came into existence in 1933 and was an instant success. Appearing in May, it had to be reprinted in September, and twice reprinted the following year. For ten years it dominated the field, and only slowly gave way to the proliferation of competing and often disgracefully similar texts which appeared. The fourth edition, 1956, with Clark Bricker, is currently (1960) doing well. This is a remarkable longevity for a chemistry text.

It was almost inevitable that the notes for the advanced course should be organised and published too. This was done by Harvey Diehl and appeared in 1943 as *Advanced Quantitative Analysis*, a companion volume to Willard and Furman. In its own less spectacular way this text too won adoption and a place in the literature of analytical chemistry.

About 1934, Willard organised a course in instrumental analysis, recognising from the very start the role physical chemistry and instruments were to play in the development of analytical chemistry. Again, the successive mimeographed notes and laboratory procedures were an accurate reflection of the development of the art: first the dipping refractometer, the interferometer and potentiometric titration apparatus, then emission spectrographic equipment, the polarograph, the glass electrode, the vacuum tube titrimeter, the photoelectric colorimeter, apparatus for graded cathode potential electrodeposition, and so on. And, here again the material was finally assembled into book form, this time with the efficient cooperation of Lynne L. Merritt, Jr. and John A. Dean. *Instrumental Methods of Analysis* was a highly successful venture, and as with the elementary book set the tone for the competition which rapidly followed.

The three texts constitute a trilogy which is unique in American scientific publications.

Willard's forceful personality dominated his teaching, but it was a very dull student indeed who could not see that behind it all was a highly competent professional, full of knowledge, and effervescent with the interest that always accompanies great creative endeavour. The teaching was always tied closely to practice, it was always up-to-date, it was aimed at developing real proficiency in the student and of having him achieve the highest possible accuracy. Even the apparent lack of sympathy was deliberate. The philosophy behind it was developed by experience and is expressed clearly in the two papers that Willard contributed to the teaching of analytical chemistry, one to the *Journal of Chemical Education* (1928) and another to the *Journal of the Association of American Medical Colleges* (1941). Literally, by example, by text books, and by the graduates he sent out into teaching positions, Willard set the pattern for the teaching of quantitative analysis for a generation.

Of Willard's Ph.D. men, about half went into college teaching: McAlpine (Michigan), G. Frederick Smith (Illinois), Kassner (Alabama), Young (Wells College), Tang (Peking), Fowler (Johns Hopkins), Hart (Carlton, Syracuse), Fogg (New Hampshire), Diehl (Iowa State), Filson (Central Michigan), G. M. Smith (Vanderbilt, Baylor), Boyle (Wayne), Merritt (Indiana), Heyn (Boston), Leininger (Michigan State), Manalo (Phillipines), Taylor (Idaho State), Freund (Oregon State), Gordon (Case), Hahn (Wayne), Dean (Tennessee). Of these many have developed research programmes of their own; two indeed have received the Fisher Award, G. Frederick Smith in 1954 and Diehl in 1956. One side-light of this secondary contribution to analytical chemistry is that some of the student's students have entered teaching, and then in turn their students have too. This process has gone on to even the fifth generation: G. Frederick Smith (Illinois), Brandt (Purdue), Pflaum (State University of Iowa), and Howick (Arkansas); and Diehl (Iowa State), Banks (Iowa State), Margerum (Purdue), and Clarke (Hercules Powder).

One of the characteristics of the American university system, particularly as practised in the mid-west, is the so-called extension system, under which the teaching activity is deliberately taken off the university campus and systematically made available to the entire population. The extension system has been especially successful in the fields of agriculture and home economics. Willard was always generous with his time in all matters pertaining to chemistry, and the numerous lectures he delivered away from the Michigan campus constituted a one-man extension programme. These lectures for the most part were delivered to the local sections of the American Chemical Society, some one hundred and fifty in number. During the 1930's, the Washington office began to organise the local section lectures into tours by the speakers. These tours were sometimes quite extensive, running to as many as twenty speaking engagements and covering a large area of the country. Willard took part in this programme enthusiastically, and at one time or another lectured before practically all of the local sections. He was an interesting and forceful speaker, and always in demand. The value of these lectures, like that of a great deal of teaching, cannot be assessed directly, but those who have appeared before the local sections can attest to the warm response and the intense appreciation shown by the local membership. Willard's influence in this direction was certainly profound.

CONCLUDING REMARKS

Reviewing Willard's research record, one is struck by the number of analytical methods he devised which have become the standard or preferred procedures. The perchloric acid dehydration of silica, the periodate method for manganese, the fluosilicic acid distillation of silica, the various oxidation-reduction procedures for chromium and vanadium, the 1,10-phenanthroline method for iron.

It is interesting to speculate why Willard did not develop an extensive programme of atomic weight determinations at Michigan. Technically he was competent, as was amply demonstrated by the work on antimony with McAlpine. Perhaps he found the work unattractive; but more likely he sensed that the chemical methods were shortly to be superseded by the mass spectrographic method and wisely refrained from beating a dying horse. In any case it is fortunate that he devoted his vast energies to other fields, for we have as a consequence the initiation of great advances in the broad fields of perchloric acid chemistry, bimetallic electrodes, ceric oxidimetry, oxidation-reduction methods, periodic acid chemistry, organic precipitating reagents, and precipitation from homogeneous solution. Atomic weight determinations and instrument design were well left to others. Here was a master chemist doing exactly what he was uniquely equipped to do.

Fifty-five years of research and teaching by Hobart H. Willard have left this world a better place to live in.

The French chemist Chevreul reached the age of one hundred and three, spanning the nineteenth century with a long lifetime of creative achievement. We hope Willard will match Chrevreul's record and that his next twenty-five years will be both pleasant and productive.

THE PH.D. STUDENTS OF HOBART H. WILLARD

1.	Lucien H. Greathouse	1917
2.	Dorothy Hall	1920
3.	R. K. McAlpine	1921
4.	Florence Fenwick	1922
5.	G. Frederick Smith	1922
6.	J. L. Kassner	1926
7.	Philena Young	1928
8.	A. W. Boldyreff	1930
9.	R. C. Gibson	1930
10.	Ning Kang Tang	1930
11.	R. D. Fowler	1931
12.	J. J. Thompson	1931
13.	R. R. Ralston	1932
14.	Frank L. Chan	1933
15.	C. S. Hart	1933
16.	H. C. Fogg	1933
17.	Edwin W. Goodspeed	1934
18.	George E. Lindemulder	1934
19.	R. C. Thielke	1935
20.	O. B. Hager	1935
21.	Headlee Lamprey	1935
22.	Ross W. Moshier	1935
23.	Dwight Williams	1936
24.	Harvey Diehl	1937
25.	M. H. Filson	1937

26. George M. Smith	1938
27. Albert J. Boyle	1938
28. Lynne L. Merritt, Jr.	1940
29. John H. Sheldon	1940
30. Taft Y. Toribara	1942
31. C. W. Zuehlke	1943
32. Arno H. A. Heyn	1944
33. Elmer Leininger	1945
34. Gloria D. Manalo	1945
35. Albert E. Taylor	1945
36. Harry Freund	1946
37. Louis Gordon	1947
38. R. B. Hahn	1948
39. A. L. Wooten	1948
40. Lowell R. Perkins	1948
41. John A. Dean	1949
42. Charles A. Horton	1950
43. Sylvia T'sai Yu	1951

For a complete list of the publications of Hobart H. Willard, see p. 316.

Talanta, 1961, Vol. 7, pp. 152 to 156. Pergamon Press Ltd. Printed in Northern Ireland

SIXTY YEARS OF ANALYTICAL CHEMISTRY

HOBART H. WILLARD

ANALYTICAL chemistry is the oldest branch of this science. In 1856, at the University of Michigan, there was built a laboratory for instruction in analytical chemistry. This was the first laboratory in the United States devoted entirely to chemistry. Later, the main interest in chemistry was in organic chemistry. But after many years analytical chemistry again assumed an important position which it still retains.

At the beginning of this century the course in qualitative analysis at the University of Michigan, which was taught by Professor Otis Coe Johnson, was a strenuous one. The class met for lectures and quiz five days a week and five afternoons were spent in the laboratory. The student analysed forty dry "unknowns", after he had laboured with a considerable number of solutions. He balanced two hundred equations. Time was perhaps not so valuable in those days; at any rate the pace was not so rapid. The reactions of the various elements were thoroughly studied, and although from a modern point of view much time was wasted, the student acquired what might be called "chemical instinct," so that he knew what sort of a reaction to expect when various compounds were brought together. This chemical instinct is, even now, best acquired in a course in qualitative analysis. It is something that is never acquired by a student who is not enthusiastic about chemistry, and this ability readily distinguishes him from the mediocre student. It has sometimes been called "chemical horse sense." It is probably the ability to co-ordinate a large number of chemical facts.

Analytical chemistry at that time was largely a study of chemical reactions. Quantitative analysis emphasised an accurate technique and the ability to carry on filtration, ignition and other operations without loss of material, with a precision not demanded in other courses. Stoichiometric relationships were essential. The skill acquired in analytical chemistry resulted in increased accuracy in other fields of chemistry.

Laboratory work involved no very expensive equipment aside from a balance, and consisted largely of relatively simple operations carried out with great care to avoid the slightest loss. Most of the experimental work involved gravimetric methods and separations, some of them rather tedious and time consuming, such as the analysis of a complex silicate in which separations were performed one after another on the same sample following the directions of Fresenius or Hillebrand, with the hope that summation of results would be reasonably close to 100%. Little attention was paid to the theory involved, but accuracy was important. The length of time required for an analysis was not a matter of prime importance although the desirability of a short process was recognised.

The elements involved were the common ones. Except for simple acid-base, redox and complex-forming reactions, titrimetric methods were somewhat less common than gravimetric. Colorimetric methods were relatively few because even visual colorimeters were rather crude and no photoelectric ones were available. The analysis of organic compounds was not included in elementary courses.

The electrolytic deposition of metals was extensively used and this technique was accelerated by Edgar F. Smith, whose first book was published in 1890. Spectroscopy was not a quantitative method but was used qualitatively. A few organic reagents were available, but it was not until 1905, with the introduction of dimethylglyoxime as a reagent for nickel, that real interest in these reagents was initiated.

The reagent chemicals commercially available were not as pure as those furnished after the introduction of quality standards, and this often necessitated further purification by the analyst. Only the reagents furnished by Kahlbaum in Germany were analysed and approached in purity our present "analytical reagent" grade, and they were available only in the larger laboratories.

Pyrex and similar glassware, resistant to thermal shock, was not available, and the best glass for chemical use was that made in Jena, Germany. It was quite resistant to chemical attack but not to sudden changes in temperature. A small amount of fused quartz was available in Germany.

Space for publication of research was not so limited fifty years ago. The author's doctoral thesis was published in the *Journal of the American Chemical Society* and a translation of it appeared in *Zeitschrift für anorganische Chemie*. The older papers make more interesting reading because they include many details which could not be included today. Those who have read some of the papers that appeared in the old journals have found them fascinating, almost like conversing with the authors, and have regretted the necessity of curtailing contemporary publications until they are often only long abstracts. The number of pages in *Analytical Chemistry* has increased from 1588 in 1949 to 2148 in 1959, an increase of 35% in the last ten years, and the increase in the number of papers in all journals is much greater.

As one looks back sixty years it is amazing to note the gigantic changes that have occurred not only in the teaching of analytical chemistry, but also in the practice of it. From a relatively mediocre position it has risen to one of the most important. This is due to many factors. Analytical chemistry has always been indispensable to other fields of chemistry; and therefore as they have increased in scope, it necessarily had to expand also. The first World War gave the chemical industry in this country a great impetus.

The number of elements included in commercial products has increased tremendously and now includes nearly everything in the periodic table. For example, the term "rare earths" is no longer appropriate because they are used so extensively. The introduction of new elements was enormously accelerated by the development of the atomic bomb, which required the use of a great variety of materials. This necessitated the development of analytical methods for these new elements, which now enter into so many commercial products.

The older analysts worked largely with macro quantities. In recent times special attention has been directed to the determination of micro and even ultramicro amounts, requiring completely different techniques, often necessitating the use of radio-isotopes. As one man has said, "We are interested in a milligram in a carload." It would be difficult to find any line of work in which the demand for new analytical methods has not increased.

Because labour costs are high, and because manufactured products are being turned out so rapidly, the classical methods of analysis have become inadequate and have been replaced to a considerable extent by methods using instruments which measure physical properties. These methods have several advantages. They are more rapid, they require less labour, they are often non-destructive, and in many cases they make possible analyses which cannot be made in any other way. Although the instruments are often very expensive, this is usually justified by the savings effected in time and personnel.

The teaching of analytical chemistry has undergone radical changes in the past sixty years. Physical chemistry has entered into the analytical course to a large extent, and a modern course lays great stress on the theory involved, such as the equilibria in redox, acidimetric and complex-forming reactions. The first effort in this direction was made by Ostwald in his *Scientific Foundations of Analytical Chemistry* in 1894, but it was not until many years later that text-books really emphasised the theory and principles involved in quantitative analysis.

The analysis of organic compounds was not usually included in a course in quantitative analysis, but now it is customary to include a certain amount of it.

In the curriculum, qualitative analysis usually followed beginning chemistry, and this was followed by quantitative analysis. Gradually qualitative analysis has been included to a considerable extent in general chemistry; and in many schools it has been discontinued as a separate course. Organic chemistry and sometimes physical chemistry now frequently precede analytical. This makes it possible to broaden extensively the scope of quantitative analysis. It is now included to a certain extent in general chemistry and this has allowed the inclusion of some simple instrumental methods in the analytical course.

At this level it is reasonable to expect the student to grasp a much broader and deeper view of the theory and principles of analytical methods than would otherwise be possible. His appreciation of the wide scope and great applicability of analytical methods is inevitably greater because by this time he understands what chemistry is. He realises that analytical chemistry is not just a collection of tests and determinations, but comprises a great body of principles and methodology for the solution of those problems in all branches of chemistry which involve physical and numerical measurements. But equally important with theoretical knowledge is the development of good techniques and certain basic skills.

Gravimetric methods are now less emphasised because they play a minor rôle in contemporary analytical practice. The determination of organic functional groups is now almost always included, whereas the old quantitative course was usually limited to inorganic substances.

Although instrumental analysis belongs in a separate course, certain of the simpler instruments, such as pH meters and colorimeters are so universally found in modern laboratories that an introduction to their use is included in most elementary analytical courses.

Chromatography, ion-exchange, solvent extraction, *etc.* are commonly included in modern courses in quantitative analysis.

Chemical "instinct", the ability to predict the nature of a chemical reaction and to represent it by means of an equation, is best acquired by the type of drill that is possible in a course in qualitative analysis. This type of training has almost disappeared from chemical education in this country and constitutes a real loss.

Statistical treatment of experimental results has assumed considerable importance, and an increase in accuracy with less labour is the result of planning a series of experiments with this in mind.

Formerly the university had to rely almost entirely on its own funds to promote research, but now this is supported to a considerable extent by grants from other sources. This has greatly encouraged and accelerated research. In 1958, one-third of the papers appearing in *Analytical Chemistry* from universities acknowledged financial support from outside sources. Without such aid much of this research would have been impossible.

The number of journals publishing papers primarily in analytical chemistry has increased due to the greater amount of research in this field. The *Analytical Edition* of *Industrial and Engineering Chemistry* appeared in 1929; in 1947, this became the separate journal, *Analytical Chemistry*. *Analytica Chimica Acta* appeared in 1947, and *Talanta* in 1958.

The greatest advance in analytical chemistry has been in the field of instrumental methods, measuring by physical means chemical properties, rates of reaction, *etc.* The course in instrumental methods of analysis at the University of Michigan was begun in 1934, and has continued to increase in popularity and importance. In recent years a course of this type has been included to a greater or less extent in practically all chemical curricula. It is interesting to note that developments in electronics have been largely responsible for the great advance in this field. It often happens that progress in one direction comes to a halt until new discoveries in a different field make possible its continuance. Close collaboration between physicists and chemists is essential, as well as between chemists in general and analytical chemists. The rise in importance of analytical groups is undoubtedly related to this co-operation because it is through co-operation that progress is made.

Success in research is a combination of different forces working toward a common objective. The trend in analytical chemistry is toward consideration of the analytical chemist as a member of a research team. Modern instrumentation has multiplied the analyst's abilities.

Analytical chemistry in the past used to involve elemental analysis—the science of measurement applied to the reactions that could be made to follow a stoichiometric equation. Today analytical chemistry involves the use of complicated instruments in complicated systems. Each quantity to be determined is usually measured on a separate sample and often without destroying the sample. Steel mills use the quantometer spectrograph to record the impurities in a sample and transmit the answer to the furnace room at the same time. Direct reading and controlling devices are the rule rather than the exception. It is possible with an infrared spectrophotometer and a computer to have the analysis typed out when a card containing the spectrum is fed into the computer.

Any problem requiring advanced knowledge in two disciplines is solved most efficiently by the creative co-operation of two experts.

Instrument manufacturers advertise new and improved instrumentation for determinations which were previously long and tedious, if not almost impossible. An extensive discussion of new instruments and their many uses is beyond the scope of this paper. It is possible only to point out their possibilities by citing a few examples.

Automatic X-ray fluorescence instruments have been developed for the determination in steel and other alloys of elements of high atomic number without destruction of the sample.

Gas chromatographic techniques, a laboratory curiosity six or seven years ago are today a major tool in the laboratory, not only for analysis, but also for process controls.

Electronic computers are being widely used in the analytical laboratory for performing many repetitive calculations.

The use of radio-isotopes has made possible a careful study of the errors involved in separations, precipitations and other processes.

In reviewing the papers in the April, 1958, number of *Analytical Chemistry* one is impressed by the fact that although most of the thirty-one subjects covered were known twenty-five or thirty years ago, they were primarily only of academic interest. Although in the late 1930's, some of the subjects were being successfully applied, it was not until the early 1940's that advances in instrumentation made possible the many advances in analytical chemistry that we know today. These advances were facilitated by better electronics, such as amplifiers and other devices.

But not only will there be progress in instrumentation; there will, it is hoped, be progress in another important field not so frequently publicised—the search for new analytical reagents. We may never attain the goal of a specific reagent for each element, but we shall make progress in this direction. The discovery of a valuable reagent may be just as important as the design of a new instrument. It may, like the latter, save valuable time and make possible analyses previously difficult, tedious or impossible, and it will probably be much less expensive. Organic chemistry opens a limitless field for research in this direction. Much progress has already been made by Fritz Feigl, by G. F. Smith and others.

During the next ten years we can expect an increasing flow of new alloys, new materials and new machinery resulting from industrial and academic research. The analytical chemist will play an ever more important part in the development of new analytical reagents, techniques, instruments and concepts to make these products a reality. His importance has been recognised by the granting each year of the Fisher Award and the Anachem Award for outstanding contributions to analytical chemistry. The new generation of analytical chemists will face a vast array of new methods, reagents and techniques. The research of today will often be the routine of tomorrow. Analytical chemistry will play a greater rôle than ever before in our academic and industrial development. Although it may not be spectacular, it is a fascinating field and its importance will be recognised more and more as time goes on.

Talanta, 1961, Vol. 7, pp. 157 to 162. Pergamon Press Ltd. Printed in Northern Ireland

THE SOLUBILITIES OF ZINC COMPLEXES OF 8-QUINOLINOL AND SOME DERIVATIVES OF 8-QUINOLINOL*

LYNNE L. MERRITT, JR. and CHARLES W. WEBER†
Indiana University, Bloomington, Indiana, U.S.A.

(*Received* 6 *October* 1960)

Summary—The solubilities of *bis*-8-quinolinolo-zinc^{II}, *bis*-2-methyl-8-quinolinolo-zinc^{II} and *bis*-5:7-dibromo-8-quinolinolo-zinc^{II} have been measured over the pH range of 4·5 to 9 at ionic strengths of 0·114 and 0·230 and at 25° and 40°. A mathematical treatment of the results gave nearly constant solubility products only when a dissolved but undissociated molecule, in addition to all of the dissociated and partly dissociated species, was considered. The relative abundance of each species of molecule in solution has been calculated.

INTRODUCTION

SEVERAL measurements of the solubility products of the slightly soluble complexes of metals with 8-quinolinol have appeared in the literature.[1–4] Except for the excellent series by Näsänen and co-workers,[4] the calculations have always been made on the assumption of complete dissociation of the complex upon solution. Näsänen adjusted the pH of a solution containing metallic ions and complexing agent until precipitation began, measured the pH and the concentration of MO_x^+ either spectrophotometrically or potentiometrically, then computed solubility products taking into account the dissociation constants of the complexes and the ionisation constants of the complexing agent. Under his conditions of low pH and low concentration of ligand, the complex MO_x^+ was the predominant species in solution.

We have measured the solubility of the zinc complexes of 8-quinolinol, 2-methyl-8-quinolinol and 5:7-dibromo-8-quinolinol using radioactive zinc-65 as tracer. The measurements were carried out at ionic strengths of 0·114 and 0·230 and at temperatures of 25° and 40° and over a pH range from about 4·5 to about 9·0. In the calculations of solubility products we have considered all species of ions and molecules which may be present in the solutions.

EXPERIMENTAL

Reagents

Bis-8-quinolinolo-zinc^{II}: Eastman Kodak reagent grade 8-quinolinol was purified by two recrystallisations from alcohol. Zinc oxide from the Oak Ridge National Laboratory, Oak Ridge, Tenn., was purified by solution in hydrochloric acid, followed by two precipitations of any acid-insoluble sulphides from 0·25*M* hydrochloric acid solution with hydrogen sulphide gas, adjustment of the pH to 3 and precipitation of zinc sulphide by hydrogen sulphide. The zinc sulphide was ignited to zinc oxide and stored in a desiccator.

The zinc complex was formed in the usual manner by addition of a 2% solution of 8-quinolinol in alcohol to the solution of zinc ion in sodium acetate-acetic acid at 60°. A very slight stoichiometric deficiency of 8-quinolinol was employed. The precipitate was allowed to stand for 24 hr, filtered, washed with water and air-dried. The complex was redissolved in hydrochloric acid and re-precipitated by the addition of sodium acetate solution, then washed and dried as before.

---

* Abstracted from a thesis presented to the Graduate School of Indiana University by Charles W. Weber in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1953.

Contribution No. 961 from the Chemical Laboratories of Indiana University.

† Present address: Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.

Bis-*2-methyl-8-quinolinolo-zinc*^{II}: The organic reagent was prepared according to the method of Merritt and Walker[5] and purified by vacuum distillation. The zinc complex was prepared in the same manner as the *bis*-8-quinolinolo-zinc^{II}.

Bis-*5*:*7-dibromo-8-quinolinolo-zinc*^{II}: The reagent was prepared by the method of Phillips[6] which is essentially that employed by Berg.[7] It was purified by reprecipitation from hydrochloric acid solution by partial neutralisation of the acid and recrystallisation from an acetone-benzene mixture. The zinc complex was formed in the same manner as the *bis*-8-quinolinolo-zinc^{II} complex except that the organic reagent was employed as a 0·06% solution in 3*N* hydrochloric acid containing 20–30% of acetone.

Buffer solutions: Buffer solutions of sodium acetate-sodium barbital-hydrochloric acid mixtures were prepared as suggested by Michaelis.[8] Sodium chloride was used to adjust the ionic strength to either 0·114 or 0·230.

Solubility measurements

Radioactive tracer techniques were used for determination of the solubilities. The zinc isotope ^{65}Zn ($t_{1/2}$ = 250 days) was employed.

In general, 600 ml of buffer solution was prepared at one time, divided into 150-ml portions and placed in contact with excess precipitate in 250-ml glass-stoppered Pyrex bottles. The samples were then rotated slowly in a constant-temperature water bath. From time to time samples were withdrawn through 10-mm diameter Corning No. 39535 medium-porosity fritted glass discs. Subsequent filtrations and sample countings were made to show that one filtration was sufficient to separate the solid completely and that no radioactive species of the solution was preferentially adsorbed on the discs. The pH of the filtered solutions was measured with a Beckman Model G pH meter, carefully standardised with buffer solutions of known pH,at the temperature of the water bath. Since pH is a critical factor, the pH of three or four identical runs was always measured and a precision of about 0·02 pH units was considered acceptable.

The filtered solutions were allowed to come to room temperature and 25-ml portions were pipetted into Marinelli type double-walled beakers and counted with a bismuth-wall Geiger-Müller tube. All measurements were corrected for background, then compared with the activity, measured at approximately the same time, of a solution of a weighed amount of the original zinc oxide used in preparing the complexes, dissolved in hydrochloric acid. Sufficient counts were registered so that the standard deviation of the counts was always below 5% of the sample activity corrected for background.

Samples were withdrawn at intervals and measured until the corrected activity remained constant over a period of 2 weeks in order to ensure that equilibrium had been attained. Usually 6-8 weeks were necessary.

RESULTS

The results of the solubility measurements are given in Tables I–III.

CALCULATIONS

Attempts were made to calculate solubility product constants from these results assuming complete ionisation of the dissolved material. If this is done the calculated solubility products vary by a factor of about 6000 over the pH range 4·5 to 9. Inclusion of stepwise dissociation of the complexes improves the result somewhat, but satisfactory values are only obtained after the presence of a dissolved but undissociated molecule is included. The following treatment, involving all known stability constants[9] of the *bis*-8-quinolinolo-zinc^{II} and the ionisation constants of the 8-quinolinol,[10] leads to the best values of the solubility product constants. This treatment has been applied only to the *bis*-8-quinolinolo-zinc^{II} complex since all necessary data for the other complexes are not known.

The reactions to be considered and their respective equilibrium constants are given below. The symbol HO_x stands for the 8-quinolinol molecule. Activity coefficients are neglected.

TABLE I. SOLUBILITY OF *Bis*-8-QUINOLINOLO-ZINC^{II} IN VERONAL-ACETATE BUFFERS

pH	μ	T, °*C*	Total Zn in solution, *M*
4·84	0·230	25	$1{\cdot}277 \times 10^{-5}$
5·90	0·230	25	$5{\cdot}05 \times 10^{-6}$
7·15	0·230	25	$1{\cdot}79 \times 10^{-6}$
8·17	0·230	25	$7{\cdot}30 \times 10^{-7}$
8·70	0·230	25	$4{\cdot}75 \times 10^{-7}$
4·63	0·114	25	$4{\cdot}43 \times 10^{-6}$
4·72	0·114	25	$4{\cdot}33 \times 10^{-6}$
5·83	0·114	25	$2{\cdot}40 \times 10^{-6}$
5·95	0·114	25	$2{\cdot}32 \times 10^{-6}$
6·73	0·114	25	$9{\cdot}72 \times 10^{-7}$
8·83	0·114	25	$2{\cdot}16 \times 10^{-7}$
4·60	0·114	40	$9{\cdot}46 \times 10^{-6}$
4·62	0·114	40	$10{\cdot}5 \times 10^{-6}$
6·22	0·114	40	$5{\cdot}04 \times 10^{-6}$
6·40	0·114	40	$3{\cdot}30 \times 10^{-6}$
8·06	0·114	40	$1{\cdot}10 \times 10^{-6}$
8·11	0·114	40	$8{\cdot}04 \times 10^{-7}$
8·25	0·114	40	$4{\cdot}35 \times 10^{-7}$

TABLE II. SOLUBILITY OF *Bis*-2-METHYL-8-QUINOLINOLO-ZINC^{II} IN VERONAL-ACETATE BUFFERS; $\mu = 0{\cdot}114$

25°		40°	
pH	Total zinc concentration, *M*	pH	Total zinc concentration, *M*
4·86	$1{\cdot}20 \times 10^{-5}$	5·21	$2{\cdot}32 \times 10^{-5}$
5·11	$1{\cdot}09 \times 10^{-5}$	5·22	$2{\cdot}13 \times 10^{-5}$
6·79	$7{\cdot}60 \times 10^{-7}$	6·66	$3{\cdot}13 \times 10^{-6}$
8·84	$2{\cdot}09 \times 10^{-7}$	6·73	$2{\cdot}64 \times 10^{-6}$
		8·24	$8{\cdot}74 \times 10^{-7}$
		8·44	$9{\cdot}57 \times 10^{-7}$

TABLE III. SOLUBILITY OF *Bis*-5:7-DIBROMO-8-QUINOLINOLO-ZINC^{II} IN VERONAL-ACETATE BUFFERS; $\mu = 0{\cdot}114$

25°		40°	
pH	Total zinc concentration, *M*	pH	Total zinc concentration, *M*
4·50	$3{\cdot}12 \times 10^{-5}$	4·60	$3{\cdot}40 \times 10^{-5}$
4·66	$2{\cdot}44 \times 10^{-5}$	4·61	$3{\cdot}05 \times 10^{-5}$
6·69	$1{\cdot}52 \times 10^{-6}$	4·62	$2{\cdot}96 \times 10^{-5}$
6·73	$1{\cdot}44 \times 10^{-6}$	6·56	$3{\cdot}06 \times 10^{-6}$
8·28	$5{\cdot}32 \times 10^{-7}$	6·71	$2{\cdot}45 \times 10^{-6}$
8·39	$4{\cdot}10 \times 10^{-7}$	8·06	$9{\cdot}86 \times 10^{-7}$
8·55	$3{\cdot}87 \times 10^{-7}$		

$$\mathrm{Zn(O_x)_2} \rightleftarrows \mathrm{ZnO_x^+} + \mathrm{O_x^-};\quad k_2 = \frac{[\mathrm{Zn(O_x)_2}]}{[\mathrm{Zn(O_x)^+}][\mathrm{O_x^-}]} = 7{\cdot}95 \times 10^9 \qquad (1)$$

$$\mathrm{ZnO_x^+} \rightleftarrows \mathrm{Zn^{++}} + \mathrm{O_x^-};\quad k_1 = \frac{[\mathrm{ZnO_x^+}]}{[\mathrm{Zn^{++}}][\mathrm{O_x^-}]} = 8{\cdot}13 \times 10^{10} \qquad (2)$$

$$\mathrm{HO_x} \rightleftarrows \mathrm{H^+} + \mathrm{O_x^-};\quad k_a' = \frac{[\mathrm{H^+}][\mathrm{O_x^-}]}{[\mathrm{HO_x}]} = 1{\cdot}95 \times 10^{-10} \qquad (3)$$

$$\mathrm{HO_x} + \mathrm{H^+} \rightleftarrows \mathrm{H_2O_x^+};\quad k_b' = \frac{[\mathrm{HO_x}][\mathrm{H^+}]}{[\mathrm{H_2O_x^+}]} = 1{\cdot}20 \times 10^{-5} \qquad (4)$$

$$\mathrm{Zn(O_x)_2}\,(s) \rightleftarrows \mathrm{Zn(O_x)_2}(1) \qquad (5)$$

Let the subscript T indicate the total concentration of any dissolved material. Then

$$\mathrm{Zn_T} = [\mathrm{Zn^{++}}] + [\mathrm{ZnO_x^+}] + [\mathrm{Zn(O_x)_2}] \qquad (6)$$

and $$\mathrm{O_{xT}} = 2[\mathrm{Zn_T}] = [\mathrm{ZnO_x^+}] + [\mathrm{O_x^-}] + [\mathrm{HO_x}] + [\mathrm{H_2O_x^+}] + 2[\mathrm{Zn(O_x)_2}]. \qquad (7)$$

Let $$p = \frac{[\mathrm{Zn(O_x)_2}]}{[\mathrm{Zn_T}]} = 2t \qquad (8)$$

$$t = \frac{[\mathrm{Zn(O_x)_2}]}{[\mathrm{O_{xT}}]} \qquad (9)$$

$$u = \frac{[\mathrm{Zn^{++}}]}{[\mathrm{Zn_T}]} \qquad (10)$$

$$v = \frac{[\mathrm{ZnO_x^+}]}{[\mathrm{Zn_T}]} = 2w \qquad (11)$$

$$w = \frac{[\mathrm{Zn(O_x)^+}]}{[\mathrm{O_{xT}}]} \qquad (12)$$

$$x = \frac{[\mathrm{H_2O_x^+}]}{[\mathrm{O_{xT}}]} \qquad (13)$$

$$y = \frac{[\mathrm{HO_x}]}{[\mathrm{O_{xT}}]} \qquad (14)$$

and $$z = \frac{[\mathrm{O_x^-}]}{[\mathrm{O_{xT}}]}. \qquad (15)$$

Then $$2t + w + x + y + z = 1 \qquad (16)$$

and $$p + u + v = 1. \qquad (17)$$

Now $$K_{\mathrm{S.P.}} = [\mathrm{Zn^{++}}]\,[\mathrm{O_x^-}]^2 = 4uz^2[\mathrm{Zn_T}]^3 \qquad (18)$$

and it can be further shown that

$$z^3 + z^2\frac{1}{2k_2[\mathrm{Zn_T}]} + z\left[\frac{E - k\,[\mathrm{Zn_T}]}{4k_1k_2[\mathrm{Zn_T}]^2E}\right] - \frac{1}{4k_1k_2[\mathrm{Zn_T}]^2E} = 0 \qquad (19)$$

where $$E = \frac{[\mathrm{H^+}]^2}{k_a'k_b'} + \frac{[\mathrm{H^+}]}{k_a'} + 1. \qquad (20)$$

The cubic equation (19) could be solved rigorously. Descartes rule of signs indicates not more than one positive root, however, and this was obtained by successive approximations. Since z represents a mole fraction, only a positive root has physical significance. The solutions of equation (19) for the corresponding values of the concentrations of ions and molecules in solution and the values of $K_{S.P.}$ calculated according to equation (18) for bis-8-quinolinolo-zinc^{II} are given in Table IV.

TABLE IV. CONCENTRATIONS OF IONS IN SOLUTION AND KS.P. VALUES FOR *Bis*-8-QUINOLINOLO-ZINC^{II} AT 25°

	pH	O_x^-	Zn^{2+}	ZnO_x^+	$Zn(O_x)^2$	KS.P.
$\mu = 0{\cdot}230$	5	$7{\cdot}92 \times 10^{-11}$	$9{\cdot}79 \times 10^{-7}$	$6{\cdot}30 \times 10^{-6}$	$3{\cdot}97 \times 10^{-6}$	$6{\cdot}14 \times 10^{-27}$
	6	$1{\cdot}56 \times 10^{-10}$	$1{\cdot}56 \times 10^{-8}$	$1{\cdot}98 \times 10^{-6}$	$2{\cdot}46 \times 10^{-8}$	$3{\cdot}80 \times 10^{-27}$
	7	$2{\cdot}10 \times 10^{-10}$	$4{\cdot}29 \times 10^{-8}$	$7{\cdot}32 \times 10^{-7}$	$1{\cdot}23 \times 10^{-6}$	$1{\cdot}89 \times 10^{-27}$
	8	$2{\cdot}34 \times 10^{-10}$	$1{\cdot}45 \times 10^{-8}$	$2{\cdot}75 \times 10^{-7}$	$5{\cdot}10 \times 10^{-7}$	$7{\cdot}92 \times 10^{-28}$
	9	$2{\cdot}44 \times 10^{-10}$	$8{\cdot}43 \times 10^{-9}$	$1{\cdot}67 \times 10^{-7}$	$3{\cdot}25 \times 10^{-7}$	$5{\cdot}02 \times 10^{-28}$
$\mu = 0{\cdot}114$	5	$4{\cdot}41 \times 10^{-11}$	$6{\cdot}42 \times 10^{-7}$	$2{\cdot}30 \times 10^{-6}$	$8{\cdot}1 \times 10^{-7}$	$1{\cdot}25 \times 10^{-27}$
	6	$1{\cdot}20 \times 10^{-10}$	$9{\cdot}47 \times 10^{-8}$	$9{\cdot}25 \times 10^{-7}$	$8{\cdot}8 \times 10^{-7}$	$1{\cdot}36 \times 10^{-27}$
	7	$1{\cdot}76 \times 10^{-10}$	$1{\cdot}85 \times 10^{-8}$	$2{\cdot}64 \times 10^{-7}$	$3{\cdot}7 \times 10^{-7}$	$5{\cdot}68 \times 10^{-28}$
	8	$2{\cdot}24 \times 10^{-10}$	$7{\cdot}77 \times 10^{-9}$	$1{\cdot}41 \times 10^{-7}$	$2{\cdot}5 \times 10^{-7}$	$3{\cdot}88 \times 10^{-28}$
	9	$2{\cdot}41 \times 10^{-10}$	$4{\cdot}31 \times 10^{-9}$	$8{\cdot}43 \times 10^{-7}$	$1{\cdot}61 \times 10^{-7}$	$2{\cdot}50 \times 10^{-28}$

DISCUSSION

Certain assumptions and approximations have been made in obtaining these results. Activity coefficients have been neglected except, of course, for the hydrogen ion. Any formation of $Zn(OH)_3^-$ or $Zn(OH)_4^{2+}$ has also been neglected. A calculation using the values for the dissociation constants of these basic zinc ions as given by Dirkse, Postmus and Vandenbosch[11] indicates that only at pH 9 would there be any appreciable amount of $Zn(OH)_3^-$ ion present.

The results clearly indicate that the undissociated molecule and the partially dissociated molecule are the species present in largest concentrations over the pH range 5 to 9. Below a pH of about 5·8 the $Zn(O_x)^+$ ion is the predominant form, but above this pH the $Zn(O_x)_2$ species is predominant.

It is interesting to note that the concentration of the $Zn(O_x)_2$ molecule increases with decreasing pH. One might expect that the concentration of the undissociated molecule, which is in direct equilibrium with the solid, would remain constant. There are at least two possible explanations for the solubility behaviour of this species. Firstly, the molecule may be partially dissociated by the acid, forming ions of the type $Zn(O_x)(HO_x)^+$ or $Zn(HO_x)_2^{2-}$. The formation of an ion of this type would not be included in measurements of k_2, but would be counted as $Zn(O_x)_2$ molecules in this experiment. As second possibility is that the water molecules which bind the *bis*-8-quinolinolo-zinc^{II} molecules together in the crystal[12] are weakened by competing for hydrogen ions to form oxonium ions. A third possibility is that k_1 or k_2 or both are in error; however, a ten-fold decrease in the value of k_2 results in the solubility of $Zn(O_x)_2$ molecules being still 5 to 6 times greater at pH 5 than at pH 8. Thus it would appear that the k_1 and k_2 values would have to be in error by several orders of magnitude, which seems unlikely.

The values for the solubility product obtained here are in fair agreement with the value $pS_0 = 24{\cdot}500$, obtained by Näsänen,[4] considering the fact that Näsänen has extrapolated his values to zero ionic strength, his temperature was 20° and that he used somewhat different values for the dissociation and ionisation constants involved.

It will be interesting to calculate the absorption spectra of each species of ion using the concentrations found in this paper. Another application would be to determine the values of the dissociation constants and the solubility product by selecting the best values of the constants by the method of least squares. Further work along these lines is being carried out.

Acknowledgment—This work was supported by the U.S. Atomic Energy Commission under contract AT(11-1)-120.

Zusammenfassung—Die Loslichkeit von Bis-oxin-zink, Bis-2-methyl-oxin-zinc und Bis-5,7-dibrom-oxin-zink wurde gemessen im pH-Bereich 4,5-9 bei ionaler Konzentration 0·114 und 0·230 sowie bei 25° und 40°C. Mathematische Behandlung der Ergebnisse ergab ein nahezu konstantes Löslichkeitsproduct nur unter der Annahme, dass eine gelöste aber undissoziierten Molekul neben allen anderen dissoziierten oder teilweise dissoziierten Partikeln anwesend ist. Die relative Menge aller in der Lösung vorhandener Spezien wurde errechnet.

Résumé—Les solubilités du bis-8-quinolinolo-zinc (11), du bis-2-méthyl-8-quinolinolo-zinc (11) et du bis-5-7-dibromo-8-quinolinolo-zinc (11) ont été mesurées dans le domaine de pH 4,5-9 à des forces ioniques de 0,114 et 0,230 à 25° et 40°. Une étude mathématique des résultats donnait des produits de solubilité à peu près constants seulement quand on considèrait une molécule dissoute, mais non dissociée ajoutée à toutes les espèces dissociées et partiellement dissociées. L'abondance relative de chaque sorte de molécule en solution a été calculée.

REFERENCES

[1] W. Treadwell and A. Ammann, *Helv. Chim. Acta*, 1938, **21**, 1249.
[2] J. P. Phillips and H. P. Price, *J. Amer. Chem. Soc.*, 1951, **73**, 4414.
[3] S. Lacroix, *Analyt. Chim. Acta*, 1947, **1**, 260.
[4] R. Näsänen, *Acta Chem. Scand.*, 1947, **1**, 260; *ibid.*, 1951, **5**, 1199, 1293; R. Näsänen and Urho Penttinen, *Acta Chem. Scand.*, 1952, **6**, 837; R. Näsänen, *Suomen Kem.*, 1953, **26B**, 11-15; *ibid.*, 1955, **28B**, 123 and other papers in this series.
[5] L. L. Merritt, Jr. and J. K. Walker, *Analyt. Chem.*, 1944, **16**, 387.
[6] J. P. Phillips, M. A. Thesis, Indiana University, Bloomington, Indiana, U.S.A., 1947.
[7] R. Berg, *Z. anorg. Chem.*, 1932, **204**, 208.
[8] L. Michaelis, *Biochem. Z.*, 1947, **234**, 139.
[9] *Discussion on Coordination Chemistry*, Report No. BRL/146, Butterwick Research Laboratories, Welwyn, England, September 21, 1950, p. 30.
[10] J. P. Phillips and L. L. Merritt, Jr., *J. Amer. Chem. Soc.*, 1948, **70**, 410.
[11] T. P. Dirkse, C. Postmus, Jr. and R. Vandenbosch, *ibid.*, 1954, **76**, 6022.
[12] L. L. Merritt, Jr., R. T. Cady and B. W. Mundy, *Acta Cryst.*, 1954, **7**, 473.

Talanta, 1961, Vol. 7, pp. 163 to 174. Pergamon Press Ltd. Printed in Northern Ireland

BATHOPHENANTHROLINEDISULPHONIC ACID AND BATHOCUPROINEDISULPHONIC ACID, WATER SOLUBLE REAGENTS FOR IRON AND COPPER

DAVID BLAIR and HARVEY DIEHL
Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

(*Received* 29 *September* 1960)

Summary—Bathophenanthrolinedisulphonic acid and bathocuproïnedisulphonic acid have been isolated in solid form as sodium salts and characterised. Both materials retain the high sensitivity of the parent materials as spectrophotometric reagents, for iron and copper respectively. They are water soluble and unlike the parent reagents may be used in aqueous perchlorate solutions. Interferences are about the same as with the parent reagents, but the pH range for maximum colour formation extends two pH units further into the alkaline region. Iron^{II} tribathophenanthrolinedisulphonic acid is an excellent oxidation-reduction indicator, changing sharply from red to green in the cerate titration of iron^{II}; it may be used in solutions containing perchloric acid.

THE initial paper of Smith, McCurdy and Diehl[1] on bathophenanthroline (4:7-diphenyl-1:10-phenanthroline), a highly sensitive reagent for the spectrophotometric determination of iron, has been followed by several other papers detailing applications of the reagent to various materials bearing traces of iron.[2] In a like manner, bathocuproïne (2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline), originally proposed by Smith and Wilkins,[3] is finding numerous applications[4] because its unqualified specificity and high sensitivity make it the superior reagent for the spectrophotometric determination of traces of copper.

The difficulty encountered in the use of these reagents in water solution is their low solubility in water. Both are soluble in alcohols, and also in water as the hydrochlorides, but in the neutral solutions needed for maximum colour development with the metals, the excess reagent tends to precipitate, rendering the solutions turbid. Even this is satisfactory if the procedures of the original authors are followed, for Smith and his co-workers extract the metal derivatives into amyl or hexyl alcohol and in these solvents make the final photometric measurement. The advantages of such extraction are considerable, for a significant concentration can be effected and the blank can be reduced essentially to zero by extracting from the various reagent solutions any iron and copper present. Workers with heavy loads of routine work, however, find the extraction a handicap, but in omitting it, *i.e.*, in making the photometric measurement on the water solution, are plagued with the turbidity difficulty.

Trinder[5] solved this problem by sulphonating bathophenanthroline, and later Zak[6] followed with a sulphonation of bathocuproïne. Both succeeded in providing a sensitive, water soluble reagent, free from turbidity in use. The art was thus advanced and the daily capabilities of the clinical analyst increased. As with pioneers at all times and stations, Trinder and Zak left problems for others: Can the sulphonated products be isolated in solid form suitable for commercial distribution and shipping? What is the composition of the sulphonated reagents? What is the nature of their metal derivatives? What are their sensitivities and the degree to which they are affected by foreign elements? Then too, is the perchlorate of the iron^{II} derivative of sulphonated bathophenanthroline water soluble so that it may be used as an oxidation-reduction indicator in a perchloric acid solution, in contrast to its parent material?

We have attempted to answer these questions.

EXPERIMENTAL

Apparatus and reagents

Spectrophotometric data were secured using a Cary Model 12 Recording Spectrophotometer and a Beckman DU Spectrophotometer using 1-cm matched cells. pH measurements were made with a Beckman Model G pH meter with Beckman No. 30740 amber bulb glass electrode. Potential measurements were made with a Leeds and Northrup No. 7552 potentiometer. The thermobalance used was one built in this laboratory.

The starting materials, bathophenanthroline and bathocuproïne, were obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio. The commercial chlorosulphonic acid used was first subjected to distillation to insure the absence of iron and copper. The Amberlite IR-120 used was a reagent-grade material. The water used was first distilled, then passed through a monobed ion-exchange resin.

Bathophenanthrolinedisulphonic acid (4:7-*diphenyl*-1:10-*phenanthrolinedisulphonic acid*)

Synthesis. One g of bathophenanthroline and 10 ml of freshly distilled chlorosulphonic acid were stirred vigorously (glass-coated magnetic stirring bar) for 20 hr at 25°. The mixture was cooled in ice and 100 ml of de-ionised water was added carefully. The mixture was then heated in a boiling water bath until a clear solution was obtained. Water and hydrochloric acid were removed by heating with aspiration leaving the excess sulphuric acid and the sulphonated material.

Concentrated ammonia was added until in excess. The resulting solution was evaporated to dryness on a steam plate. The residue was pulverised and treated with 200 ml of 95% ethanol. The mixture was heated to boiling, stirred for 30 min and the ammonium sulphate filtered out using suction. The filtrate was evaporated to dryness on a steam plate. The residue was dissolved in 100 ml of de-ionised water and the solution passed through a column of Amberlite IR-120 (a strong cation-exchange resin) in the hydrogen form. The resulting acidic solution was partially neutralised with iron-free sodium bicarbonate and the carbon dioxide formed expelled by boiling while the solution was still slightly acidic. The pH of the solution was then adjusted to 8·5 with dilute sodium hydroxide. The solution was evaporated on a hot plate and the residue pulverised. Yield 98%. Found: C 53·87, H 2·85, N 5·05, S 11·87, Na 8·77 (Huffman Microanalytical Laboratory, Wheatridge, Colorado) giving an empirical formula of $C_{24\cdot2}H_{15\cdot3}N_{2\cdot0}S_{2\cdot0}Na_{2\cdot1}$; disodium bathophenanthrolinedisulphonate: $C_{24}H_{14}N_2S_2Na_2O_6$. Equivalent weight (determined by passing a weighed sample of the sodium salt dried at 110° through a column of IR-120 in the hydrogen form and titration with standard sodium hydroxide, see Fig. 1): 263·0, 264·5 (first preparation), 264·5 (second preparation); calculated for $C_{24}H_{15}Na_2(SO_3Na)$ 434·4; for $C_{24}H_{14}N_2(SO_3Na)_2$ 536·5/2 or 268·2; for $C_{24}H_{13}N_2(SO_3Na)_3$ 638·5/3 or 212·8.

Properties. The disodium salt, a light tan solid, is extremely soluble in water. It is hygroscopic but after drying at 110° for 2 hr shows no change in weight up to 275° (thermobalance). It shows a light blue fluorescence under ultraviolet light.

The free acid is a syrupy liquid, highly hygroscopic, and is difficult to obtain in the solid form. It proved impossible to prepare an ammonium salt of stoichiometric composition.

Iron^{II} derivative. A solution of iron^{II} sulphate was treated with hydroxylamine hydrochloride, a ten-fold excess of disodium bathophenanthrolinedisulphonate, and sodium acetate. The absorption spectrum of the deep red solution was obtained on the Cary spectrophotometer (Fig. 2); at the wavelength of maximum absorption, 535 mμ, the molar extinction coefficient was 22,140.

The combining ratio of the iron^{II} and bathophenanthrolinedisulphonate ions was determined by a spectrophotometric titration, the iron concentration being held constant in a series of solutions and the concentration of reagent varied. Straight lines were obtained for the sloped and horizontal portions of the curve and the sharp break fell at the ratio Fe:bathophenanthrolinedisulphonate = 1:3·17.

The pH range over which iron^{II} tribathophenanthrolinedisulphonic acid is stable was determined by preparing a series of solutions, each solution having the same amount of iron, sodium sulphite and an excess of bathophenanthrolinedisulphonate; the pH was adjusted with hydrochloric acid or sodium hydroxide and after 1 hr the absorbancy of each solution was measured. Results are presented graphically in Fig. 3.

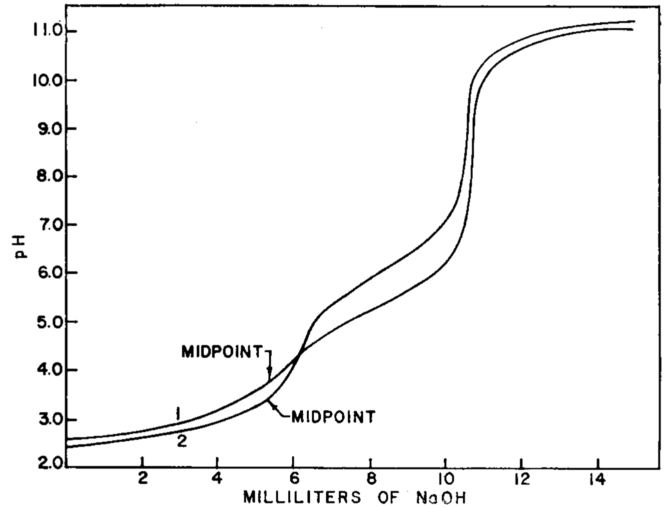


FIG. 1.—Titration of bathophenanthrolinedisulphonic acid (curve 1) and of bathocuproïnedisulphonic acid (curve 2).

Bathocuproïnedisulphonic acid (2:9-*dimethyl*-4:7-*diphenyl*-1:10-*phenanthrolinedisulphonic acid*)

Synthesis. Identical with that given above for bathophenanthrolinedisulphonic acid. Yield 97% Found: C 52·41, H 3·69, N 4·57, S 10·40, Na 8·11 (Huffman Microanalytical Laboratory) giving an empirical formula of $C_{26\cdot9}H_{26\cdot0}N_{2\cdot0}S_{2\cdot0}Na_{2\cdot2}$; disodium bathocuproïnedisulphonate is $C_{26}H_{18}N_2S_2Na_2O_6$. Equivalent weight found (method given above, Fig. 1): 278·0 (first preparation), 273·4, 273·0 (second preparation); calculated for $C_{26}H_{19}N_2SO_3Na$ 462·5, for $C_{26}H_{18}N_2(SO_3Na)_2$ 564·6/2 or 282·3, for $C_{26}H_{17}N_2(SO_3Na)_3$ 666·6/3 or 222·2.

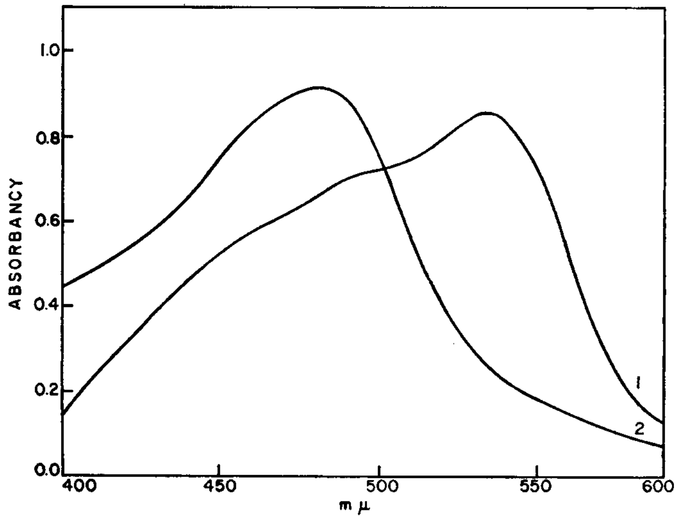


FIG. 2.—Absorption spectra of iron^{II} tribathophenanthrolinedisulphonic acid (curve 1) and of copper^{I} dibathocuproïnedisulphonic acid (curve 2).

Properties. The disodium salt, a light tan solid, is extremely soluble in water; it is hygroscopic but once dried (110°, 2 hr) it shows no change in weight on heating to 275°. It shows a light blue fluoresence under ultraviolet light.

The free acid is a syrupy liquid, highly hygroscopic and difficult to obtain in the crystalline form: It was impossible to prepare an ammonium salt of stoichiometric composition.

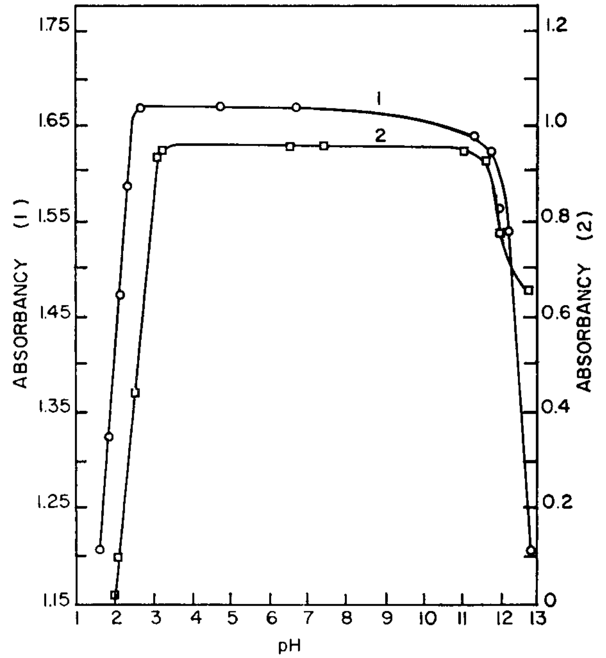


FIG. 3.—pH range for complete formation of iron^{II} tribathophenanthrolinedisulphonic acid (curve 1) and of copper^{I} dibathocuproïnedisulphonic acid (curve 2).

Copper^{I} derivative. A solution of copper sulphate was treated with hydroxylamine hydrochloride and a ten-fold excess of bathocuproïnedisulphonate, then buffered with sodium acetate. The absorption spectrum of the orange coloured solution was obtained on the Cary spectrophotometer (Fig. 2); at the wavelength of maximum absorption, 483 mμ, the molar extinction coefficient was 12,250.

The combining ratio was determined by a spectrophotometric titration; found Cu: bathocuproïnedisulphonate = 1:2·28.

The pH range over which copper is converted completely to copper^{I} dibathocuproïnedisulphonic acid was measured in the same fashion as described above for iron^{II} tribathophenanthrolinedisulphonic acid; the results are shown in Fig. 3.

Determination of iron with bathophenanthrolinedisulphonic acid

The spectrophotometric determination of iron with bathophenanthrolinedisulphonic acid was worked out by Trinder in the original paper.[5] We sought here to extend the studies of the interferences and to show that the method can be used in solutions containing perchloric acid, such as those resulting from the wet ashing of plant and animal material.

Interferences. The disturbing effects of various ions on the spectrophotometric determination of iron was determined on solutions made up to contain $6{\cdot}5 \times 10^{-7}$ moles of iron and $9{\cdot}5 \times 10^{-6}$ moles of bathophenanthrolinedisulphonate in a total volume of 50·0 ml. In all cases the order of addition of the reagents was the same, first the interfering ion, second the iron, next the hydroxylamine hydrochloride, then the sulphonated reagent, and finally the sodium acetate buffer. See Table 1. The method of calculating the relative error is that of Fortune and Mellon.[7]

TABLE 1—EFFECT OF VARIOUS IONS ON THE DETERMINATION OF IRON WITH BATHOPHENANTHROLINEDISULPHONIC ACID

Ion	Interfering ion concentration, *ppm*	Added as	Relative error* % of 0·726 *ppm* of Fe taken
Cu^{2+}	0·9	$CuSO_4$	+2·2
†Cu^{2+}	9·4	$CuSO_4$	+3·2
Co^{2+}	1·2	$CoSO_4$	+1·1
†Co^{2+}	5·8	$CoSO_4$	0·0
Ni^{2+}	1·4	$NiSO_4$	+1·1
†Ni^{2+}	5·5	$NiSO_4$	0·0
Zn^{2+}	13·8	$ZnSO_4$	+0·3
Mn^{2+}	25·3	$MnSO_4$	−1·1
Cr^{3+}	5·8	$K_2Cr_2O_7$	+1·6
Cr^{3+}	29·2	$K_2Cr_2O_7$	+4·7
Be^{2+}	14·6	$Be(ClO_4)_2$	+2·2
Al^{3+}	121·3	$Al_2(SO_4)_3$	Prec.
Mg^{2+}	58·7	$MgSO_4$	+0·3
Ca^{2+}	189	$Ca(C_2H_3O_2)_2$	−1·1
Sr^{2+}	571	$Sr(NO_3)_2$	0·0
Cd^{2+}	35·5	$Cd(NO_3)_2$	0·0
Sn^{4+}	307	$SnCl_4$	Prec.
Th^{4+}	546	$Th(NO_3)_4$	+0·3
UO_2^{2+}	653	$UO_2(NO_3)_2$	+1·6
Li^+	627	$LiCl$	0·0
ClO_4^-	17780	$NaClO_4$	+2·7
CN^-	536	KCN	No colour
PO_4^{3-}	1122	KH_2PO_4	0·0
F^-	543	NaF	+1·1
$C_2H_3O_2^-$	15320	$NH_4C_2H_3O_2$	0·0
Br^-	895	KBr	−2·3
I^-	1040	NaI	−0·8
Cl^-	5180	KCl	−0·8
NO_2^-	873	$NaNO_2$	−2·0
SO_4^{2-}	3470	$(NH_4)_2SO_4$	0·0
ClO_3^-	818	$KClO_3$	−0·8
SCN^-	1200	$NaSCN$	−1.7
$S_2O_3^{2-}$	1074	$Na_2S_2O_3$	Prec.
BO_3^{3-}	1800	$Na_2B_4O_7$	+0·3
BrO_3^-	1380	$KBrO_3$	+0·3
MoO_4^{2-}	93·2	Na_2MoO_4	0·0
$C_6H_5O_7^{3-}$	1627	$H_3C_6H_5O_7$	−1·7
$S_2O_8^{2-}$	1626	$(NH_4)_2S_2O_8$	−9·7

* Calculated using

$$\% \text{ Relative Error} = \frac{C_1 \frac{A_2}{A_1} - C_1}{C_1} 100$$

where C and A refer to concentration and absorbancy, respectively, and subscripts 1 and 2 to solutions without and with the interfering ion, respectively.[7]

† Solutions containing a large excess ($2 \cdot 5 \times 10^{-5}$ moles) of bathophenanthrolinedisulphonate.

Determination of iron in yeast. As a check on the use of bathophenanthrolinedisulphonic acid for the determination of iron, a commercial yeast (Fleischmann's "Active Dry") was selected as a suitable and homogeneous material requiring wet ashing. A sample weighing 2 g was transferred to a 250-ml conical flask. Five ml of concentrated sulphuric acid were added and a reflux head[8] was placed in the neck of the flask. A blank determination was carried along simultaneously starting with the sulphuric acid. The yeast was charred by heating the mixture on a gas hot-plate for 15 min. The mixture was cooled, then 20 ml of equal parts by volume of 72% perchloric acid and 70% nitric acid were added. The reflux head was replaced and the mixture was boiled in such a fashion that the water and nitric acid were expelled in about 15 min and perchloric acid began to condense on the walls of the flask. This smooth refluxing of perchloric acid without undue escape of perchloric acid was continued 10 min. The mixture was then cooled and the reflux head and flask washed with approximately 30 ml of de-ionised water.

To this solution was added 5 ml of a 10% solution of hydroxylamine hydrochloride and 10 ml of a 0·1% solution of disodium bathophenanthrolinedisulphonate. Ammonium hydroxide was added until the pH of the solution reached 7 to 8 as shown by pH paper. The pH was then brought to between 4 and 5 by the dropwise addition of perchloric acid. The solution was then transferred to a 100-ml volumetric flask, diluted to the mark with de-ionised water and mixed. The absorbancy was then measured in a 1-cm cell at 535 mμ.

A calibration curve was prepared following the procedure of the paragraph immediately above, starting with various volumes of a standard iron solution (0·036 mg of iron/ml), prepared by dissolving electrolytic iron ignited in moist hydrogen (G. Frederick Smith Chemical Company, Columbus, Ohio) in sulphuric acid and diluting and aliquoting and again diluting as appropriate. The calibration curve was linear, indicating conformity to Beer's law, over the range 0 to 3·6 ppm of iron.

Known amounts of iron were added to certain samples of the yeast before digestion. The results on the yeast and on the spiked samples are summarised in Table II.

Table II—Determination of iron in dry yeast with bathophenanthrolinedisulphonic acid

Sample number	Iron added, *mg*	Iron found, *mg*	Iron in yeast, *ppm*	
1	none	0·100	50·0	
2	none	0·102	51·0	
3	none	0·101	50·5	
4	none	0·101	50·5	
5	none	0·101	50·5	
6	none	0·099	49·5	
		Av. 0·101	Av. 50·3	
			Iron recovered, *mg*	Error, *mg*
7	0·036	0·139	0·038	+0·002
8	0·036	0·143	0·042	+0·006
9	0·036	0·138	0·037	+0·001
10	0·072	0·172	0·071	−0·001
11	0·072	0·169	0·068	−0·004
12	0·072	0·173	0·072	0·0

Determination of copper using bathocuproïnedisulphonic acid

The use of bathocuproïnedisulphonic acid for the spectrophotometric determination of copper was described by Zak.[6] We have extended the study by an investigation of the ions which could interfere with the method and have applied the reagent to the determination of copper in yeast in the presence of the perchlorate ion as a check on the method.

Interferences. **A solution was prepared by adding first the ion under study, second 1·9 × 10^{-6} mole of copper, next the hydroxylamine hydrochloride, then 1·4 × 10^{-5} mole of disodium bathocuproïnedisulphonate, and finally the sodium acetate buffer.** The solution was diluted to a volume of **50·0 ml and the absorbancy was measured at 483 mμ.** The disturbance was reported as relative error **in the amount of copper taken, Table III.**

TABLE III.—EFFECTS OF VARIOUS IONS ON THE DETERMINATION OF COPPER WITH BATHOCUPROÏNEDISULPHONIC ACID

Ion	Interfering ion concentration, *ppm*	Added as	Relative error % of 2·41 ppm of Cu taken
Fe^{2+}	5·8	$FeSO_4$	+0·2
Fe^{2+}	57·8	$FeSO_4$	+1·2
Co^{2+}	1·2	$CoSO_4$	0·0
Co^{2+}	5·9	$CoSO_4$	+1·4
Ni^{2+}	1·4	$NiSO_4$	0·0
Ni^{2+}	6·9	$NiSO_4$	+1·4
Zn^{2+}	126	$ZnSO_4$	−0·3
Mn^{2+}	316	$MnSO_4$	0·0
Cr^{3+}	5·8	$K_2Cr_2O_7$	−0·2
Cr^{3+}	29·2	$K_2Cr_2O_7$	+3·1
Be^{2+}	14·6	$Be(ClO_4)_2$	+1·1
Al^{3+}	90	$Al_2(SO_4)_3$	Prec.
Mg^{2+}	67	$MgSO_4$	0·0
Ca^{2+}	170	$Ca(C_2H_3O_2)_2$	−0·2
Sr^{2+}	571	$Sr(NO_3)_2$	−2·1
Cd^{2+}	360	$Cd(NO_3)_2$	−0·2
Sn^{4+}	351	$SnCl_4$	Prec.
Th^{4+}	525	$Th(NO_3)_4$	−0·2
UO_2^{2+}	555	$UO_2(NO_3)_2$	+6·1
Li^+	642	$LiCl$	−0·2
ClO_4^-	16550	$NaClO_4$	0·0
CN^-	550	KCN	No colour
PO_4^{3-}	1284	KH_2PO_4	−0·3
F^-	696	NaF	−1·2
$C_2H_3O_2^-$	15660	$NH_4C_2H_3O_2$	−1·2
Br^-	1000	KBr	0·0
I^-	840	NaI	−0·6
Cl^-	5130	KCl	−2·1
NO_2^-	882	$NaNO_2$	−0·2
SO_4^{2-}	3060	$(NH_4)_2SO_4$	−2·1
ClO_3^-	905	$KClO_3$	−1·1
SCN^-	975	$NaSCN$	−16·5
$S_2O_3^{2-}$	1330	$Na_2S_2O_3$	+3·2
BO_3^{3-}	1940	$Na_2B_4O_7$	−0·3
BrO_3^-	1028	$KBrO_3$	−0·3
MoO_4^{2-}	81	Na_2MoO_4	−0·2
$C_6H_5O_7^{3-}$	1627	$H_3C_6H_5O_7$	−0·8
$S_2O_8^{2-}$	1567	$(NH_4)_2S_2O_8$	−15·4

Determination of copper in yeast. Two g of the same yeast analysed for iron were analysed for **copper. The procedure for destroying the organic matter was the same as detailed in the first paragraph above on the determination of iron in yeast.**

To this solution were added 5 ml of a solution 10% in hydroxylamine hydrochloride and 2% in citric acid. Then 5 ml of a 0·1 % solution of disodium bathocuproïnedisulphonate were added. Ammonium hydroxide was added until the pH reached 7 to 8 as indicated by pH paper. The solution was then brought to pH 4 to 5 by the dropwise addition of dilute perchloric acid. The solution was diluted to exactly 100 ml and the absorbancy measured at 483 mμ.

A calibration curve was prepared by applying this same procedure to various volumes of a standard copper solution (0·079 mg of copper/ml), by dissolving electrolytically purified copper in nitric acid, converting to copper sulphate by evaporation with sulphuric acid and diluting as appropriate. The calibration curve was linear, indicating conformity to Beer's law, over the range 0 to 6·35 ppm of copper.

Known amounts of copper were added to some of the samples as a check on the accuracy of the method. The results are reported in Table IV.

TABLE IV—DETERMINATION OF COPPER IN DRY YEAST WITH BATHOCUPROÏNEDISULPHONIC ACID

Sample number	Copper added, *mg*	Copper found, *mg*	Copper in yeast, *ppm*	
1	none	0·053	26·6	
2	none	0·053	26·6	
3	none	0·052	26·0	
4	none	0·053	26·7	
5	none	0·052	26·0	
6	none	0·051	25·6	
		Av. 0·052	Av. 26·2	
			Copper recovered, *mg*	Error, *mg*
7	0·079	0·125	0·073	−0·006
8	0·079	0·129	0·077	−0·002
9	0·079	0·126	0·074	−0·005
10	0·158	0·203	0·151	−0·007
11	0·158	0·201	0·149	−0·009
12	0·158	0·202	0·150	−0·008

Iron^{II} tribathophenanthrolinedisulphonic acid as a redox indicator

Because iron^{II} tribathophenanthrolinedisulphonic acid does not form an insoluble perchlorate, it became of interest to learn if it could be used as an oxidation-reduction indicator in solutions containing perchloric acid.

Preparation of indicator solution. To 5·0 ml of 0·0375*M* iron^{II} perchlorate was added 0·302 g of disodium bathophenanthrolinedisulphonate. The resulting solution was diluted to 50 ml, giving a solution 0·00375*M* in iron^{II} tribathophenanthrolinedisulphonic acid.

Standard reduction potential. The formal reduction potential of iron^{II} tribathophenanthrolinedisulphonic acid was determined in both 1*M* sulphuric acid and 1*M* perchloric acid. A solution approximately equimolar in iron^{II} sulphate and iron^{II} tribathophenanthrolinedisulphonic acid and 1*M* in sulphuric acid was titrated with sulphatoceric acid prepared by dissolving cerium^{IV} hydroxide in sulphuric acid and adjusting the sulphuric acid concentration to 1*M*. A platinum foil and a saturated calomel electrode with agar salt bridge were used as electrodes. Two sharp breaks were obtained in the titration curve and the horizontal portion of the curve corresponding to the titration of the iron^{II} bathophenanthrolinedisulphonic acid was sufficiently broad (because of the large amount taken) to permit locating the mid-point with certainty. The mid-point of the first horizontal portion of the curve corresponded to values of the formal reduction potential of the iron^{III}–iron^{II} couple in

1M sulphuric acid already reported. The titration was repeated replacing the sulphuric acid with 1M perchloric acid in both the titrant and the solution titrated. The results are reported in Table V.

TABLE V.—FORMAL REDUCTION POTENTIALS OF IRON$^{\text{II}}$ TRIBATHOPHENANTHROLINEDISULPHONIC ACID IN 1M SULPHURIC ACID AND IN 1M PERCHLORIC ACID

	1M Sulphuric acid	1M Perchloric acid
E° on hydrogen scale, potentiometric*	1·09 V	1·01 V
E° on hydrogen scale, visual†	1·15 V	1·14 V

* From mid-point of titration curve.
† At colour change: green, no red remaining.

Use in the determination of iron in iron ore. A sample of iron ore weighing 0·2 to 0·3 g was transferred to a 500-ml conical flask. To this were added 15 ml of a mixture of equal volumes of 70% perchloric acid and 85% phosphoric acid.[9] A reflux head[8] was inserted into the neck of the flask and the mixture was heated on a hot plate until the ore had dissolved. The mixture was cooled and 70 ml of water added. The reflux head was replaced by a stirring rod and the mixture boiled for 4 min. The solution was cooled and 30 ml of dilute sulphuric acid (1 : 1) added. The solution was then passed

TABLE VI.—DETERMINATION OF IRON IN VARIOUS ORES. CERATE TITRATION USING IRON$^{\text{II}}$ BATHOPHENANTHROLINEDISULPHONATE

Sample	Iron found, %	Average and standard deviation	Iron reported, %
NBS No. 29a	69·30	69·30	69·54
	69·36	$\sigma = 0·07$	
	69·26		
	69·21		
	69·37		
NBS No. 26	58·23	58·24	58·62*
	58·32	$\sigma = 0·08$	
	58·33		
	58·13		
	58·22		
Lerch Brothers, Incorporated, 1953 Standard†	58·03	58·04	58·19
	58·03	$\sigma = 0·04$	
	57·98		
	58·08		
	58·08		

Electrolytic iron (standardisation)	Normal concentration of cerate solution
	0·07350
	0·07338
	0·07323
	0·07335
	0·07327
	Av. 0·07335
	$\sigma = 0·00010$

* Based on a small number of determinations and not certified.
† Lerch Brothers, Incorporated, Hibbing, Minnesota.

through an amalgamated zinc reductor. The reductor was washed with dilute sulphuric acid (1:20), care being taken not to allow any air to be drawn into the zinc column during the washing operation. Four drops of 0·00375*M* iron^{II} bathophenanthrolinedisulphonate indicator were added and, with vigorous stirring, the iron^{II} was titrated with 0·1*N* perchloratoceric acid. The end-point was marked by a very sharp change from red to green.

The perchloratocerate solution was standardised against electrolytic iron ignited in moist hydrogen (obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio) in exactly the same manner.

The results obtained on three iron ores are reported in Table VI.

CONCLUSIONS AND DISCUSSION

It is evident that room temperature sulphonation with chlorosulphonic acid has produced a disulphonated material from both bathophenanthroline and bathocuproïne. The parent 1:10-phenanthroline cannot be sulphonated under these conditions. It appears reasonable then to assume that the sulphonic groups have entered into the phenyl groups of bathophenanthroline and bathocuproïne, and because a sulphonic group on a phenyl ring tends to hinder further addition to the ring, that one sulphonic group has entered each of the phenyl groups in each case.

Various work has shown that 1:10-phenanthroline and its derivatives act as monoacidic bases, presumably because the spatial arrangement permits only one proton to enter easily. In these disulphonic acids it might be expected that one proton would be transferred to the ring nitrogen giving the molecule a zwitterion structure. The neutralisation titration curves, (Fig. 1) can be explained on this basis: the first titration corresponds to the neutralisation of the free sulphonic acid, the second to the neutralisation of the proton on the nitrogen. The dissociation constants are:

	pK_1	pK_2
Bathophenanthrolinedisulphonic acid	2·83	5·20
Bathocuproïnedisulphonic acid	2·65	5·80

The second acid dissociation constant of bathocuproïnedisulphonic acid is smaller than that of bathophenanthrolinedisulphonic acid, presumably because the basic character of the latter is enhanced by the presence of the 2— and 9-methyl groups.

The zwitterion structure probably accounts for the failure in either case to obtain a di-ammonium salt on neutralisation of the acids with ammonia and subsequent evaporation and drying.

In preparing either of the disulphonated products particular care must be taken to avoid the introduction of iron and copper inasmuch as the isolation scheme does not adequately separate the free acid from the highly coloured metal derivative. Distillation of the intermediates where possible and the use of reagent-grade chemicals and of de-ionised water help in producing an almost colourless product.

The combining ratios found, 3 for bathophenanthrolinedisulphonic acid and the iron^{II} ion, 2 for bathocuproïnedisulphonic acid and the copper^{I} ion, are the values expected. The combining ratio found for the copper^{I} compound, 2·28, is not as close to 2 as is desirable and we are at a loss to explain the discrepancy; possibly the starting material contained an impurity which was carried through, although the melting point of the bathocuproïne was satisfactory.

The absorption spectra recorded for the iron^{II} and copper^{I} derivatives of the sulphonated reagents (Fig. 1) are essentially the same as those reported by Zak.[6] The sensitivities of these reagents are essentially the same as those of the parent reagents.

	Wavelength of maximum absorption, $m\mu$	Molar extinction coefficient
Iron^{II} bathophenanthroline		
Smith and others[1,2]	543	22,143 (water-alcohol)
	533	22,350 (*iso*amyl)
Iron^{II} bathophenanthrolinedisulphonic acid		
Trinder[5]	535	——
This work	535	22,140
Copper^{I} bathocuproïne		
Smith and others[3,4]	479	13,900 (water)
	479	14,160 (n-hexyl)
Copper^{I} bathocuproïnedisulphonic acid		
Zak[6]	485	——
This work	483	12,250

Sulphonation has thus conferred water solubility and freedom from precipitation in a perchlorate solution without impairing the sensitivity.

The wet oxidation of yeast before the determination of its content of iron and copper proved more difficult than anticipated. In preliminary work, digestion with nitric and perchloric acids failed to effect complete destruction of the organic material and the results were erratic. The results were somewhat better with the ternary mixture of nitric, perchloric and sulphuric acids. The preliminary charring with sulphuric acid and subsequent digestion with nitric and perchloric acids produced complete destruction of all organic matter and the results for iron and copper were then satisfactory.

The citric acid added in the procedure for copper is to prevent the precipitation of any iron as the hydrous oxide.

The pH range over which the metal derivatives of the sulphonated reagents are stable extends to nearly pH 11, some two pH units further than the parent reagents; this may be useful under certain circumstances.

The use of iron^{II} bathophenanthrolinedisulphonic acid as redox indicator is very advantageous in cerate oxidimetry since it is soluble in solutions containing perchlorate, whereas the other ferroïn compounds are difficultly soluble. The colour change is vivid and the end-point sharp. The demonstration of the utility of this indicator in the determination of iron in three iron ores is admittedly a bit unconvincing in that the results on all three of the ores studied are all significantly lower than the values reported by others. It did not appear that the perchloric acid-phosphoric acid solvent[9] failed to dissolve all of the ore nor that the method lacked precision. We suggest that our values are correct.

Acknowledgement—The authors wish to express their appreciation of grants of chemicals received from the G. Frederick Smith Chemical Company of Columbus, Ohio.

Zusammenfassung—Bathophenanthrolindisulfonsäure und Bathocuproindisulfonsäure wurden als Natriumsalze isoliert. Beide Substanzen weisen die hohe Empfindlichkeit für Eisen bzw. Kupfer auf, wie die Muttersubstanzen; sind jedoch wasserlöslich und können für Bestimmungen in wässrigen Losungen (Perchlorat) verwendet werden. Die Störungen durch andere Ionen sind etwa dieselben doch wird der pH-Bereich, in dem die Bestimmungen durchgeführt werden konnen, um etwa 2 Einheiten ins alkalische Gebiet ausgedehnt. Ferro-tribathophenanthrolindisulfonat ist ein ausgezeichneter Redox-indicator (scharfer Farbumschlag von rot nach grun) in der cerimetrischen Titration von Eisen, in perchlorsäurer Lösung.

Résumé—Les acides bathophénanthrolinedisulfonique et bathocuproinésulfonique ont été isolés sous forme solide à l'état de sels de sodium, et caractérisés. Ces deux composés conservent la haute sensibilité des produits apparentés comme réactifs spectrophotométriques respectivement pour le fer et le cuivre. Ils sont solubles dans l'eau, et contrairement aux réactifs apparentés ils peuvent être utilisés dans des solutions aqueuses de perchlorate. Les interférences sont à peu près les mêmes qu'avec les réactifs apparentés, mais le domaine de pH où la formation de la couleur est la plus importante s'étend de 2 unités dans la région alcaline. L'acide tribathophénanthrolinedisulfonique ferreux est un excellent indicateur d'oxydo-réduction, qui vire nettement du rouge au vert dans le dosage du fer ferreux par le cerate; il peut être utilisé dans des solutions contenant de l'acide perchlorique.

REFERENCES

[1] G. Frederick Smith, W. H. McCurdy, Jr. and H. Diehl, *Analyst*, 1952, **77**, 418.

[2] H. Diehl and G. Frederick Smith, *The Iron Reagents: Bathophenanthroline*, 2:4:6-*Tripyridyl-s-triazine*, *Phenyl-2-pyridyl Ketoxime*. G. Frederick Smith Chemical Company, Columbus, Ohio, 1960, p. 13.

[3] G. Frederick Smith and D. H. Wilkins, *Analyt. Chem.*, 1953, **25**, 510.

[4] H. Diehl and G. Frederick Smith, *The Copper Reagents: Cuproine, Neocuproine, Bathocuproine.* G. Frederick Smith Chemical Company, Columbus, Ohio, 1958, p. 39.

[5] P. Trinder, *J. Clin. Pathology*, 1956, **9**, 170.

[6] B. Zak, *Clinica Chim. Acta*, 1958, **3**, 328.

[7] W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem. Analyt.* 1938, **10**, 60.

[8] G. Frederick Smith and V. R. Sullivan, *ibid.*, 1935, **7**, 302.

[9] C. A. Goetz and E. P. Wadsworth, Jr., *ibid.* 1956, **28**, 375.

Talanta, 1961, Vol. 7, pp. 175 to 180. Pergamon Press Ltd. Printed in Northern Ireland

A POLAROGRAPHIC STUDY OF D-GLUCURONOLACTONE

ROGER J. THIBERT*® and ALBERT J. BOYLE
Department of Chemistry, Wayne State University, Detroit, Michigan, U.S.A.

(*Received* 26 *February* 1960)

Summary—A polarographic study of D-glucuronolactone using a dropping mercury electrode is made. The effects on the wave of various supporting electrolytes, buffers, and maximum suppressors are investigated. The diffusion current shows a linear relationship to concentration for lithium chloride and potassium chloride as supporting electrolytes in the range of 10–100 μg/ml. Pyruvate interferes whereas D-glucose does not.

INTRODUCTION

THE fact that D-glucuronolactone (D-glucurone) is a lactone and is potentially reducible at the dropping mercury electrode suggested the possibility of a polarographic determination. Aldoses and ketoses give kinetic currents and their waves depend on the transformation of the non-reducible cyclic hemi-acetal form to the aldehydo- or keto-form at the electrode.[1,2] Carbohydrates may also be determined polarographically by forming their hydrazones, then reducing them at the dropping mercury electrode.[3,4]

A polarographic study of D-glucuronic acid was reported by Ishidate and Shimozawa.[5] These investigators were not able to obtain reproducible waves and the results were not quantitative for either D-glucuronic acid or D-glucurone. In this communication, an investigation of the effect of the supporting electrolyte, maximum suppressor, pH, types of buffers, and the interference of glucose is discussed.

EXPERIMENTAL

Apparatus

A Beckman pH-meter, Model G, was used to measure pH. An E. H. Sargent polarograph, Model XXI, with a Heyrovský-type cell was used to obtain the polarograms. A polarimeter with monochromator assembly, Rudolph 503, O. C. Rudolph and Sons, served to measure the specific rotation of D-glucurone solutions.

Reagents

The prepared D-glucurone solutions presented a specific rotation [$\alpha_D{}^{27}$] of +20·3°. Polarograms obtained after digestion of D-glucurone solutions with nitric-perchloric acid mixture[6,7] gave the same wave as the supporting electrolyte (0·02*N* potassium chloride).

Procedure

The solutions to be analysed were prepared by mixing the appropriate concentrations of D-glucurone, supporting electrolyte, and maximum suppressor in a 100-ml volumetric flask and diluting to volume with distilled water. After proper mixing, the solution to be analysed was transferred to a 25-ml Heyrovský-type polarographic cell. Nitrogen was passed through the solution for 10 min and a polarogram was obtained for each solution, using a drop rate of 4 sec. The polarograms were run through the range of 0·0 to −3·0 V versus the mercury pool.

---

[*] Research Fellow, Michigan Heart Association. Present address: Essex College, Assumption University of Windsor, Windsor, Ontario, Canada.

RESULTS AND DISCUSSION

Supporting electrolytes

The relationship between diffusion current and concentration of D-glucurone using 0·2*N* potassium chloride solution as the supporting electrolyte and 0·005% gelatin as the maximum suppressor is given in Table I.

TABLE 1. EFFECT OF D-GLUCURONE CONCENTRATION ON DIFFUSION CURRENT

D-Glucurone concentration, *μg/ml*	Diffusion current, *mA*
100	1·41
80	1·00
80	1·02
60	0·882
40	0·495
20	0·176
20	0·148
20	0·159
10	0·096
10	0·132

The half-wave potential was observed to be —1·56 V versus the mercury pool. The polarographic wave has a sharp maximum at about —1·6 to —1·7 V versus the mercury pool using 0·005% gelatin as the maximum suppressor. Further work revealed that 0·01% gelatin completely suppresses the maximum but the total wave height is somewhat reduced.

Lithium chloride as a supporting electrolyte proved to be superior to potassium chloride if 0·005% gelatin was used as the maximum suppressor. The wave exhibits no maximum and, as is shown in Table II, the relationship of concentration to diffusion current is much more nearly linear than is the case with potassium chloride.

TABLE II. EFFECT OF D-GLUCURONE CONCENTRATION ON DIFFUSION CURRENT

D-Glucurone concentration, *μg/ml*	Diffusion current, *mA*
100	1·23
80	0·888
60	0·612
60	0·623
60	0·576
40	0·366
20	0·120
20	0·111
10	0·062

A typical polarogram using lithium chloride as the supporting electrolyte and 0·005% gelatin as the maximum suppressor is shown in Fig. 1. The half-wave potential is —1·60 V versus the mercury pool. Attempts to use ammonium chloride as a supporting electrolyte were not successful since the electrolyte gave a wave starting at —1·65 V versus the mercury pool.

Degree of hydrolysis

The influence of time on the wave height of D-glucurone was investigated. It was observed that a three-weeks old solution had a similar diffusion current (1·41 mA) to a one-day old solution (1·40 mA). The polarogram was run using 100 μg/ml of D-glucurone in 0·2*N* potassium chloride solution as the supporting electrolyte and 0·005% gelatin as the maximum suppressor. If the fresh solution is heated before analysis, the diffusion current is much less (1·02 mA), pointing to some hydrolysis. Standard solutions of D-glucurone were always stored at 0°–5°, thereby slowing down hydrolysis.

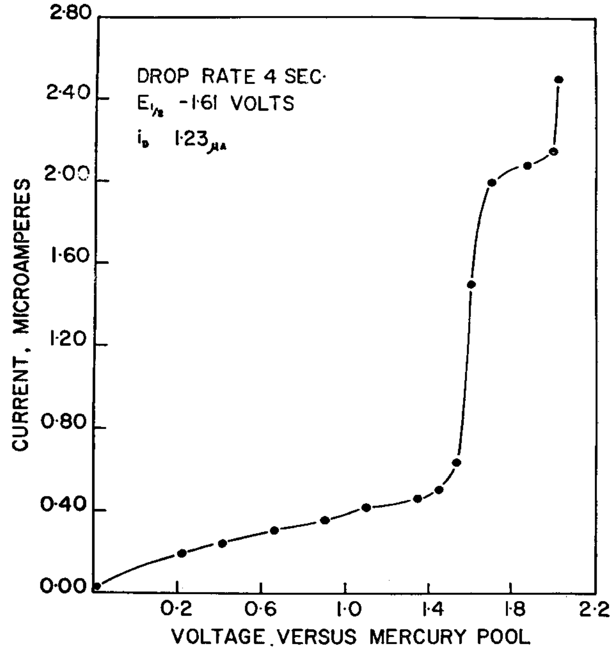


FIG. 1.—Polarogram of 100 μg/ml of D-glucurone using 0.02*N* LiCl as the supporting electrolyte.

Reduction of D*-glucurone in the presence of hydrochloric acid*

Polarograms of 100 μg/ml of D-glucurone in 0·1*N* potassium chloride solution using 4 drops of methyl orange solution (0·1 % in water) as the maximum suppressor, were run at various hydrogen ion concentrations. The effect of hydrogen ion concentration on the diffusion current is shown in Table III.

At acid concentrations above $1 \times 10^{-4}M$, the D-glucurone wave cannot be obtained, but rather a very large wave, beginning at about —1·5 V versus the mercury pool and going off scale rapidly, is observed. Under basic conditions no wave is obtained; upon neutralisation with hydrochloric acid, the wave re-appears. The wave exhibits a more pronounced maximum using methyl orange as the maximum suppressor, but the wave height is somewhat elevated.

TABLE III. EFFECT OF HYDROGEN ION CONCENTRATION ON DIFFUSION CURRENT

Concentration of HCl, *moles/litre*	Diffusion current, *mA*
1×10^{-4}	1·23
1×10^{-5}	1·68
1×10^{-6}	1·80
no acid present	1·70

Interference

The use of any of the standard buffer mixtures, completely suppressed the wave. The buffers usually caused the appearance of a gradual wave at about −1·32 to −1·7 V versus the mercury pool. This gradual wave completely eliminated the D-glucurone wave. The buffer systems used were: phthalate buffer,[8] pH 4; Coleman buffers, pH 2, 6, 9; K_2HPO_4–KH_2PO_4 buffer,[8] pH 6; $NaC_2H_3O_2$–$HC_2H_3O_2$ buffer,[9] pH 4; $(C_2H_5)_4NOH + H_3PO_4$ buffer, pH 2·1, 4·1, 6·0, 8·0, 9·4; barbiturate buffer, pH 6, Li_2HPO_4–LiH_2PO_4 buffer, pH 6. Even upon dilution, these buffers inhibited the D-glucurone wave. So extreme is the effect with any form of phosphate buffer, that if, for example, one drop of 0·1*M* potassium dihydrogen phosphate solution is added to the 25–ml polarographic cell containing 100 μg/ml of D–glucurone with potassium chloride as the supporting electrolyte containing 0·005% gelatin as the maximum suppressor, the D–glucurone wave is entirely suppressed. This suggested the possibility of an indirect polarographic determination of phosphate. Present studies indicate that this indirect method for phosphate is feasible. Barbiturate buffer enhanced the wave height because it exhibited a wave of its own in the region of the D-glucurone wave.

Pyruvic acid, when added to D-glucurone solutions, interferes with the D-glucurone wave height. The relationship is not linear, nor is it additive. (Pyruvic acid is converted to lactic acid at the dropping mercury electrode.[10])

Determination of D*-glucurone in the presence of* D*-glucose*

A D-glucose solution (1000 μg/ml) was analysed in 0·1*N* potassium chloride solution using 0·005% gelatin as the maximum suppressor. At sensitivities of 0·003, 0·004, 0·006, and 0·01 mA/mm, the polarograms showed a break at −1·80 V versus the mercury pool in each case (*i.e.* no characteristic wave was observed). A solution of 50 μg/ml of D-glucurone and 1000 μg/ml of D-glucose in 0·1*N* potassium chloride solution using 0·005% gelatin as the maximum suppressor was analysed in the usual manner. The usual D-glucurone wave was obtained with a diffusion current of 0·60 mA and half-wave potential of −1·56 V versus the mercury pool (Fig. 2).

CONCLUSION

D-Glucurone exhibits a polarographic wave in potassium chloride or lithium chloride as the supporting electrolyte using gelatin as the maximum suppressor. It is suggested that this wave is due to the lactone since it disappears at high pH levels (hydrolysis occurs) and decreases in magnitude upon heating solutions of D-glucurone before analysis.

The wave obtained with D-glucurone is not due to metal ions, since digestion to dryness of D-glucurone solutions with nitric-perchloric acid mixture causes the wave to disappear.

The complete inability of the system to function in the presence of any type of buffer sets it apart from many types of organic reductions which require well defined media with respect to pH.[11] The type of reduction occurring does not appear to be of the reversible type with controlled pH, but rather of the catalytic type in which the overvoltage of hydrogen is decreased by the lactone, and the diffusion current obtained is proportional to the concentration of the reducible species in solution.

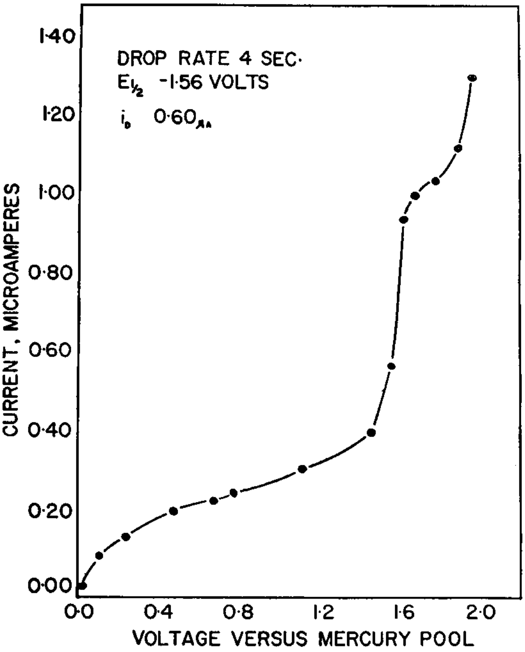


FIG. 2.—Polarogram of a mixture of 50 μg/ml of D-glucurone and 1000 μg/ml of D-glucose in 0.1*N* KCl as the supporting electrolyte.

Zusammenfassung—Eine polarographische Studie mit D-Glucurono-lacton an der tropfenden Quecksilberelektrode wird mitgeteilt. Der Einfluss verschiedener Grundlösungen, Elektrolyte, Puffer und Maximasuppressoren auf die Welle wurde studiert. In Lithium- oder Kaliumchlorid als Grundlösungen ist die Beziehung zwischen Diffusionsstrom und Konzentration linear im Bereich 10–100 μg per ml. Pyruvate stören während D-Glucose ohne Einfluss ist.

Résumé—Les auteurs ont fait une étude polarographique de la D-glucuronolactone en utilisant une électrode á gouttes de mercure. Les actions de différents électrolytes supports, des tampons et des suppresseurs de maximum sur la vague ont été étudiées. Le courant de diffusion varie linéairement avec la concentration dans le domaine 10 μg–100 μg par ml pour les électrolytes supports: chlorure de lithium et chlorure de potassium. Le pyruvate gêne, mais non le D-glucose.

REFERENCES

[1] I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience Publishers, New York, 2nd Ed., 1952. Vol. 2, p. 720.

[2] S. M. Cantor and Q. P. Peniston, *J. Amer. Chem. Soc.*, 1940, **62**, 2113.

[3] L. Mester and A. Major, *ibid.*, 1955, **77**, 4297.

[4] J. W. Haas and C. C. Lynch, *Analyt. Chem.*, 1957, **29**, 479.

[5] M. Ishidate and T. Shimozawa, *J. Pharm. Soc. Japan.*, 1944, **64**, 53.

[6] G. Frederick Smith, *Mixed Perchloric, Sulphuric and Phosphoric Acid and their Applications in Analysis.* The G. Frederick Smith Chemical Co., 1942. p. 10.

[7] G. Frederick Smith, *Analyt. Chim. Acta*, 1953, **8**, 397.

[8] H. H. Willard, L. L. Merritt and J. A. Dean, *Instrumental Methods of Analysis.* D. Van Nostrand Company, Inc., New York, 1951. p. 182.

[9] F. C. Koch and M. E. Hanke, *Practical Methods in Biochemistry.* The Williams and Wilkins Company, Baltimore, 6th. Ed., 1953. p. 522.

[10] I. M. Kolthoff and J. J. Lingane, *Polarography.* Interscience Publishers, New York, 2nd. Ed., 1952. Vol. 2, p. 730.

[11] O. H. Muller, *Polarography*, in A. Weissberger, *Technique of Organic Chemistry.* Interscience Publishers, New York, 1949. Vol. 1, Part 2, p. 1833.

Talanta, 1961, Vol. 7, pp. 181 to 186. Pergamon Press Ltd. Printed in Northern Ireland

THE SPECTROFLUOROMETRIC DETERMINATION OF ANTHRACENE, FLUORENE AND PHENANTHRENE IN MIXTURES

GLENN A. THOMMES* and ELMER LEININGER
Kedzie Chemical Laboratory, Michigan State University, East Lansing, Michigan, U.S.A.

(*Received* 8 *July* 1960)

Summary—A procedure is presented for the spectrofluorometric determination of mixtures of anthracene, fluorene and phenanthrene. The determination depends on differences in fluorescence emission spectra and on selective excitation of anthracene fluorescence. Some of the fluorescence and absorption spectra involved overlap, but these difficulties can be overcome by empirical corrections. The average relative error in this method is less than 5% over the concentration range 0 to 5 ppm.

THE use of the spectrofluorometer has greatly facilitated the fluorometric resolution of mixtures of compounds, particularly those depending on selective excitation and significant differences in fluorescent emission spectra.

The fluorescence spectra, uncorrected for instrumental differences of sensitivity with wavelength, of anthracene, fluorene and phenanthrene in absolute methyl alcohol solution are shown in Fig. 1. Casual observation suggests a possible resolution of a mixture of these hydrocarbons in the following manner:

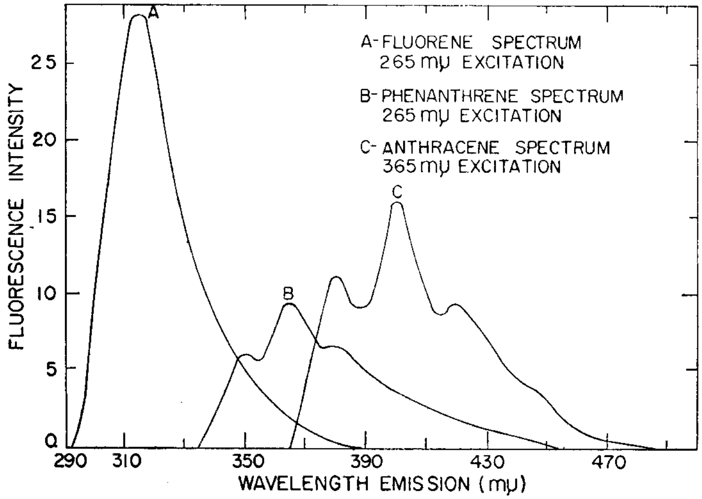


FIG. 1.—Fluorescence spectra of hydrocarbons

(*a*) Only anthracene is fluorescent under 365 mμ-excitation. Therefore, irradiation at this wavelength and measurement of the fluorescence intensity at 400 mμ should yield, directly, the anthracene concentration.

---

* Present address: E. I. du Pont de Nemours and Co., Inc. Photo Products Department, Parlin, New Jersey, U.S.A.

(*b*) Although excitation with 265 mμ-radiation causes all three compounds to fluoresce, the fluorescence intensity measured at 316 mμ should be a measure of the fluorene concentration.

(*c*) At 350 mμ, under 265 mμ-irradiation, a fluorescence intensity measurement should be the sum of the phenanthrene and fluorene emissions at this wavelength. Since the fluorene concentration would be known from (*b*), the phenanthrene concentration could be determined providing the fluorescence intensities are additive.

In practice, however, the resolution is complicated by the fact that the absorption spectra of anthracene and phenanthrene[3] interfere. Anthracene absorbs at 350 mμ and both anthracene and phenanthrene absorb at 316 mμ. Consequently, only the anthracene emission at 400 mμ, under 365 mμ-excitation, is free from interference and the fluorescence readings at both 316 and 350 mμ are dependent on the concentrations of all three compounds.

Since the concentration of anthracene can be measured independently, a correction can be made for the interaction of anthracene with the fluorescent emission of the other hydrocarbons at 350 and 316 mμ. For example, if the assumption is made that the interaction is only due to absorption, the observed fluorescence intensity, I_f^a, is equal to the fluorescence intensity in the absence of anthracene, I_f°, minus the intensity absorbed by the anthracene present. Thus:

$$I_f^a = I_f^\circ - I_f^\circ(1 - 10^{-K_AC_A}) = I_f^0 \times 10^{-K_AC_A}$$

where K_A is the product of the molar absorptivity of anthracene at the wavelength of fluorescence measurement and the path length of the fluorescent emission, and C_A is the molar concentration of anthracene.

If the above assumptions were correct, a plot of $\log I_f^\circ - \log I_f^a$ versus C_A should be linear. Two such plots, showing the effect of anthracene on the fluorescence of fluorene at 350 and 316 mμ are shown in Figs. 2 and 3. Although the plots are not linear, they may be used for correction purposes.

The curves were obtained by observing the decrease in the fluorescence intensity of fluorene at 316 and 350 mμ as a function of anthracene concentration. The decrease was only a function of the anthracene concentration and was independent of the fluorene concentration. Furthermore, the 350 mμ-correction is also satisfactory for use with phenanthrene fluorescence.

With the above information and the appropriate calibration curves, mixtures of anthracene and phenanthrene or anthracene and fluorene can be resolved easily.

Mixtures containing phenanthrene and fluorene appear to be more difficult because of the mutual dependence of their fluorescence intensities at both 316 and 350 mμ. However, a simple graphical method[4] can be used to resolve this difficulty. Any combination of 316 mμ- and 350 mμ-fluorescence intensities must be unique for the concentrations of phenanthrene and fluorene involved. The fluorescence intensities of a series of fluorene and phenanthrene mixtures were measured at 316 and 350 mμ. These were plotted against each other and the points corresponding to identical fluorene concentrations were joined. Likewise, the points corresponding to identical phenanthrene concentrations were joined. The resulting calibration grid,

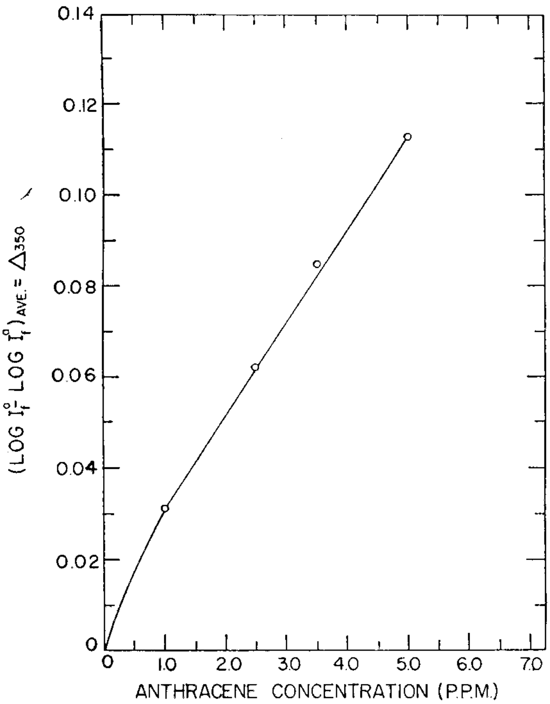


FIG. 2.—Anthracene absorption of 350 mμ emission

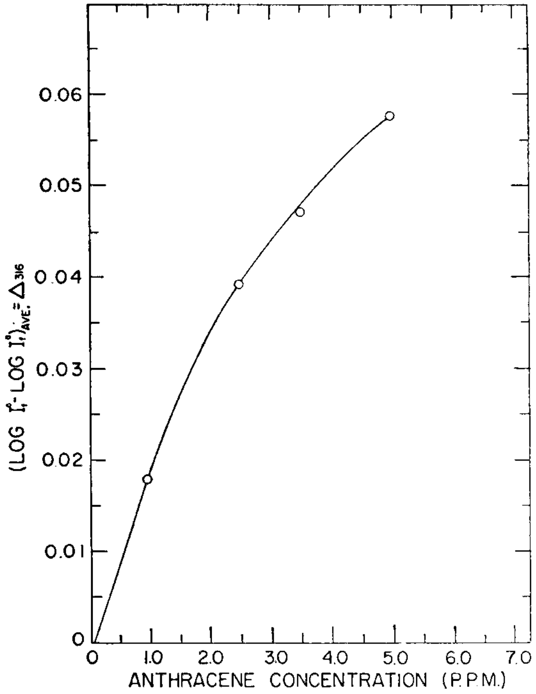


FIG. 3.—Anthracene absorption of 316 mμ emission

shown in Fig. 4, serves as a standard calibration curve for both fluorene and phenanthrene. If anthracene is present the 316- and 350 mμ-measurements must be corrected for anthracene absorption before using the calibration grid.

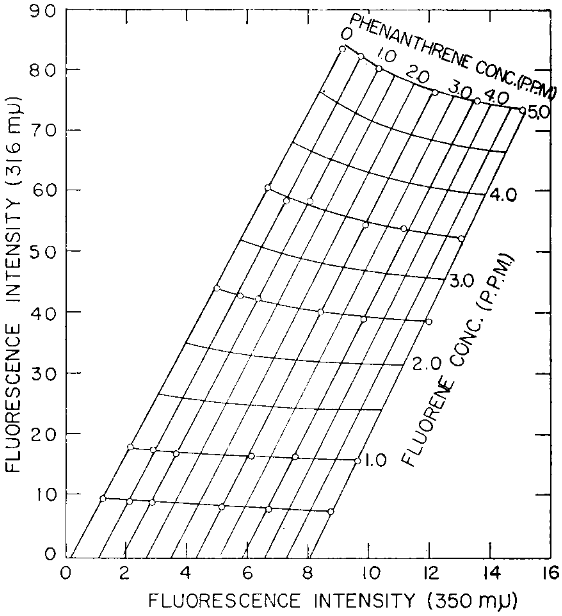


FIG. 4.—Calibration grid

EXPERIMENTAL

Reagents

The anthracene and phenanthrene were purified by azeotropic distillation, under reduced pressure, with ethylene glycol and diethylene glycol according to the procedure of Feldman *et al.*[2] The fluorene was purified by repeated vacuum sublimation. The starting materials in all of the purification procedures were Eastman White Label Chemicals. Baker's analysed absolute methanol was used as the hydrocarbon solvent.

Stock solutions of the three purified hydrocarbons were prepared which contained 0·5 mg of hydrocarbon per ml of solution. All subsequent solutions used were prepared by direct methanolic dilution of these stock solutions.

Apparatus

The spectrofluorometer employed was that described by the writers in a previous study.[5] The instrument was calibrated each time before use with a standard solution containing 3·50 ppm of anthracene. The instrument was set to read 17·0 at 400 mμ under 365 mμ-excitation. The methanolic solution of anthracene was chosen as a calibration standard because of the well known oxygen quenching of the fluorescence of polynuclear hydrocarbons.[1,6] Employing a standard which is also subject to oxygen quenching should eliminate any effect of day-to-day fluctuations in oxygen concentration.

Calibration graphs

A series of solutions of the three hydrocarbons was prepared to cover the range from 0·5 to 5·0 ppm. Each solution was made by transferring an aliquot portion of the appropriate standard stock solution to a 100 ml-volumetric flask, diluting to the mark with absolute methyl alcohol and mixing thoroughly.

The anthracene readings were obtained by measuring the fluorescence intensities of the anthracene solutions at 400 mμ under 365 mμ-excitation. The anthracene calibration curve was prepared from these data.

The calibration grid for phenanthrene and fluorene was prepared by measuring fluorescence intensities at 350 mμ and 316 mμ under 265 mμ-excitation of mixtures of phenanthrene and fluorene. The mixtures were prepared to cover the ranges of 0–5 ppm of phenanthrene and 0–5 ppm of fluorene.

The correction curve for anthracene absorption was prepared as stated before.

Calibration curves of the three hydrocarbons show linearity over the concentration range of 0–5 ppm; consequently, this was used as the upper concentration limit in this study. However, the plots are smooth curves above 5 ppm and the concentration range could probably be extended.

Procedure

A series of unknown solutions were prepared comprising the four types of possible mixtures. These were prepared by dilution of aliquot portions drawn from standard stock solutions. The solutions were then excited with 365 mμ-radiation and the fluorescence intensity, if any, was measured at 400 mμ. This measurement is used directly with the anthracene calibration curve, to obtain the concentration of anthracene present. The wavelength of excitation is changed to 265 mμ and fluorescence intensity measurements are made at 316 and 350 mμ. These measurements are corrected for anthracene absorption, if it is present, and are used with the calibration grid to obtain the concentrations of phenanthrene and fluorene present. If initial measurements indicate that the concentration of any of the hydrocarbons is greater than 5 ppm, a suitable dilution with methyl alcohol can be made to bring the concentrations into the proper range.

TABLE I. RESULTS OF HYDROCARBON MIXTURE ANALYSIS

Anthracene			Phenanthrene			Fluorene		
Taken, *ppm*	Found (400 mμ), *ppm*	Percent error	Taken, *ppm*	Found, *ppm*	Percent error	Taken, *ppm*	Found, *ppm*	Percent error
0·75	0·73	−2·6	4·00	4·06	+1·5	—	—	—
1·00	1·00	0	1·00	1·05	+5·0	—	—	—
1·50	1·44	−4·2	—	—	—	3·00	3·07	+2·3
2·00	1·95	−2·5	—	—	—	3·00	2·14	+7·0
3·00	2·95	−1·7	—	—	—	1·00	1·05	+5·0
—	—	—	1·00	0·85	−15·0	3·00	3·04	+1·3
—	—	—	2·00	1·90	−5·0	2·00	2·05	+2·5
—	—	—	3·00	2·92	−2·7	1·00	0·98	−2·0
—	—	—	3·50	3·75	+7·1	1·00	1·00	0
—	—	—	3·50	3·50	0	2·50	2·52	+0·8
—	—	—	5·00	5·05	−1·0	3·80	3·45	−1·4
1·00	0·97	−3·0	2·00	1·78	11·0	3·00	3·15	+5·0
2·00	1·97	−1·5	3·00	2·93	−2·3	2·00	2·20	+10·0
2·00	1·97	−1·5	2·00	2·10	+5·0	2·00	2·20	+10·0
3·00	2·93	−2·3	1·00	0·99	−1·0	1·00	1·02	+2·0
3·50	3·50	0	3·00	3·00	0	3·00	3·20	+6·7
1·50	1·52	+1·4	4·00	4·34	+8·5	1·00	1·05	+5·0

RESULTS

The results obtained on the mixtures prepared are summarised in Table I. The average errors found in the determinations of the three hydrocarbons were as follows:

Anthracene, $E_{ave.} = 1·9\%$
Phenanthrene, $E_{ave.} = 4·6\%$
Fluorene, $E_{ave.} = 4·1\%$

The maximum error observed was 15%; however, errors of this order of magnitude are exceptional and in the majority of determinations the error is less than ±5%.

Acknowledgement—The authors are indebted to the Eastman Kodak Company for financial support during this investigation.

Zusammenfassung—Ein Methode zur spektrofluorimetrischen Bestimmung von Anthracen, Phananthren und Fluoren wird mitgeteilt. Die Bestimmung beruht auf den Unterschieden in den Fluoreszenspektren und der selektiven Anregung der Anthracenfluorescenz. Einige der Fluoreszenz- und Absortionsspektren überschneiden sich, jedoch kann diese Schwierigkeit durch Anbringen einer empirischen Korrektur überwunden werden. Der mittlere relative Fehler der Methode ist weniger als 5% im Konzentrationsbereich 0–5 ppm.

Résumé—Les auteurs présentent un procédé de dosage spectrofluorométrique de mélanges d'anthracène, de phénanthrène et de fluorène. Le dosage dépend des différences des spectres d'émission fluorescents et de l'excitation sélective de la fluorescence de l'anthracène. Certains des spectres de fluorescence et d'absoprtion considérés se recouvrent, mais ces difficultés peuvent être surmontées par des corrections empiriques. L'erreur relative moyenne dans cette méthode est inférieure à 5 pour cent dans le domaine de concentration 0–5 p.p.m.

REFERENCES

[1] E. J. Bowen and A. H. Williams, *Trans. Faraday Soc.*, 1939, **35**, 765.
[2] J. Feldman, P. Panteges and M. Orchin, *J. Amer. Chem. Soc.*, 1951, **73**, 4341.
[3] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds.* John Wiley and Sons, Inc., New York, 1950
[4] J. W. Collat and L. B. Rodgers, *Analyt. Chem.*, 1955, **27**, 961.
[5] G. A. Thommes and E. Leininger, *ibid.*, 1958, **30**, 1361.
[6] H. Weil-Malherbe and J. Weiss, *Nature*, 1942, **149**, 172; 1943, **151**, 449; *J. Chem. Soc.*, 1944, 541 and 544.

Talanta, 1961, Vol. 7, pp. 187 to 194. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF CALCIUM IN LITHIUM SALTS

RODNEY L. OLSEN and HARVEY DIEHL
Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.
and
PETER F. COLLINS and R. B. ELLESTAD
Lithium Corporation of America, Bessemer City, North Carolina, U.S.A.

(*Received* 10 *November* 1960)

Summary—Two procedures are described for the determination of traces of calcium in lithium salts. In both procedures the calcium is titrated with very dilute EDTA and the end-point is determined fluorometrically with Calcein as indicator. This titration is carried out in the presence of the lithium salt in one procedure; in the other, a preliminary separation of the calcium is made on the chelating exchange resin, Dowex A-1.

THE determination of small amounts of calcium in lithium compounds is of some significance owing to the detrimental effects of calcium in certain commercial uses of lithium salts. The ethylenediaminetetra-acetate (EDTA) titration offers an obvious way of circumventing the tedious gravimetric oxalate method but unfortunately the usual indicator, Eriochrome Black T, does not function properly in the presence of large amounts of lithium. We have now found that the fluorescein-methylene-iminodiacetic acid indicator (Calcein) of Diehl and Ellingboe[1] provides a fairly satisfactory fluorometric method of locating the end-point in this titration, but that if sufficient time is available greater precision can be obtained by making a preliminary separation of the calcium from the lithium with the chelating resin Dowex A–1.

Dowex A-1 is a co-polymer of divinylbenzene and styrene into which iminodiacetic acid groups have been introduced. The resin has a strong affinity for those cations which form non-ionised compounds with iminodiacetic acid and according to data published by the Dow Chemical Company,[2] calcium can be efficiently separated from sodium with this resin. This suggests that calcium might be similarly separated from lithium and this has proved true. Samples containing lithium chloride in amounts many times more than equivalent to the capacity of the resin in the column may be passed through the column; the calcium is absorbed quantitatively although only up to the point where calcium equivalent to about 1% of the capacity of the column has been taken up. The calcium is eluted with $2N$ hydrochloric acid, the acid neutralised with potassium hydroxide, and the calcium titrated with EDTA, the visual end-point with Calcein being satisfactory but the fluorometric end-point being better.

EXPERIMENTAL

Apparatus and reagents

Dowex A-1 *chelating resin column:* Seal together two lengths of borosilicate tubing, one of 15-mm inside diameter and 15 cm long and the other of 6-mm inside diameter and 10 cm long. Draw down the smaller end somewhat so that it will retain a small plug of borosilicate wool to support the resin. Connect a borosilicate nozzle of small bore to the bottom of the column by means of a piece of surgical rubber tubing so that the flow-rate can be adjusted with a screw clamp. Transfer to the column 2·0 to 2·5 ml of Dowex A-1 chelating resin in the water-swollen, salt form. The upper, larger-diameter portion of the column serves as a reservoir.

Calcein: Dissolve 0·1 g of Calcein W (the sodium salt of Calcein, available from the G. Frederick Smith Chemical Company, Columbus, Ohio) in 100 ml of water. This solution is satisfactory for several weeks. Alternatively prepare this stock solution from Calcein (the free acid, also available from the same company) by dissolving 0·1 g in 100 ml of water containing 0·5 ml of $2N$ potassium hydroxide; a solution prepared in this way is stable for only 3 or 4 days, presumably because of the excess alkali. From this stock solution prepare daily a 0·0033 % solution by diluting 1 ml of the 0·1 % solution to 30 ml with de-ionized water.

Water and other reagents. Use only demineralized water (passage through Amberlite MB-1) in making up the various solutions and in the analysis. Use hydrochloric acid and potassium hydroxide which are low in calcium as determined by running through the entire procedure but omitting the lithium chloride. Use potassium hydroxide rather than sodium hydroxide as it gives less fluorescence with Calcein.[3]

Preparation of calcium-free lithium chloride: Filter a hot, concentrated solution of lithium chloride through a sintered-glass filter of fine or medium porosity. Filter paper has no strength in hot, concentrated solutions of lithium chloride and invariably breaks under the weight of the liquid. Cool the solution to room temperature and filter off the crystals of lithium chloride which form using a sintered-glass filter. Prepare a saturated solution (about 43 %) of this lithium chloride in water and store the solution in a polyethylene bottle.

Prepare an ion-exchange column containing about 20 ml of Dowex A-1 chelating resin in the salt form. Pass 100 ml of $2N$ hydrochloric acid through the column and then 50 ml of water. Pass through the column 60 ml of $2N$ lithium hydroxide to which disodium dihydrogen ethylenediaminetetra-acetate equivalent to 6 mg of calcium has been added. Wash the column very thoroughly with water. The column is now in the lithium form and free of calcium.

Dilute the saturated lithium chloride solution to a concentration of about 100 mg per ml. Make the solution basic by the addition of 5 ml of $2N$ lithium hydroxide per litre of lithium chloride solution. Pass up to 4 litres of this solution through the column at the rate of 10 ml per min. Store the resulting calcium-free solution in a polyethylene bottle or concentrate to recover crystalline lithium chloride.

Calcium-free potassium hydroxide solution: This may be prepared with a Dowex A-1 resin column, by a procedure similar to that described for the preparation of calcium-free lithium chloride.

Photofluorometer. Two different photofluorometers were used at the two laboratories where this work was done, a Coleman Model 12 Electronic Photofluorometer provided with filters No. 12–223 (exciting beam) and No. PC-2 (fluorescent beam) and a non-commercial instrument constructed from a Sylvania 4-watt Black Lite, a Wratten K3 filter, a Weston 856RR, helium-filled Photronic photoelectric cell, and a General Electric galvanometer, 0·001 μA/mm. Pyrex test-tubes were used as cells in both instruments.

Recommended procedure for the determination of calcium in lithium salts with preliminary separation of calcium

Throughout this determination, when liquid is being passed through the column of Dowex A-1, use a flow-rate of not more than 2 ml per min. Prepare the resin column by passing through it 10 ml of $2N$ hydrochloric acid. Wash the column with 10 ml of water added in small portions. Pass 3 ml of $2N$ potassium hydroxide through the column and follow with 10 ml of water. Avoid an excess of potassium hydroxide as any calcium in it is retained by the resin. The resin approximately doubles in size on passing from the hydrogen to the potassium form. The resin should not be stored in the hydrogen form because this causes a decrease in its capacity.

Weigh 2 g of the lithium salt (chloride, bromide or sulphate) to be analysed. Dissolve it in 25 ml of water and make the solution basic with 2 or 3 drops of $2N$ potassium hydroxide. Pass the solution through the column. Wash the column with 5 ml of water. Discard the liquid which has passed through the column. Elute the calcium with 4 ml of $2N$ hydrochloric acid. Wash the column with two 3-ml portions of water. Neutralise the eluate with $2N$ potassium hydroxide and add an excess of 1 ml. Add 1 drop of 0·1 % solution of Calcein and titrate with $0{\cdot}005M$ disodium dihydrogen ethylenediaminetetra-acetate, observing the end-point visually. The end-point is marked by a sharp decrease in the fluorescent colour. The change is somewhat more easily observed under ultraviolet light. Alternatively, and with better results, the titration may be carried out as a fluorometric titration as described below.

Standardise the EDTA solution by titrating a suitable aliquot of a standard calcium solution prepared by dissolving calcium carbonate in hydrochloric acid; use Calcein as indicator.

Samples larger than 2 g may be used and as little as 0·0002% of calcium detected in lithium chloride. With larger samples use a correspondingly greater volume of water and a slightly lower flow-rate.

Procedure for the determination of calcium in lithium salts by the EDTA-Calcein-fluorometric method without prior separation

Employ procedure (A) or (B) or a slight modification thereof depending on the characteristics of the fluorometer.

(A) *Using the Coleman Model* 12 *electronic photofluorometer.* Weigh directly into a fluorometer cuvette a sample of 100 mg of the lithium salt (chloride, bromide or sulphate) to be analysed. Dissolve the sample in about 10 ml of water and make the solution basic by the addition of 1·0 ml of 2*N* potassium hydroxide. Add 5 drops of 0·0033% Calcein. Titrate with 0·00025*M* disodium dihydrogen ethylenediaminetetra-acetate.

After the addition of each increment of EDTA stir the solution by bubbling through it a stream of air introduced through a length of very small-bore polyethylene tubing. Measure the fluorescence after each addition. Plot the fluorescence intensities found against the volume of EDTA added and draw straight lines through the vertical and horizontal portions of the results. From the end-point, as indicated by the intersection of the lines, calculate the calcium in the sample.

(B) *Using the locally constructed photofluorometer with Wratten K*3 *filter.* Weigh a sample of 1 g of the lithium salt (chloride, bromide or sulphate) to be analysed directly into the fluorometer cell. Dissolve the sample in about 27 ml of water and make the solution basic by the addition of 3·0 ml of 2*N* potassium hydroxide. Add 5 drops of a 0·1% solution of Calcein. Titrate with 0·0005*M* disodium dihydrogen ethylenediaminetetra-acetate. Continue as given in the second paragraph of procedure (A) above.

RESULTS AND DISCUSSION

Several samples of lithium chloride were analysed according to the recommended procedure involving the prior separation of the calcium on the Dowex A-1 resin. Additional calcium was added to some of the samples. The results of some of the analyses are summarised in Tables I and II. It was found that owing to the very large ratio of lithium to calcium in the samples, the resin would only take up about 1% of its theoretical capacity for calcium (theoretical capacity: 15 mg of calcium for 2·5 ml of resin; limit: 1% of this or 0·15 mg of calcium). This puts a limitation on the size of the sample and the amount of calcium which can be handled in one determination. Although the method does not possess the simplicity that might be desired, it does permit the detection of as little as 0·0002% calcium.

The fluorometric titration procedure, Procedure (A), was tested on 100-mg samples of lithium chloride, purified by the ion-exchange procedure given above, to which 2–20 μg of calcium were added. The results are given in Table III. A typical titration curve for a sample containing 5 μg of calcium is shown in Fig. 1. Procedure (B) was tested on 1-g samples of various lithium salts "spiked" with various amounts of calcium; the results are given in Table III and a typical titration curve, for a sample containing 50 μg of calcium, is shown in Fig. 2.

The fluorometric titration method without prior concentration of the calcium with the Dowex A-1 resin is the more rapid of the two procedures. The precision is satisfactory, but 0·001% of calcium is the least amount that can be determined in lithium chloride by this method. Concentration of the calcium by the ion-exchange

TABLE I.—DETERMINATION OF CALCIUM IN LITHIUM SALTS BY THE RECOMMENDED PROCEDURE INVOLVING PRELIMINARY SEPARATION OF CALCIUM WITH DOWEX A-1

Lithium salt taken,	Calcium found,	
g	μg	%*
Visual end-point		
LiCl (Lot A)		
15·0	34	0·00022
20·0	34	0·00016
LiCl (Lot B)		
2·0	26	0·0011
LiCl (Lot C)		
2·0	35	0·0016
10·0	120	0·0012
Fluorometric end-point		
LiCl (Lot A)		
2·0	6·8	0·00019
2·0	6·4	0·00017
2·0	7·4	0·00022
LiCl (Lot D)		
2·0	7·1	0·00020
2·0	6·4	0·00017
2·0	6·7	0·00018
LiBr (Lot E)		
2·0	48·5	0·0023
2·0	47·5	0·0022
2·0	46·5	0·0021
Li_2SO_4 (Lot F)		
2·0	10·0	0·00035
2·0	9·7	0·00033
2·0	9·8	0·00034
Blank		
0·0	3·0	—
0·0	2·8	—
0·0	3·1	—

Lot A. Purified by Dowex A-1 method described above; average = 0·00020% calcium.

Lot B. Purified by simple recrystallisation; average = 0·0011% calcium.

Lot C. As received from Lithium Corporation of America; average = 0·0014% calcium.

Lot D. Purified by Dowex A-1 method described above; average = 0·00019% calcium.

Lot E. Commercial material, Lithium Corporation of America: average = 0·0022% calcium.

Lot F. Commercial material, Lithium Corporation of America; average = 0·00034% calcium.

* % Calcium found is calculated after subtracting the average blank, 3·0 μg, from the calcium found.

TABLE II.—DETERMINATION OF CALCIUM IN LITHIUM CHLORIDE BY THE RECOMMENDED PROCEDURE INVOLVING PRELIMINARY SEPARATION OF THE CALCIUM WITH DOWEX A-1

Lithium chloride taken, g	Calcium added, μg	Total calcium* present, μg	Calcium found, μg	Error, μg
Visual end-point				
Lot A. 20·0	200	243	196	−47
Lot B. 2·0	50	75	74	−1
2·0	100	125	120	−5
Fluorometric end-point				
Lot A. 2·0	20	26·9	28·3	+1·4
2·0	20	26·9	27·8	+0·9
2·0	20	26·9	27·6	+0·7

Lot A. Purified by Dowex A-1 method described above; value of 0.00020 % calcium (from Table 1) used in calculating total calcium present.

Lot B. Purified by simple recrystallisation; value of 0·0011 % calcium (from Table 1) used in calculating the total calcium present.

* Total calcium values include 2·9 μg added with reagents.

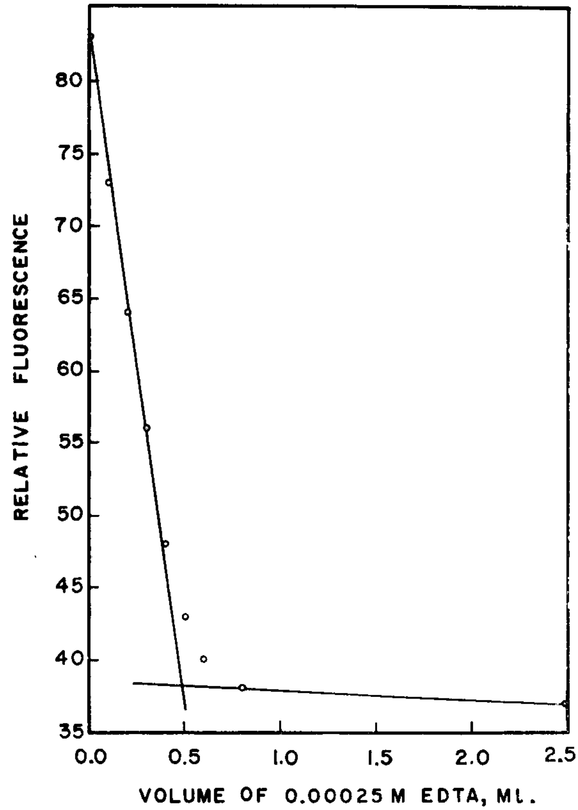


FIG. 1.—Fluorometric titration of 5 μg of calcium in 100 mg of lithium chloride with EDTA using Calcein indicator [Procedure (A), Coleman Model 12 Fluorometer].

procedure followed by the fluorometric titration extends the sensitivity to 0·0002% of calcium. The precision is good unless too large a sample is taken. The visual titration following concentration also permits the detection of as little as 0·0002% of calcium but does not possess the precision of the fluorometric titration and generally requires the use of larger samples. This, in turn, requires proportionately longer time.

The methods are applicable to lithium chloride, bromide and sulphate and undoubtedly to other lithium salts.

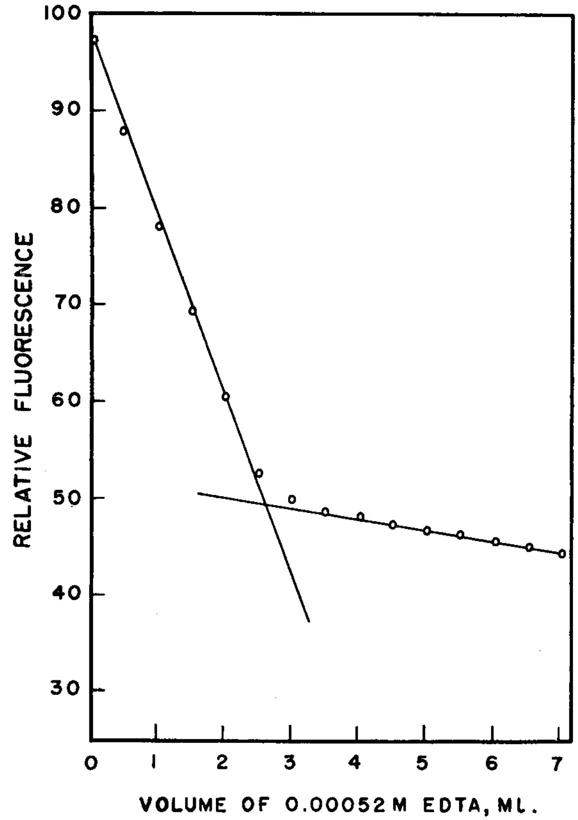


FIG. 2.—Fluorometric titration of 50 μg of calcium in 1 g of lithium chloride with EDTA using Calcein indicator [Procedure (B), Collins Fluorometer].

Magnesium, provided it is not a major constituent, does not interfere with the determination of calcium. Aluminium, up to at least 0·1%, causes no interference. Iron above 0·1% does cause interference.

Although it was reported by Diehl and Ellingboe[1] that strontium and barium are titrated together with calcium at pH 12 by EDTA using Calcein as indicator, barium was found not to interfere in the procedures described here. Thus, using 1-g samples of lithium chloride containing 26 μg of calcium (as determined by fluorometric titration) to which were added 276 μg and 552 μg of barium, 27·8 and 27·2 μg of calcium were found [Procedure (*B*)]. Also, in the presence of lithium bromide, barium is not titrated. It may be that the potassium hydroxide contained sufficient carbonate to precipitate all the barium; sodium hydroxide was used in the original procedure of

TABLE III.—DETERMINATION OF CALCIUM IN LITHIUM SALTS BY THE FLUOROMETRIC TITRATION PROCEDURE WITHOUT PRELIMINARY SEPARATION

Calcium added, μg		Total calcium present, μg	Total calcium found, μg	Error, μg
0·100-g Sample [Procedure (A) Coleman Fluorometer]				
LiCl (Lot A)*	2·0	2·2	1·5	−0·7
	2·0	2·2	2·0	−0·2
	2·0	2·2	2·2	0·0
	5·0	5·2	4·6	−0·6
	5·0	5·2	4·9	−0·3
	5·0	5·2	5·1	−0·1
	10·0	10·2	9·5	−0·7
	10·0	10·2	9·9	−0·3
	10·0	10·2	9·7	−0·5
	20·0	20·2	19·7	−0·5
	20·0	20·2	19·8	−0·4
	20·0	20·2	20·1	−0·1
1·00-g Sample [Procedure (B), Collins Fluorometer]				
LiCl (Lot D)	0·0	1·9	7·3	+5·4
	10·0	11·9	14·0	+2·1
	10·0	11·9	11·5	−0·4
	10·0	11·9	14·3	+2·4
	10·0	11·9	15·4	+3·5
	20·0	21·9	23·6	+1·7
	20·0	21·9	25·8	+3·9
	20·0	21·9	23·7	+1·8
	20·0	21·9	24·1	+2·2
	25·0	26·9	28·1	+1·2
	25·0	26·9	27·4	+0·5
	50·0	51·9	52·3	+0·4
	50·0	51·9	53·1	+1·2
	50·0	51·9	52·9	+1·0
	50·0	51·9	52·7	+0·8
	50·0	51·9	55·0	+3·1
	50·0	51·9	53·5	+1·6
	50·0	51·9	54·4	+2·5
	50·0	51·9	54·1	+2·2
	50·0	51·9	52·9	+1·0
	50·0	51·9	56·2	+4·3
	50·0	51·9	54·7	+2·8
	100·0	101·9	103·7	+1·8
	100·0	101·9	100·8	−1·1
	100·0	101·9	103·1	+1·2
	100·0	101·9	101·2	−0·7
	100·0	101·9	103·1	+1·2

Table III (*contd.*)

Calcium added, μg		Total calcium present, μg	Total calcium found, μg	Error, μg
LiBr (Lot E)	0·0	22·2	23·1	+0·9
	50·0	72·2	71·6	−0·6
	50·0	72·2	73·5	+1·3
	100·0	122·2	122·8	+0·6
Li_2SO_4 (Lot F)	10·0	13·4	21·4	+8·0
	50·0	53·4	56·7	+3·3
	50·0	53·4	55·6	+2·2
	100·0	103·4	104·1	+0·7
	100.0	103·4	104·0	+0·6
	50·0	53·4	56·3	+2·9

* Lot designations same as in Table I.

Diehl and Ellingboe but is supplanted here by potassium hydroxide because of the significantly lower fluorescence of potassium with Calcein. Strontium is not titrated in the procedure here described but does render the end-point less distinct. Zinc does not interfere at all.

Zusammenfassung—Zwei Methoden zur Bestimmung von Calcium in Lithiumsalzen werden beschrieben. In beiden Verfahren wird Calcium mit sehr verdünnter ÄDTA-Lösung titriert unter Verwendung von Calcein als Fluorescenzindicator. Bei einer Methode wird das Calcium in Anwesenheit der Lithiumsalze titriert, in der anderen wird das Calciumzverst mittels des chelierenden Ionenaustauschers DOWEX A-1 abgetrennt.

Résumé—Les auteurs décrivent deux méthodes de dosage du calcium dans les sels de lithium. Dans les 2 méthodes, le calcium est dosé avec de l'EDTA très dilué et le point équivalent est déterminé par fluorimétrie avec la calcéïne comme indicateur. Le titrage est réalisé en présence du sel de lithium dans une méthode; dans l'autre, on fait une séparation préliminaire du calcium sur une résine échangeuse d'ions Dowex A–1.

REFERENCES

[1] H. Diehl and J. L. Ellingboe, *Analyt. Chem.*, 1956, **28**, 882.

[2] The Dow Chemical Company Technical Service and Development: *Dowex Chelating Resin A*-1. Technical Bulletin Code No. 164-80. Midland, Michigan, January 1959.

[3] J. Körbl, F. Vydra and R. Přibil, *Talanta*, 1958, **1**, 281.

Talanta, 1961, Vol. 7, pp. 195 to 211. Pergamon Press Ltd. Printed in Northern Ireland

CO-PRECIPITATION IN SOME BINARY SULPHATE SYSTEMS

ALLEN I. COHEN*
Department of Chemistry, Syracuse University,† Syracuse 10, New York, U.S.A.

and

Louis Gordon®
Department of Chemistry and Chemical Engineering, Case Institute of Technology,
Cleveland 6, Ohio, U.S.A.

(*Received* 30 *September* 1960)

Summary—Studies have been made of the distribution behaviour of tracers with alkaline earth sulphates, using the technique of precipitation from homogeneous solution. The co-precipitation of strontium with barium sulphate and of lead, lanthanum, and yttrium, separately, with barium sulphate, and with strontium sulphate, were investigated. Although there was qualitative correlation between the observed values of the distribution coefficient and the theoretical solubility product ratios for each of the binary systems studied, the divergence between theory and observation was so great that it seems unlikely that there is any quantitative correlation.

I—CO-PRECIPITATION OF STRONTIUM WITH BARIUM SULPHATE

THE co-precipitation of trace impurities with barium salts as carriers has been the object of many studies, a number of which have been concerned with the application and significance of the homogeneous and logarithmic distribution equations.[1]

Several investigators have considered the effect of the fractional rate of precipitation on the logarithmic distribution coefficient.[2,3] For example, Hermann[3] precipitated lanthanum oxalate from homogeneous solution in the presence of actinium. Where the fractional rate of precipitation was constant, Hermann obtained a rate constant from a plot of "log of the carrier concentration in solution" versus "time". In experiments designed to obtain *varying* fractional rates, a plot of rate constant versus the observed distribution coefficient, extrapolated to zero rate of precipitation, gave a value of λ which Hermann designated as the "maximum (or minimum) limiting distribution coefficients". Hermann attributed the change in the distribution coefficient, *i.e.* variable co-precipitation results, to differing states of supersaturation.

Riehl[4] has also considered the effect of supersaturation on the distribution coefficient with systems in which barium chloride, with radium tracer present, was crystallised from initially quite supersaturated solutions. In Riehl's experiments, the fractional supersaturation‡ varied from nearly 1 at the beginning of precipitation to zero at the end; in contrast, Hermann has postulated that the fractional supersaturation should be constant for the process of precipitation from homogeneous solution.

---

* Present Address: Squibb Institute for Medical Research, New Brunswick, New Jersey, U.S.A.

† Work performed at Syracuse University, U.S.A.

‡ Defined as (a − b)/a, where a is the concentration of the barium in the supersaturated solution and b is the concentration of the barium in the final saturated solution.

Hermann derived a modification of the logarithmic distribution equation from Riehl's equation, assuming S′ (fractional supersaturation) to be constant:

$$\log \frac{t_f}{t_i} = \frac{\lambda}{1 + (\lambda - 1)S'} \log \frac{c_f}{c_i} \tag{1}$$

where t_f, t_i, c_f, and c_i refer to the final and initial concentrations of the tracer and carrier respectively. Where S' is zero, then the usual form of the logarithmic distribution equation, *i.e.*

$$\log \frac{t_f}{t_i} = \lambda \log \frac{c_f}{c_i} \tag{2}$$

is obtained. If the value of λ calculated from equation (2) is dependent upon supersaturation (or on the fractional rate of precipitation), this could then explain the inability to relate distribution coefficient and solubility products.[2]

Studies of the distribution behaviour of tracers with alkaline earth sulphates, using the technique of precipitation from homogeneous solution, are described in this paper. The co-precipitation of strontium with barium sulphate and of lead, lanthanum, and yttrium, separately, with barium sulphate, and with strontium sulphate, were investigated

EXPERIMENTAL

Reagents

All chemicals were reagent-grade. Barium nitrate was purified by recrystallisation from water. To prepare barium-free strontium solutions, a strontium nitrate solution was slowly evaporated and fifteen consecutive 5-g portions of the crystals were discarded; because barium nitrate is less soluble than strontium nitrate, it should concentrate in the discarded solid. The supernatant solution was then diluted to the desired concentration. The solutions of barium and strontium were also used in the later co-precipitation studies involving lead, lanthanum, and yttrium as tracers.

Sulphamic acid was purified[5] and stored in a desiccator until ready for use.

Radioactive Tracers

Both γ- and β-emitting isotopes were used. Strontium-90, from the Oak Ridge National Laboratories, was initially used as a source of carrier-free strontium. The sample was over 2 years old and it was assumed that there was no other activity present but that of strontium and its daughter yttrium-90. However, for a greater part of the study, carrier-free strontium-85, obtained from Nuclear Science and Engineering Corporation, was used because of the convenience of measuring γ activity. The half-life was found experimentally to be 65 days.[6]

High specific activity barium-133 from Oak Ridge National Laboratories was used as a source of γ activity. Barium-140, Oak Ridge National Laboratories, 12·6-day half-life, a γ- and β-emitter, was used when carrier-free barium was required.

Apparatus

A conventional single channel scintillation spectrometer with stabilised high voltage source was used both for γ-ray spectroscopy and for regular γ counting. The γ activity was determined as described by Gordon and Ginsburg.[7] The β activity was measured with an end-window proportional counter flushed with 90% argon-10% methane gas. Precipitations were carried out in the reaction vessel described by Gordon and Rowley.[8] Photometric titrations were performed in an Evelyn colorimeter and pH measurements were taken with a Beckman model H-2 line-operated pH meter.

Method of precipitation of barium sulphate

Barium sulphate was precipitated with sulphamic acid as previously described.[8] In most instances, 40 mg of sulphamic acid per 21 ml of reaction mixture were used. In all cases, 400 mg of ammonium chloride were also added to increase the particle size of the precipitate.[8] Reactions were carried out at 80°. In a few experiments the barium was precipitated for comparison purposes by direct mixing with a solution containing sulphate; in some instances, pre-formed barium sulphate was used. In experiments where the amount of strontium was made so large that the carrier in effect became strontium sulphate, the amount of added sulphamic acid was also made larger than that used in the precipitation of barium in order to decrease the time of initial precipitation of strontium sulphate; however, other conditions were essentially the same as for the precipitation of barium sulphate.

Methods of Analysis

Barium was determined either by photometric titration with EDTA[9] or by radio-assay with previously added barium-133. Strontium was determined either by photometric titration or by radio-assay with strontium-85. Carrier-free strontium-85 was determined by scintillation methods, and carrier-free strontium-90 was determined, in the presence of its daughter, by applying the unmodified form of the Kirby equation.[10] A modified equation, $a_1/A_1 = C_4/C_2$, was employed when the samples were allowed to stand for more than 2 months, where a_1 is the activity of the parent in the unknown, A_1 is the activity of the parent in the standard, C_4 is the counting rate of the mixture, and C_2 is the counting rate of the standard. Two-ml aliquots of the filtrate or of the dissolved precipitate were evaporated, then counted. The efficiency of β counting was determined with Ra-DEF standards of known activity; the concentration of the strontium-90 was thus determined to be approximately 10^{-9} *M*.

Procedure

The following were added to a 100-ml volumetric flask: an aliquot of stock barium (or strontium) nitrate solution, tracer isotope, carrier tracer if the carrier was to be determined by radio-assay, sulphamic acid, and ammonium chloride. The solution was diluted to volume and a 20-ml aliquot pipetted into the reaction cell. One ml of rinse water was used and the cells were then sealed and reacted in an oil bath at 80° ± 0·4° for a desired period of time. When the cell was opened, the filtrate and precipitate were separated by centrifugation.[8] The filtrate was then transferred to a 100-ml volumetric flask and 10 ml of concentrated ammonium hydroxide added to the solution which was then diluted to volume. The resulting solution was analysed for the appropriate alkaline earth cation either by photometric titration, by scintillation counting, or by spectroscopy. The filter frit and its solid contents were placed in a beaker to which was added 50 ml of solution which was 0·02*M* in EDTA and 6·4*M* in ammonium hydroxide. The contents were heated to 80° for several hr to dissolve the precipitate. In cases where the carrier concentration in the precipitate was determined by photometric titration, a known excess of ammoniacal EDTA solution was added and back-titrated with a standard magnesium solution. However, in most cases radio-assay was used.

RESULTS AND DISCUSSION

Precipitation of Barium in the Presence of Trace Quantities of Strontium

Experimental data and results for the co-precipitation of carrier-free strontium-90 and of strontium-85 with barium sulphate are summarised in Tables I and II. The average value of λ in Table I is 0·0143 and in Table II it is 0·0120. A much closer adherence to the logarithmic than the homogeneous distribution equation is definitely indicated. A least squares plot of the results of Table II yielded the equation, $\lambda = 0{\cdot}0114 + 0{\cdot}0009f$ where f is the fraction of barium precipitated; a least squares analysis was made only for the results of Table II because of the greater agreement among the results, which was probably due to the greater reliability of the methods of analysis.

The co-precipitation values of the two tables are plotted in Fig. 1 along with the theoretical curves for λ equal to 0·0143 and to 0·0120. The difference in the two distribution coefficients could easily be due to differences in pH and hence in the fractional rates of precipitation of the barium sulphate. Rate constants (arbitrary units) were determined in a manner analogous to that of Hermann. For the results of Table I, where the experiments were conducted at pH 0·65, the rate constant for the precipitation of barium sulphate was $-(3{\cdot}11 \times 2{\cdot}3) \times 10^{-3}$ per min. For the results of Table II, the rate constants were calculated to be $-(0{\cdot}35 \times 2{\cdot}3) \times 10^{-3}$ per min for pH 1·60,

$-(0{\cdot}58 \times 2{\cdot}3) \times 10^{-3}$ per min for pH 1·30, and $-(1{\cdot}08 \times 2{\cdot}3) \times 10^{-3}$ per min for pH 1·25. These values are in qualitative agreement with the previously published results[11] for the hydrolysis of sulphamic acid; with the fractional hydrolysis rate increasing with decreasing pH, presumably the fractional rate of precipitation of barium sulphate would also increase. At pH 0·65, the increased fractional rate of precipitation of barium sulphate would be expected, as was found, to result in a larger value of the distribution coefficient.

The fractional rate of precipitation was also increased by increasing the concentration of sulphamic acid, *i.e.* using 150 mg rather than 40 mg of sulphamic acid. The rate constant was determined to be $-(5{\cdot}95 \times 2{\cdot}3) \times 10^{-3}$ per min at pH 1·1.

TABLE I. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM-90 WITH BARIUM SULPHATE[a]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %	$\lambda \times 10^2$	$D \times 10^2$
255	26·7	0·28	0·95	0·71
		(0·37)	(1·25)	(1·06)
475	57·1	0·88	1·00	0·70
		(0·92)	(1·09)	(0·70)
597	70·2	1·20	1·00	0·52
		(1·23)	(1·02)	(0·53)
701	80·3	1·64	0·97	0·39
		(1·66)	(1·03)	(0·42)
816	90·26	2·55	1·09	0·27
		(2·41)	(1·05)	(0·27)
649	91·2	4·28	1·80	0·43
		(4·19)	(1·76)	(0·42)
723	96·57	5·73	1·75	0·22
		(5·74)	(1·75)	(0·22)
780	97·21	4·35	1·27	0·13
		(4·34)	(1·24)	(0·13)
942	97·90	4·46	1·18	0·10
780	97·92	6·93	1·85	0·16
		(7·17)	(1·93)	(0·16)
1000	98·64	3·82	0·91	0·052
1100	98·91	7·73	1·78	0·092
1315	99·02	6·72	1·50	0·074
		(6·55)	(1·46)	(0·069)
1184	99·09	5·47	1·20	0·053
		(5·37)	(1·19)	(0·052)
2750	99·25	11·37	2·47	0·090
		(10·80)	(2·34)	(0·092)
1318	99·26	8·25	1·80	0·067
		(8·21)	(1·75)	(0·067)
1392	99·35	7·43	1·53	0·053
		(7·21)	(1·49)	(0·051)
1946	99·50	9·13	1·81	0·050
		(8·97)	(1·77)	(0·050)
1987	99·56	9·60	1·88	0·049
		(9·46)	(1·85)	(0·049)

[a] 40 mg of sulphamic acid, 19·80 mg of barium, and 400 mg of ammonium chloride in 21-ml volume; final concentration of strontium-90, 2×10^{-9} *M*; pH = 0·65; reaction temperature, 80°.

[b] The results in parentheses were obtained by use of the modified Kirby equation as described in text.

The values of the distribution coefficients are given in Table III. The single experiment in the table in which only 14 mg of sulphamic acid were used gave a distribution coefficient of 0·0106 which is qualitatively correct for the much slower fractional rate of precipitation obtained. The approximately linear relationship of λ with the fractional rate of precipitation (using previously described rate constants) is shown in Fig. 2.

The value of the distribution coefficient obtained by Gordon, Reimer, and Burtt[12]

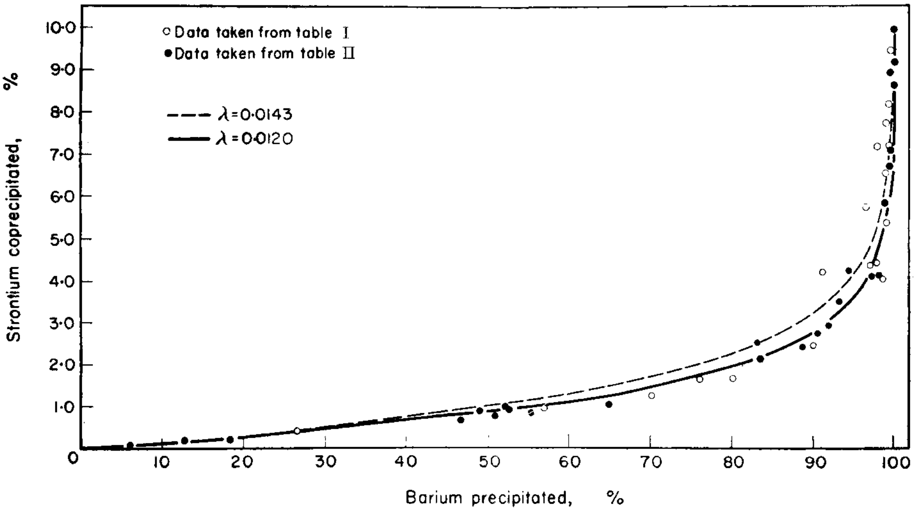


FIG. 1.—Co-precipitation of carrier-free strontium with barium sulphate.

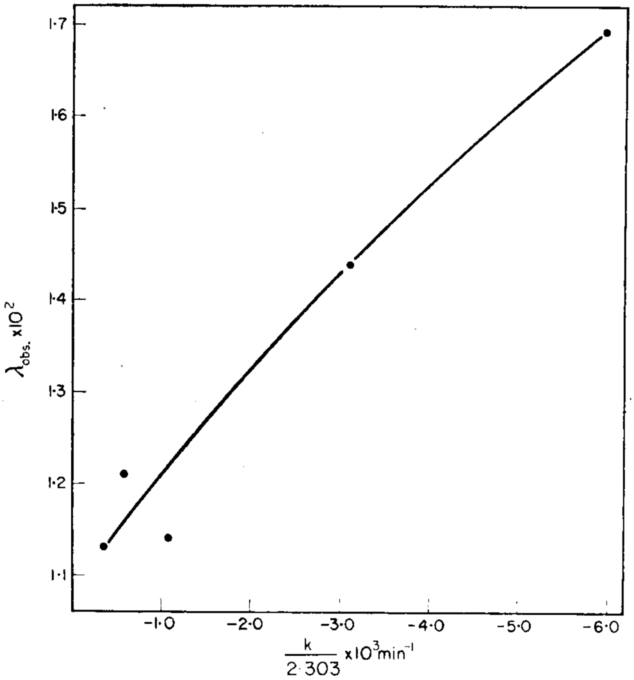


FIG. 2.—Distribution coefficient as a function of fractional rate of precipitation.

TABLE II. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM-85 WITH BARIUM SULPHATE[a]

Reaction time, *min*	pH	Method of analysis of barium[b]	Barium precipitated, %	Strontium co-precipitated, %	$\lambda \times 10^2$	D $\times 10^2$
106	1·60	T	6·2	0·071	1·30	1·08
204	1·60	T	12·8	0·18	1·31	1·23
306	1·60	T	18·4	0·18	0·88	0·80
639	1·60	T	46·7	0·63	1·00	0·72
850	1·60	T	49·1	0·84	1·25	0·88
898	1·60	T	51·0	0·74	1·04	0·72
587	1·60	T	52·2	0·93	1·28	0·87
950	1·60	T	52·7	0·87	1·17	0·79
1104	1·60	T	55·6	0·81	1·00	0·65
1232	1·60	T	65·0	0·99	0·94	0·54
1089	1·60	T	76·1	1·65	1·16	0·54
839	1·25	G	83·2	2·47	1·40	0·51
1596	1·60	T	83·5	2·12	1·19	0·43
1726	1·60	T	88·9	2·40	1·10	0·31
1906	1·60	T	90·78	2·74	1·17	0·29
1814	1·60	T	91·89	2·91	1·18	0·27
1438	1·60	T	91·90	3·10	1·25	0·28
971	1·25	G	93·28	3·49	1·32	0·26
615	1·25	G	94·46	4·26	1·50	0·26
1675	1·60	T	97·40	4·10	1·15	0·11
2185	1·60	T	98·21	4·10	1·04	0·078
1141	1·25	G	98·82	5·86	1·36	0·074
2466	1·60	T	99·37	6·71	1·37	0·046
2151	1·60	T	99·37	7·11	1·46	0·049
898	1·30	G	99·83	7·74	1·23	0·014
3619	1·60	T	99·85	9·96	1·61	0·017
1295	1·25	G	99·90	6·78	1·02	0·0073
1053	1·30	G	99·90	9·16	1·39	0·048
2713	1·60	T	99·90	8·62	1·31	0·0094
759	1·30	G	99·91	7·31	1·10	0·0079

[a] 40 mg of sulphamic acid, 19·80 mg of barium, 400 mg of ammonium chloride, 1 microcurie of barium-133 (where used), and 20 microcuries of strontium-85; reaction temperature, 80°.

[b] T indicates determination of barium by photometric titration with EDTA; G indicates determination of barium by γ counting of barium-133; determination of strontium was by γ counting of strontium-85.

in 20% methanol solutions by the hydrolysis of methyl sulphate at 83° was 0·03 for several different ratios of carrier to tracer concentrations. The differences between this value and those obtained in the present study may be attributed either to a significant difference in the fractional rate of precipitation, or to variation in the carrier to tracer ratios, or to the media used. For example, in their study, 15 hr were required to precipitate 94% of the barium while in the present study the time necessary to precipitate 92% of the barium was approximately 32 hr, which could easily account for the larger constant obtained, *i.e.* 0·03.

Experiments were performed in which there was direct mixing of solutions of barium and sulphate, where the fractional rate of precipitation would be considerably increased. The results are shown in Table IV. The value of λ was approximately 1·0 (for the first two experiments of the table conducted at the lower temperature of 25°).

It is somewhat difficult to compare this value of λ obtained at 25° with previous values of λ ($\simeq$0·01) obtained at 80° because of the temperature dependence of the distribution coefficient. However, a value of λ approaching unity would be expected for rapid precipitation regardless of temperature. Perhaps more striking are the results for the last two experiments of Table IV in which λ was determined to be 0·027 for the slower method of precipitation and to be 0·22 for the rapid method, after a long period of digestion which could only have served to reduce the latter value from some previously greater value.

TABLE III. EFFECT OF CHANGE OF FRACTIONAL RATE OF PRECIPITATION UPON CO-PRECIPITATION[a]

Reaction time, *min*	Sulphamic acid, *mg*	Barium precipitated, %	Strontium co-precipitated, %	$\lambda \times 10^2$	D $\times 10^2$
5839	14·0	86·3	2·09	1·06	0·34
105	150·0	54·3	1·26	1·62	1·08
156	150·0	85·8	3·40	1·77	0·58
201	150·0	87·8	3·47	1·68	0·45
429	150·0	99·50	15·25	3·54	0·095
255	150·0	99·83	10·20	1·69	0·019
480	150·0	99·80	15·62	2·73	0·37
375	150·0	99·86	12·67	2·09	0·021

[a] 19·80 mg of barium, 400 mg of ammonium chloride, 1 microcurie of barium-133, and 10 microcuries of strontium-85; pH = 1·1; reaction temperature, 80°; analyses of barium and strontium were performed by scintillation spectrometry.

TABLE IV. EFFECT OF METHOD OF PRECIPITATION ON DISTRIBUTION COEFFICIENT[a]

Reaction time, *min*	pH	Reaction temperature, °*C*	Method of precipitation	Method of analysis		Barium precipitated, %	Strontium co-precipitated, %	λ	D
				Carrier	Tracer				
120	0·65	25	Direct mixing	b	c	98·82	98·69	0·98	0·90
120	0·65	25	Direct mixing	b	c	98·82	98·41	0·97	0·84
14490	1·25	80	Homogeneous[d]	e	e	99·91	16·30	0·027	0·0002
14490	1·25	80	Direct mixing	e	e	99·83	75·40	0·22	0·005

[a] 19·80 mg of barium, 54 mg of ammonium sulphate, 1 microcurie of barium-133 (where used), and 20 microcuries of strontium-85.

[b] Barium determined by photometric titration with EDTA.

[c] Strontium determined by β counting (Kirby method).

[d] 40 mg of sulphamic acid used in place of ammonium sulphate.

[e] Barium and strontium both determined by scintillation spectroscopy.

Variation of the Mole Fraction Ratio of Barium to Strontium

Several experiments were performed in which the mole fraction of barium in the initial barium-strontium mixture (0·144 millimoles total) ranged from 0·896 to virtually zero, *i.e.* for the precipitation of strontium sulphate in the presence of a trace quantity of carrier-free barium-140. In general, conditions were employed similar to those of the previous experiments where barium was precipitated in the presence of carrier-free strontium (*cf.* Table II) with the exception that the pH was made 1·25 in all cases.

Analysis of the various mixtures was usually made by utilising both barium-133 and strontium-85 in the reaction mixtures; where barium-140 was used, the strontium present was determined by photometric titration with EDTA and Phthalein Purple as indicator. In those instances involving the precipitation of carrier-free barium with strontium it was also necessary to use a quantity of sulphamic acid larger than 40 mg (either 60 or 400 mg were employed) because strontium sulphate did not begin to precipitate even after more than 1·5 days when a quantity of 40 mg of sulphamic acid was used.

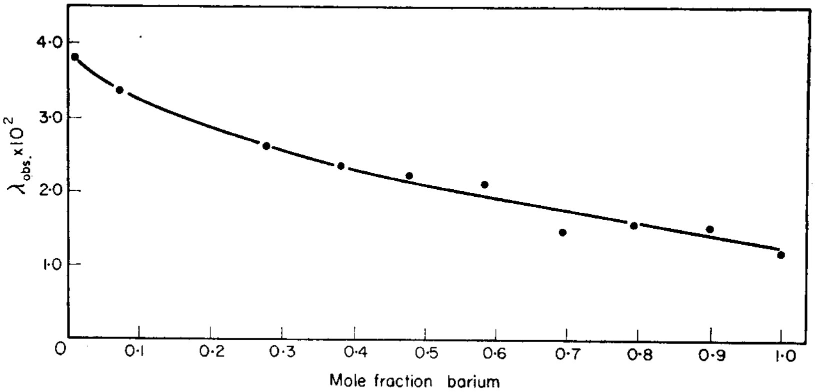


FIG. 3.—Change in distribution coefficient with mole fraction of barium. The value of λ = 1·2 (mole fraction of barium = 1) is taken from Table II.

In Fig. 3 are plotted the average values of λ for each experiment to show the variation of the distribution coefficient with mole fraction (except for the values for the co-precipitation of carrier-free barium-140 with strontium sulphate). Each point on the curve represents the average in most instances of four separate precipitations. Because 1 microcurie, 0·24 mg of barium, of high specific activity barium-133 used in these experiments, could by itself be precipitated with 40 mg of sulphamic acid, it must be assumed that the barium has in all cases acted as the carrier for strontium, except where carrier-free barium-140 was used; the latter, in the quantity normally used could not be precipitated in any appreciable quantity.

TABLE V. CO-PRECIPITATION OF CARRIER-FREE BARIUM WITH STRONTIUM SULPHATE[a,b]

Reaction time, *min*	pH	Sulphamic acid added, *mg*	Barium co-precipitated, %	Strontium precipitated, %	$\lambda \times 10^2$	$D \times 10^2$
1373	1·20	60·0	33·85	5·87	14·6	12·2
1790	1·20	60·0	98·89	55·14	17·8	1·38
1473	1·20	60·0	91·61	20·05	8·59	2·30
1540	1·20	60·0	99·94	29·28	4·67	0·0249
298	1·10	400·0	26·60	9·33	31·6	28·4
347	1·10	400·0	68·8	12·6	11·5	6·52
405	1·10	400·0	96·75	21·1	6·92	0·90

[a] 0·144 millimoles of strontium, 400 mg of ammonium chloride, 1 microcurie of varium-133, and 2 microcuries of strontium-85; reaction temperature, 80°.

[b] Carrier and tracer analyses were made by scintillation spectrometry.

The results for the co-precipitation of carrier-free barium with strontium sulphate, shown in Table V, are quite erratic; no explanation can be given for the lack of agreement within these results.

Effect of Digestion on the Co-precipitation of Strontium with Excess Barium Present

By using 14 mg of sulphamic acid it was possible to precipitate only 95% of the barium present as is shown in Table VI. The extent of co-precipitation of the added strontium-85 increased only very slightly with time, the increase being of the order of 0·06% per 1000 min over the approximately 7000 min digestion period.

TABLE VI. EFFECT OF DIGESTION ON CO-PRECIPITATION OF STRONTIUM WITH BARIUM SULPHATE[a, b]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %	λ $\times 10^2$	D $\times 10^2$
9246	95·29	2·40	0·88	0·13
13022	95·29	2·60	0·86	0·13
16427	95·19	2·83	0·95	0·15

[a] 19·80 mg of barium, 14 mg of sulphamic acid, 1 microcurie of barium-133, 2·0 microcuries of strontium 85, 400 mg of ammonium chloride; pH = 1·1; reaction temperature, 80°.

[b] Carrier and tracer analyses were made by scintillation spectrometry.

Co-precipitation of Strontium upon Pre-formed Barium Sulphate

Pre-formed barium sulphate was prepared by precipitating stable barium, with barium-133 present, from homogeneous solution. This resulted in a precipitate containing about 1 microcurie of activity per 34 mg of barium sulphate. Twenty ml of solution containing 0·4 g of ammonium chloride and carrier-free strontium-85 were added to the 34 mg of active barium sulphate in the reaction cell, along with 1 ml of rinse water, and allowed to react for various periods of time at 80°. The results of several experiments are shown in Table VII and indicate that the co-precipitation is about the same as that obtained when the barium is precipitated from homogeneous solution.

TABLE VII. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM UPON PREFORMED BARIUM SULPHATE IN ABSENCE OF EXCESS SULPHATE[a]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %
33	100	1·72
70	98·94	2·94
90	97·34	2·80
92	98·20	2·72
160	98·31	3·18
2668	98·29	5·28
4080	99·63	6·42
5305	99·16	6·02
10170	98·93	5·98
18748	99·15	5·43
34500	98·60	6·57

[a] Carrier and tracer analyses made by scintillation spectrometry.

Similar experiments were performed in which 32·6 mg of ammonium sulphate were added to determine the effect of excess sulphate. As shown in Table VIII, the co-precipitation of strontium is quite extensive and increased with time of digestion.

Effect of Temperature on the Co-precipitation of Strontium

Barium sulphate was precipitated from homogeneous solution at 90°; the results are shown in Table IX. Although the distribution coefficient is greater (*cf.* 2×10^{-2} at 90° with $1{\cdot}4 \times 10^{-2}$ at 80°), it is difficult to determine the exact cause of the increased co-precipitation. This might be attributed to the increase in the fractional hydrolysis rate of the sulphamic acid, hence an increase in fractional precipitation rate. Distribution coefficients at various temperatures should be compared only at identical fractional precipitation rates.

TABLE VIII. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM UPON PREFORMED BARIUM SULPHATE IN PRESENCE OF EXCESS SULPHATE[a]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %
40	100	16·5
407	100	31·5
786	100	36·6
1455	100	49·7

[a] Carrier and tracer analyses made by scintillation spectrometry.

TABLE IX. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM WITH BARIUM SULPHATE AT 90°[a,b]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated %	$\lambda \times 10^2$	$D \times 10^2$
175	57·4	1·72	2·04	1·30
257	97·76	7·62	2·09	0·19
328	99·30	10·66	2·27	0·054
384	99·87	11·43	1·83	0·017

[a] 19·80 mg of barium, 1 microcurie of barium-133, 2·0 microcuries of strontium-85, 40 mg of sulphamic acid, and 400 mg of ammonium chloride; pH = 1·3.

[b] Carrier and tracer analyses made by scintillation spectrometry.

II—CO-PRECIPITATION OF LEAD WITH (A) BARIUM SULPHATE AND WITH (B) STRONTIUM SULPHATE

ALTHOUGH Popov[13] has reported that lead is co-precipitated only on the surface of barium sulphate crystals, other workers[14] have considered that the co-precipitation of lead for this system follows the homogeneous distribution law. These conflicting claims warranted a further study of this system by the present techniques.

From the solubility products, it would be predicted that lead would co-precipitate with barium sulphate by derichment in the crystal, *i.e.* a distribution coefficient less than 1. In the other case, the co-precipitation of lead with strontium sulphate should occur by enrichment in the crystal.

EXPERIMENTAL

Radioactive tracers

(*a*) *Lead with barium sulphate.* Barium-133 was employed as the carrier isotope. Lead-210 (Radium D), half-life 19·4 years, Atomic Energy of Canada Ltd., was used as tracer. Lead-210 is the parent in the decay scheme of bismuth-210, half-life 5 days, and polonium-210, half-life 138 days.[6] Fresh samples were used because they showed no high-energy γ peak, whereas aged samples indicated the presence of polonium-210.

(*b*) *Lead with strontium sulphate.* Strontium-85 was used as carrier isotope and lead-210 as tracer.

Procedures

(*a*) *Lead with barium sulphate.* The general procedure used in the study of the co-precipitation of strontium with barium sulphate was employed except for the substitution of 2·0 g of ammonium nitrate for ammonium chloride; 40 mg of sulphamic acid were used in all cases. The maximum concentration of lead present was calculated to be $1{\cdot}4 \times 10^{-6}$ *M*. Analyses were performed by scintillation spectrometry to determine both carrier and tracer concentrations.

(*b*) *Lead with strontium sulphate.* The procedure used in the precipitation of lead was identical with that for the co-precipitation of lead with barium sulphate except for the use of 60 mg of sulphamic acid. Analyses were performed by scintillation spectrometry.

RESULTS AND DISCUSSION

The results of Table X and Fig. 4 indicate co-precipitation by derichment of lead with barium sulphate and a much closer adherence to the logarithmic than to the homogeneous distribution equation. The average value of λ is equal to 0·188. In a separate experiment, it was found that considerably more lead co-precipitated with the barium when the latter was precipitated by the direct addition of sulphate.

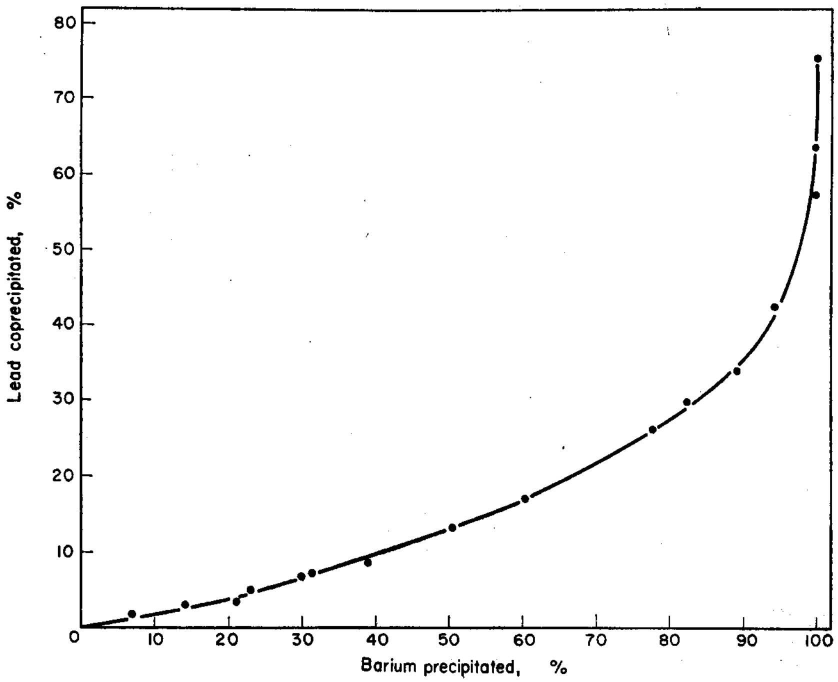


FIG. 4.—Co-precipitation of lead with barium sulphate.

The results of Table XI and Fig. 5 confirm co-precipitation by enrichment of lead in the strontium sulphate. Adherence of the results to the logarithmic distribution equation is only slightly better than to the homogeneous distribution equation.

III—CO-PRECIPITATION OF LANTHANUM AND OF YTTRIUM WITH (A) BARIUM SULPHATE AND WITH (B) STRONTIUM SULPHATE

CO-PRECIPITATION studies similar to the preceding have usually involved tracer and carrier ions of similar charge, *e.g.* radium and barium. However, there have been a few studies involving dissimilarly charged ions, *e.g.* zinc with iron^{III} periodate,[7] manganese^{II} with basic tin^{IV} sulphate,[15] rare earths with thorium iodate,[16] and yttrium with barium sulphate[12]

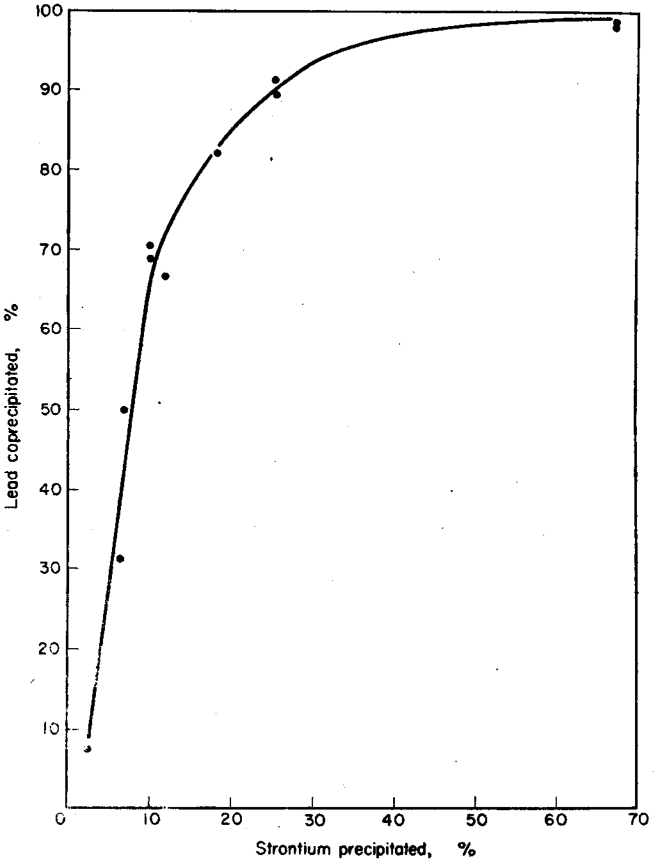


FIG. 5.—Co-precipitation of lead with strontium sulphate.

EXPERIMENTAL

Radioactive tracers

Barium-133 and strontium-85 from the previous investigations were used. Lanthanum-140 was prepared by separating it from barium-140 by precipitation of barium nitrate in fuming nitric acid;[17] the half-life of the lanthanum-140 was determined to be 40 hr. Yttrium-90 was separated from its parent, strontium-90, in a similar manner. Its half-life was determined to be the same as the reported value, *i.e.* 64 hr.

Procedure

The procedures used for the co-precipitation of lanthanum were similar to those for the co-precipitation of strontium with barium sulphate and lead with strontium sulphate. Analyses were by scintillation spectrometry.

The procedure used with yttrium in the case of barium sulphate was that of direct precipitation with ammonium sulphate in order to provide a comparison with a previous study in which barium sulphate was precipitated from homogeneous solution.[12] To a 21-ml volume of solution (containing 0·144 millimole of strontium or barium, 400 mg of ammonium chloride, and yttrium isotope) 47 mg of ammonium sulphate were added. The reaction mixture was allowed to stand for 60 min at 25°, the phases separated by centrifugation and analysed. Yttrium-90 was assayed by scintillation spectroscopy. Its high-energy β-rays were converted to bremsstrahlung (X-ray photons), through interaction of the β-rays with 0·6-cm aluminium absorbers placed between the sample and the scintillation crystal. Yttrium-90, through the resultant 55 Kev radiation, could thus be assayed by scintillation spectrometry in the presence of the other γ-emitters.

TABLE X. CO-PRECIPITATION OF LEAD WITH BARIUM SULPHATE

Reaction time, *min*	Barium precipitated, %	Lead co-precipitated, %	λ	D
80	5·87	1·47	0·245	0·239
145	14·1	2·86	0·192	0·179
117	21·0	3·18	0·137	0·124
200	23·0	4·76	0·187	0·167
180	30·0	6·59	0·191	0·165
270	31·2	7·02	0·195	0·166
169	39·0	8·51	0·131	0·145
450	50·4	13·1	0·200	0·148
259	60·3	15·92	0·188	0·125
720	77·7	26·3	0·203	0·102
312	82·4	29·8	0·204	0·0907
873	89·1	33·9	0·187	0·0626
496	94·12	42·39	0·195	0·0460
600	99·60	57·1	0·153	0·00534
1156	99·66	63·5	0·177	0·00593
1099	99·81	75·33	0·223	0·000581

TABLE XI. CO-PRECIPITATION OF LEAD WITH STRONTIUM SULPHATE

Reaction time, *min*	Strontium precipitated, %	Lead co-precipitated, %	λ	D
365	2·44	7·68	3·23	3·33
368	7·02	49·9	9·50	13·2
482	6·49	31·3	5·60	6·57
435	10·0	70·6	11·6	2·16
389	10·6	69·0	10·4	18·8
345	11·9	66·8	8·70	14·9
482	18·3	82·2	8·54	20·6
413	25·4	89·7	7·76	25·6
451	25·4	91·4	8·37	31·2
482	54·0	98·67	5·56	63·3
540	67·3	98·58	3·80	33·7
575	67·3	97·95	3·48	23·2
[a]	74·1	94·47	2·14	5·97

[a] Strontium precipitated by direct addition of sulphate.

When strontium was used as the carrier (0·144 millimole), it was precipitated from homogeneous solution by the addition of ten times the stoichiometric amount of sulphamic acid (t = 80°).

RESULTS AND DISCUSSION

Co-precipitation of lanthanum with barium sulphate is by derichment in the crystal and is appreciable only in the range where 95 to 100% of the barium sulphate is precipitated as is indicated by Fig. 6 and Table XII. Although calculations (not shown) indicated that the system did not adhere very closely to either distribution equation, this should not preclude actual conformity to either type of distribution because of the

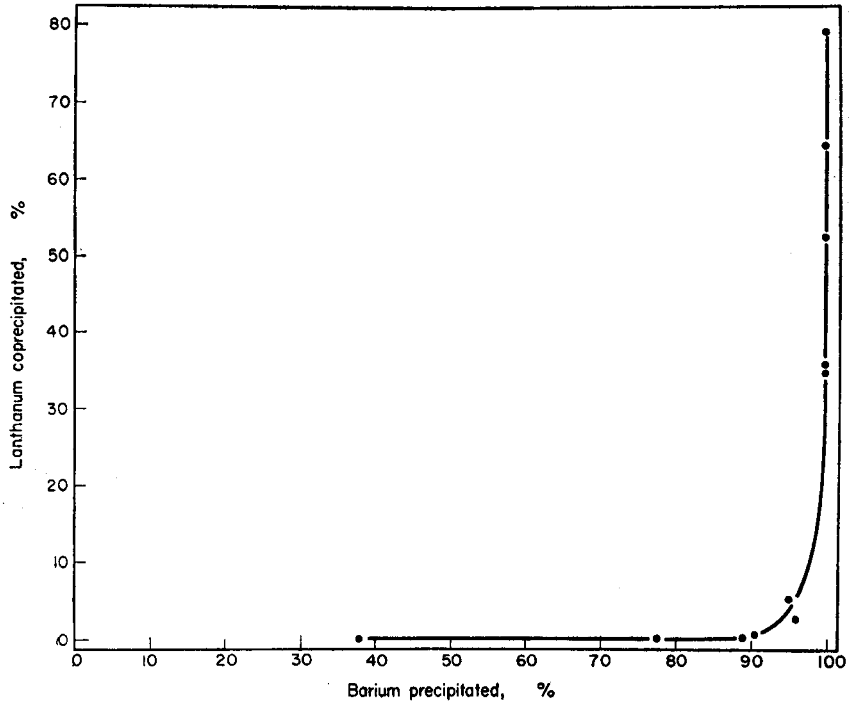


Fig. 6.—Co-precipitation of lanthanum with barium sulphate.

Table XII. Co-precipitation of lanthanum with barium sulphate

Reaction time, *min*	Barium precipitated, %	Lanthanum co-precipitated, %
431	77·5	0·17
539	88·5	0·69
568	90·76	1·23
636	95·91	2·66
760	95·40	5·35
846	98·94	9·0
1070	99·25	21·5
1132	99·25	25·3
1262	99·51	36·0
1341	99·53	35·0
1745	99·47	64·3
1310	99·53	52·2
1950	99·50	79·3
a	99·9	87·5

[a] Barium precipitated by direct addition of sulphate; precipitate digested for 60 min.

experimental uncertainties of analysis in the present case and particularly because of the limited range over which the data were obtained.

Co-precipitation of lanthanum with strontium sulphate is by enrichment in the crystal. The results are shown in Table XIII. Calculations of the distribution coefficients, λ and D, show that the logarithmic distribution equation is more closely obeyed than is the homogeneous distribution equation. Modified distribution equations[18] have been derived which show a functional dependence of distribution coefficient upon initial concentration of carrier ion if the carrier and tracer ions are of dissimilar charge. The two initial concentrations of strontium used in the present case were so slightly different that it was not possible to determine this functional dependence. The values of λ and D in Table XIII were calculated from the unmodified equations.

TABLE XIII. CO-PRECIPITATION OF LANTHANUM WITH STRONTIUM SULPHATE

Reaction time, *min*	Strontium precipitated, %	Lanthanum precipitated, %	λ	D
Sulphamic acid added: 400 mg; initial concentration of strontium: $8{\cdot}2 \times 10^{-3}\ M$				
265	1·74	2·92	1·69	1·70
343	47·8	74·9	2·13	3·26
445	47·7	81·1	2·57	4·70
373	60·4	85·7	2·10	3·93
392	64·9	86·7	1·93	3·53
491	71·9	92·06	2·00	4·53
543	76·2	96·47	2·33	8·54
Sulphamic acid added: 400 mg; initial concentration of strontium: $8{\cdot}7 \times 10^{-3}\ M$				
300	11·8	13·0	1·11	1·12
360	44·0	56·4	1·43	1·65
425	74·1	90·0	1·71	3·15
570	82·9	98·3	2·31	11·9
Sulphamic acid added: 60 mg; initial concentration of strontium: $8{\cdot}2 \times 10^{-3}\ M$				
1277	1·11	0·96	0·351	0·86
1544	10·9	12·4	1·15	1·16
1650	22·4	37·8	1·87	2·11
Direct addition of sulphate				
0	84·6	85·8	1·04	1·10

The co-precipitation of yttrium with barium sulphate precipitated from homogeneous solution with dimethyl sulphate has been shown[12] to be negligible up to 95% of the barium precipitated. In the present case, even though a conventional procedure was employed, the quantity of yttrium co-precipitated with barium sulphate or with strontium sulphate was also found to be negligible. For example, when the barium was virtually completely precipitated, only 0·8% of the yttrium co-precipitated; when 75·3% of the strontium was precipitated, only 1·04% of the yttrium co-precipitated.

The result obtained with the rare earths indicate the possibility of fractionation of rare earth isotopes. For example, yttrium did not co-precipitate with barium sulphate whereas lanthanum could be made to co-precipitate extensively. Thus, a considerable fractional separation of these rare earth isotopes could be attained. From the results obtained, it would appear that strontium sulphate could be used in a similar manner.

CONCLUSIONS

The systems studied generally showed a much closer adherence to the logarithmic distribution equation than to the homogeneous equation. The characteristic slight change[19] of distribution coefficient with change in the fraction of carrier precipitated is evident in varying degrees in the present systems.

The observed (average) values of the logarithmic distribution coefficients for the several systems studied are shown in Table XIV along with the theoretical values of the distribution coefficients calculated from the solubility product ratios.[20] It should be noted that only in the case of the strontium-lead system is there any close correlation between the observed and the theoretical values of the distribution coefficients; this may be a purely fortuitous case inasmuch as the other systems, and studies of some rare earth oxalate systems[2] as well, have not shown the predicted correlation. In view of the dependence of the distribution coefficient upon fractional precipitation rate, it seems unlikely that such a correlation exists. The only correlation which did hold in all of the present cases was a qualitative relationship between solubility product ratio and the experimentally observed value of the distribution coefficient, *i.e.* whether impoverishment or enrichment would occur.

TABLE XIV. COMPARISON OF $\lambda_{\text{observed}}$ AND $\lambda_{\text{theoretical}}$

Carrier	Tracer	λ_{obs}	$\lambda_{\text{calc}} = \dfrac{K_{sp}(\text{carrier})}{K_{sp}(\text{tracer})}$	$\dfrac{\lambda_{\text{calc}}}{\lambda_{\text{obs}}}$
Barium	Strontium	0·012	$8{\cdot}17 \times 10^{-4}$	$6{\cdot}81 \times 10^{-2}$
Barium	Lead	0·188	$9{\cdot}24 \times 10^{-3}$	$4{\cdot}91 \times 10^{-2}$
Barium	Radium	1·133[a]	$1{\cdot}31 \times 10^{4}$	$9{\cdot}85 \times 10^{3}$
Strontium	Barium	3·13 to 14·5	$1{\cdot}22 \times 10^{3}$	$3{\cdot}90 \times 10^{2}$ to $8{\cdot}41 \times 10^{1}$
Strontium	Lead	8·20	$1{\cdot}13 \times 10^{1}$	1·38
Strontium	Lanthanum	1·87	$1{\cdot}33 \times 10^{1}$	7·11

[a] Extrapolated from data of Gordon and Rowley.[8]

Although the theoretical significance of the coefficient in the logarithmic distribution equation remains unknown, the equation itself can be used empirically to predict the extent of co-precipitation (for various fractions of the carrier precipitated) under a prescribed set of reaction conditions if the average value of the distribution coefficient has been obtained experimentally. This would have practical application in separation processes in which precipitation from homogeneous solution is employed.

Acknowledgement—The authors wish to acknowledge the partial assistance of the United States Atomic Energy Commission under Contracts AT(30-1)-1213 and AT(11-1)-582.

Zusammenfassung—Unter Heranziehung der Methode der Fällung aus homogener Lösung wurden die verteillungseigenschaften von "Tracern" mit Erdalkalisulfaten studiert. Die Mitfällung von Strontium mit Bariumsulfat sowie von Blei, Lanthan und Yttrium (jedes für sich) mit Barium und Strontiumsulfat wurde untersucht. Wenn auch eine qualitative Beziehung zwischen den beobachteten Verteillungskoeffizienten und den theoretischen Werten der Löslichkeitsprodukte für jedes der Studierten binären Systeme festgestellt werden konnte, so war die Abweichungen zwischen Theorie und beobachteten Werten so gross, dass eine quantitative Beziehung als unwarhscheinlich angenommen werden musste.

Résumé—Les auteurs ont étudié le fonctionnement au point de vue partage des traceurs avec des sulfates alcalino-terreux, en utilisant la méthode de précipitation en solution homogène. Les co-précipitations du strontium avec le sulfate de baryum, et du plomb, du lauthane et de l'yttrium, séparèment avec le sulfate de baryum et avec le sulfate de strontium, ont été étudiées. Bien qu'il y ait une relation qualitative entre les valeurs observées du coefficient de partage et les rapports théoriques des produits de solubilité pour chacun des systèmes binaires étudiés, la divergence entre la théorie et l'expérience est si grande qu'il semble improbable qu'il existe une relation quantitative.

REFERENCES

[1] L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution.* John Wiley and Sons, Inc., New York, 1959.
[2] A. M. Feibush, K. Rowley and L. Gordon, *Analyt. Chem.*, 1958, **30**, 1605.
[3] J. A. Hermann, Ph.D. Dissertation, University of New Mexico, 1956.
[4] N. Riehl, *Z. phys. Chem.*, 1936, **A177**, 224.
[5] M. J. Butler, G. F. Smith and L. F. Audrieth, *Analyt. Chem.*, 1938, **10**, 690.
[6] J. Tobailem, *Ann. Phys.*, 1955, **10**, 783.
[7] L. Gordon and L. Ginsburg, *Analyt. Chem.*, 1957, **29**, 38.
[8] L. Gordon and K. Rowley, *ibid.*, 1957, **29**, 34.
[9] A. I. Cohen and L. Gordon, *ibid.*, 1956, **28**, 1445.
[10] H. W. Kirby, *ibid.*, 1952, **24**, 1678.
[11] S. H. Maron and A. R. Berens, *J. Amer. Chem. Soc.*, 1950, **72**, 3571.
[12] L. Gordon, C. C. Reimer and B. P. Burtt, *Analyt. Chem.*, 1954, **26**, 842.
[13] M. A. Popov, *Zavodskaya Lab.*, 1955, **21**, 1430.
[14] I. M. Kolthoff and G. E. Noponen, *J. Phys. Chem.*, 1938, **42**, 237.
[15] L. Gordon, H. Teicher and B. P. Burtt, *Analyt. Chem.*, 1954, **26**, 992.
[16] K. J. Shaver, *ibid.*, 1956, **28**, 2015.
[17] M. L. Salutsky and H. W. Kirby *ibid.*, 1955, **27**, 567.
[18] L. Gordon, *Rec. Chem. Progress*, 1956, **17**, 125.
[19] M. L. Salutsky, J. G. Stites and A. W. Martin, *Analyt. Chem.*, 1953, **25**, 1677.
[20] *Handbook of Chemistry and Physics.* Chemical Rubber Publishing Company, Cleveland, Ohio, 35th Ed, 1953–54.

Talanta, 1961, Vol. 7, pp. 212 to 214. Pergamon Press Ltd. Printed in Northern Ireland

A NEW PROCEDURE FOR PREPARATION OF ANHYDROUS PERCHLORIC ACID EMPLOYING ANHYDROUS MAGNESIUM PERCHLORATE

G. FREDERICK SMITH
The Noyes Laboratory, University of Illinois, Urbana, Illinois, U.S.A.

(*Received* 3 *October* 1960)

Summary—The dehydration of hydrated perchloric acid to yield anhydrous acid is described. Anhydrous (5·5% water content) magnesium perchlorate is employed as desiccant followed by distillation under reduced pressure. The new procedure is less complicated than previously described processes, and is convenient for the preparation of small amounts to be employed in studies of the preparation of anhydrous metallic perchlorates from reactions with suitable selected reagents, and for convenient lecture demonstrations.

INTRODUCTION

THE earliest investigation of anhydrous perchloric acid was made by Roscoe in 1863.[1] The first study of the preparation of oxonium perchlorate, OH_3ClO_4, as well as of other perchloric acid hydrates, was included, namely, $OH_3ClO_4 \cdot H_2O$, which was later shown to exist in two forms, α and β, with distinctive melting points. More extensive studies of these and higher hydrates were made by van Wyk[2] and by van Emster.[3] A more thorough study of these perchloric acid hydrates was provided by Smith and Goehler.[4] The anhydride of perchloric acid, chlorine heptoxide, Cl_2O_7, was first prepared by Michael and Cohn,[5] (b.p. at ordinary pressures 82°).

The multiple simultaneous separation by distillation of anhydrous perchloric acid, oxonium perchlorate and higher perchloric acid hydrates, was described by Goehler and Smith.[6] Distillation of dioxonium perchlorate at 8 to 18 mm pressure was employed for this separation. The large scale preparation of anhydrous perchloric acid by reduced pressure distillation of mixtures of fuming sulphuric acid and dioxonium perchlorate was described by Smith.[7]

The preparation of crystalline oxonium (perchlorate m.p. 49·905°)[8] is best performed by the reaction of anhydrous perchloric acid with dioxonium perchlorate by use of the following reaction:

$$HClO_4 + O_2H_5ClO_4 \rightarrow 2OH_3ClO_4.$$

The present work provides a dry distillation of aqueous perchloric acid by reaction with anhydrous magnesium perchlorate, and it is a convenient procedure for lecture demonstration as well as for the preparation of small samples of the anhydrous acid for immediate usage. Since the anhydrous perchloric acid is not stable upon long storage, the above reaction is always followed and provides a product which may be readily employed in reconversion to the anhydrous acid by distillation at reduced pressure and at 110° by the reaction:

$$OH_3ClO_4\ (110^\circ \text{ in vacuo}) \rightarrow HClO_4 + O_2H_5ClO_4.$$

The anhydrous acid forms the distillate and the 73·6% perchloric acid remains in the still pot.

EXPERIMENTAL

Reagents

Partially dehydrated magnesium perchlorate dihydrate, (app. 5% H_2O): commercially available.

Hydrated perchloric acid, 72·5% to 85%, the water azeotropic composition or stronger acid: *dioxonium perchlorate* or acid of lower water content such as oxonium perchlorate. These items are commercially available.

Dry ice for refrigeration of the cold finger distillation receiver.

Apparatus

A description, with line drawing, of the apparatus has been given by Smith.[7]

Procedure

The chilled perchloric acid for dehydration is added to the still pot in small increments and is mixed well after the addition of the anhydrous magnesium perchlorate. The proportions employed are 17–20 g of acid to 100 g of the desiccant. The latter is added in 10- to 20-g increments to 4- to5-g portions of acid, with stirring to ensure effective contact between acid and desiccant.

The still pot is then connected to the cold finger in a Dewar flask chilled by use of finely-divided dry ice. The cold finger distillate receiver is connected to the vacuum pump with an intermediate acid absorbing scrubbing tower containing Ascarite or Mikohbite to prevent any passage into the vacuum pump of acid vapours not condensed in the cold finger. The distillation is started at room temperature and the still pot is slowly heated to a maximum of 70° employing an electrically energised Glas-Col heating mantle with variable voltage energy source. A reduced pressure of 0·25 to 0·5 mm is required and the time of the distillation is 8 to 10 hr for most complete accumulation of anhydrous acid formed. A yield of 85% or better is thus provided.

If the preparation of anhydrous perchloric acid is not for use within a few hrs (12–24), there is, at room temperature, the gradual accumulation of decomposition products which gradually colour the acid yellow, then brown, and finally black at which point after 10–14 days at room temperature an explosion ensues. Storage at liquid air temperatures materially extends this time limit. The impurity thus accumulated is postulated to be ozone.

A minor contaminant of the distilled anhydrous acid is found to be the anhydride of perchloric acid, chlorine heptoxide. It is formed by dehydration in greater proportion if the reaction mixture is not distilled immediately after the preparation is provided. Its presence is shown by the fact that dilution of the anhydrous perchloric acid with sufficient water to form oxonium perchlorate leaves the chlorine heptoxide content unchanged for 72 to 96 hr before it reacts with water to form, first anhydrous perchloric acid, followed by conversion to oxonium perchlorate.

In all of the manipulations herein described it is well to keep in mind that anhydrous perchloric acid in contact with organic material produces violent explosions. If the ground-glass joints require some material to make them more effective, use perchloric acid for this purpose. Silicone greases explode in contact with anhydrous perchloric acid. The reaction between water and anhydrous perchloric acid is extremely exothermic. For this reason the conversion to oxonium perchlorate is best made by the addition of 72·5% perchloric acid until the acid is solid at approximately 50° melting point. Oxonium perchlorate (84·8% $HClO_4$) is stable indefinitely at ordinary temperatures. Its reaction, while less likely to produce explosions in contact with organic matter than the anhydrous acid, is still a hazard in contact with carbonaceous products. Chlorine heptoxide is known to be explosive when heated or subject to shock.

On the other hand 70·0 to 73·6% perchloric acid is a remarkably stable product. It may be distilled at ordinary pressure at 200–203° with but slight decomposition and this process may be employed in its purification. Dioxonium perchlorate, $O_2H_5ClO_4$ (73·605% $HClO_4$), has been described in preparation as a standard of reference in acidimetry.[9] Assuming that 10 ml of 70–72·5% perchloric acid are employed in a routine control laboratory analysis in the steel industry, cement, leather, and agricultural feed industries, there are one hundred and fifty million individual analyses carried out annually which owe their outstanding effectiveness to the use of this acid. Such widespread applicability belies the implication that reactions employing perchloric acid are hazardous. Chemists thoroughly familiar with the chemistry of perchloric acid and its salts are richly rewarded in its multiplicity of productive applications.

Zusammenfassung—Die Dehydration hydrierter Perchlorsäure zu wasserfreier Säure wird beschrieben. Wasserfreies (5·5% Wassergehalt) Magnesiumperchlorat wird als wasserentziehendes Mittel verwendet, mit anschliessender Destillation unter vermindertem Druck. Die Methode ist weniger kompliziert als früher beschriebene Verfahren und bequem um kleine Mengen wasserfreier Säure herzustellen, wie sie in den Studien zur Bereitung von wasserfreien Metallperchloraten oder für Demonstrationszwecke gebraucht werden.

Résumé—L'auteur décrit la déshydration de l'acide perchlorique hydraté pour obtenir de l'acide anhydre. Du perchlorate de magnésium anhydre (contenant 5,5 pour cent d'eau) est employé comme desséchant; une distillation sous pression réduite suit cette première opération. Cette nouvelle méthode est moins compliquée que celles décrites précèdemment; elle convient pour la préparation de faibles quantités à employer dans l'étude de la préparation des perchlorates métalliques anhydres à partir de réactions utilisant des réactifs convenablement choisis; elle convient aussi pour des démonstrations commodes de conférence.

REFERENCES

[1] H. E. Roscoe, *J. Chem. Soc.*, 1863, **16**, 82.
[2] H. J. van Wyk, *Z. anorg. Chem.*, 1902, **32**, 115.
[3] K. van Emster, *ibid.*, 1907, **52**, 270.
[4] G. Frederick Smith and O. E. Goehler, *Ind. Eng. Chem. Analyt.*, 1931, **3**, 61.
[5] A. Micheal and W. T. Cohn, *Amer. Chem. J.*, 1900, **23**, 444.
[6] O. E. Goehler and G. Frederick Smith, *Ind. Eng. Chem. Analyt.*, 1931, **3**, 55.
[7] G. Frederick Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 184.
[8] G. Frederick Smith and O. E. Goehler, *ibid.*, 1931, **3**, 58.
[9] G. Frederick Smith and W. W. Koch, *ibid.*, 1931, **3**, 52.

Talanta, 1961, Vol. 7, pp. 215 to 231. Pergamon Press Ltd. Printed in Northern Ireland

INFRARED SPECTRA OF SOME ORGANO-PHOSPHORUS EXTRACTANTS*

C. A. HORTON and J. C. WHITE
Analytical Chemistry Division, Oak Ridge National Laboratory†
Oak Ridge, Tennessee, U.S.A.

(*Received* 15 *July* 1960)

Summary—The infrared spectra of a group of organo-phosphorus compounds useful for extraction of metals from acidic aqueous solutions are presented and discussed. The spectra of a few organo-phosphorus degradation products or probable impurities are also included. Many of the organic groups responsible for some of the absorption bands are identified.

IN this paper the infrared spectra of a number of organo-phosphorus compounds which are under consideration for the extraction of various metal ions from aqueous solution are presented and discussed. The spectra of a few of the phosphorus compounds expected to occur as impurities in such extractants are also included. An attempt is made to assign some of the absorption bands to vibrations caused by specific functional groups. Other infrared investigations of less pure samples of these compounds and the spectral changes observed during various purification steps will be discussed in a subsequent report.

The functional group assignments of the bands are based on prior general correlations of the spectra of typical organo-phosphorus compounds.[4,6,7,10,11,15,17,18,19,24,27,29,31,33,37,42] Also, spectra of compounds located in catalogues by use of the A.S.T.M.-Wyandotte I.B.M. cards, and spectral reports concerning butyl phosphates,[2,11,14,15,33,35] cyclic ethers,[16] di-*n*-butyl hydrogen phosphate,[1,5,11,35] di-2-ethylhexylphosphoric acid,[5,38] dialkylphosphonates and phosphine oxides,[15,34] phosphates and phosphonates,[15] tri-*n*-butyl phosphate,[2,3,4,6,9,12,13,15,21,23,30,35,36,40] and trimethylphosphine[28] proved of value for this investigation. Discussions of hydrogen or phosphoryl inter- or intra-molecular bonding and shifts in frequency of absorption bands with changes in other substituents[8,12,25,26,32,34,39,41,43] were also helpful.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Infracord, Model 137, spectrometer with sodium chloride optics was used to record the infrared spectra for most of the compounds. A Perkin-Elmer Model 21 spectrometer was used to obtain spectra of the remaining compounds. Sodium chloride window cells of nominal path lengths of 0·05, 0·2, and 1·0 mm were used for recording spectra of solutions and sodium chloride windows were used for film spectra.

Reagents

All materials used for preparing solutions or drying them were of reagent grade. The organo-phosphorus compounds investigated were commerical grade, purified commercial grade, or synthesised and purified in this laboratory.

---

[*] Part of a paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 29 February–4 March, 1960.

[†] Work performed under contract W-7405-eng-26 with the Union Carbide Corp. for the U.S. Atomic Energy Commission.

Procedure

Solutions containing about 20% (w/v) or 1 mole/litre of the organo-phosphorus compound to be investigated were prepared in carbon tetrachloride or carbon disulphide. These were diluted by volume as necessary to ascertain the position and relative intensity of strong absorption peaks. Where traces of water were expected or solutions were turbid, the solutions were dried with anhydrous calcium or sodium sulphate, or potassium carbonate before recording the spectra. Spectra were recorded in cells of various path lengths, using reference cells of the same path lengths filled with pure solvent. In a few cases spectra of thin films on sodium chloride plates were recorded. Regions of very high absorbance for the solvents are omitted in the figures.

RESULTS

In Table I are listed the spectra presented in the figures with notes concerning the source or treatment of the samples.

TABLE I. COMPOUNDS INVESTIGATED BY INFRARED SPECTRA

Fig. No.	Name of compound	Source*	% in CCl_4	Treatment
1	Tricaprylphosphate	A	18·4	
2	Octanol-2	E	16·9	
3	Caprylphenylphosphonic acid	A	27·0	
			5·4	
4	Di-*sec*-butylphenylphosphonate	A	20·2	Dried anhyd. Al_2O_3
5	Di-*n*-butylhydrogenphosphonate	A	19·8	
6	Tri-*n*-butylphosphite	G	25·0	
7	Tris-*iso*propylphosphite	G	20·8	
			8·3	Treated 1 pellet KOH
8	Tri-*n*-octylphosphine oxide	B	19·3	
9	Tri-*n*-octylphosphine oxide	A	†	
10	Tris-(2-ethylhexyl)-phosphine oxide	A	6·7	
11	Tris-(*iso*-octyl)-thiophosphate	C	†	
12	1-Phenyl-3-*iso*hexenyl-1-phospha-3-cyclopentene-P-oxide	D	20·3	
13	Di-*n*-butylphosphoric acid	G	21·0	
14	Tri-*n*-butylphosphate (impure)	F		Distillation residue
15	Tri-*n*-butylphosphate (purer)	F		Purified by solvent washing treatments

* A Synthesised or purified at ORNL
B Eastman
C Penninsular Chemical Co.
D DuPont
E Reagent grade
F Obtained during purification treatments
G Commercial, technical grade of unknown purity
† Films, not solution

DISCUSSION

The spectra of the solvents recorded versus air were similar to previously published spectra.[3] Carbon tetrachloride spectra in the 6·4 μ (1560 cm^{-1}) and 12 to 14 μ (715 to 835 cm^{-1}) regions were unsuitable for use owing to over-compensation of a band and very high absorbance, respectively. Although carbon disulphide is usually used only for the 7·5 to 15 μ (655 to 1335 cm^{-1}) region, spectra obtained between 2·3 to 3·3, 3·7 to 4·2 and 4·9 to 5·9 μ were useful in this study and bands observed for the organo-phosphorus extractants in these regions confirmed those observed using carbon tetrachloride as solvent. Since neither of these solvents contain C-H groups, solute-solvent hydrogen bonding effects were minimal in the spectra.

Although cyclohexane, xylene, or saturated aliphatic hydrocarbons are generally preferable to carbon tetrachloride or carbon disulphide as diluents for extractions, their complex spectra made the former solvents unsuitable for this infrared study.

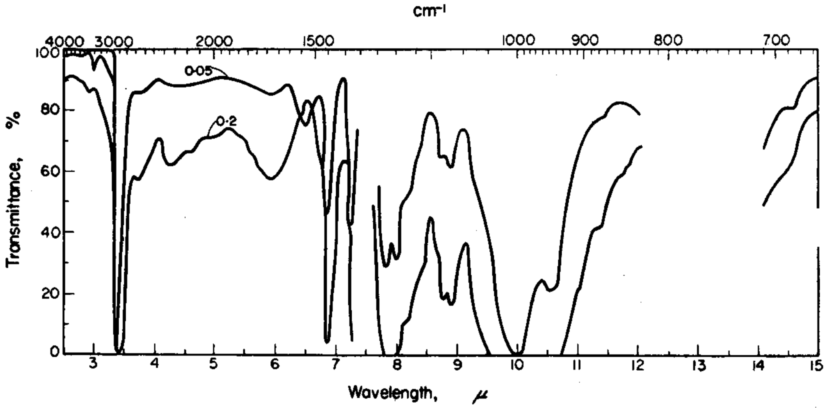


FIG. 1.—Tricaprylphosphate

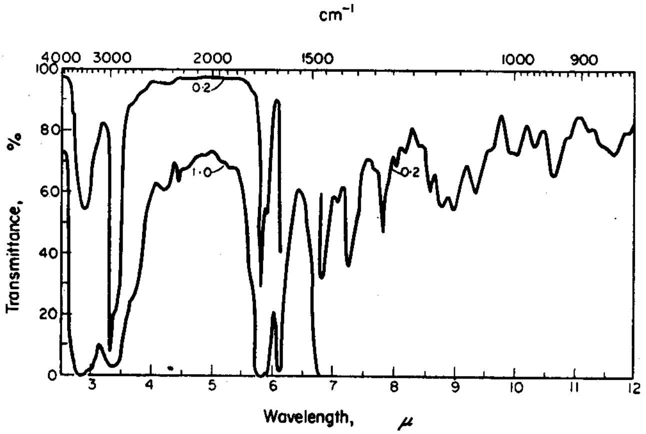


FIG. 2.—Octanol-2

A. *Tricaprylphosphate*. The infrared spectrum of our purest sample of tricaprylphosphate, $(CH_3\text{—}(CH_2)_5\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}O\text{—})_3\ P \rightarrow O$, is presented in Fig. 1. This may be compared to the spectrum of octanol-2 (capryl alcohol), Fig. 2. The alcohol shows a band at 3355 cm^{-1} attributable to an —OH vibration of a loose polymer hydrogen-bonded type, while the phosphate has a band at 3560 cm^{-1} attributable to a single-bridged intermolecular hydrogen-bonded type —OH vibration. The CH_3- and CH_2-stretching (2960 and 2920 cm^{-1}), —CH_2 scissor (1465 cm^{-1}), C-H bending (1380), and methyl rocking (1140) vibrations are at the same positions for both compounds. In Fig. 1, the strong band at 1255 cm^{-1} is due to the phosphoryl, P → O, stretching vibration, calculated to appear at 1176 cm^{-1};[8] whereas the 1160 and strong 1000 cm^{-1} bands are due to C—O—(P—) or (C)—O—P vibrations and the 970 and 940 cm^{-1} bands to vibrations of the C—O—P type.

Like other samples of this phosphorus compound, a trace of acidic impurity is indicated by the shoulder at 2700 cm^{-1}, typical of P—OH type compounds. The band at 2380 cm^{-1} is indicative of some unreacted alcohol in the phosphate rather than a P—H type impurity, inasmuch as the alcohol has a strong band at 2380 cm^{-1}.

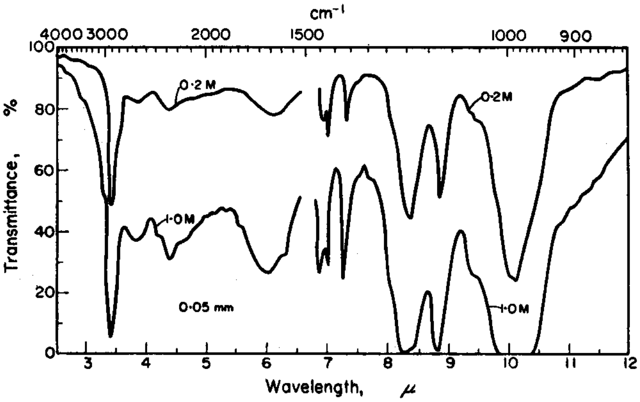
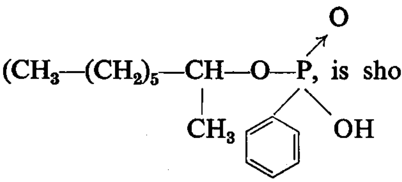
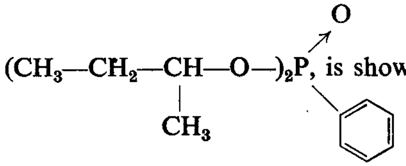


FIG. 3.—Caprylphenylphosphonic acid

B. *Caprylphenylphosphonic acid.* The spectrum of caprylphenylphosphonic acid,


$(CH_3-(CH_2)_5-CH(CH_3)-O-P(\rightarrow O)(C_6H_5)-OH)$, is shown in Fig. 3. It is a composite of the spectra of octanol-2, phosphonic acid, and mono-substituted benzene except for the absence of the 3355 cm^{-1} band of the alcohol, Fig. 2. The P—OH group vibration band is centred at 2640 cm^{-1}, a broad band with an absorbance of only 0·42 in a 1-mm cell for a 1M solution. The bands in the 2200 to 2400 cm^{-1} region indicate some phosphine P—H impurities in the preparation. The broad group of partially resolved bands between 2200 and 2400 cm^{-1} are probably phenyl vibrations. The phosphoryl stretching band is the band at 1240 cm^{-1}, as calculated.[8] The strong band at 1130 cm^{-1} is the P—O-aryl vibration, and the still stronger band at 985 cm^{-1} is due to P—O—R group vibrations. Another strong band at 685 cm^{-1}, not shown in Fig. 3, is due to the mono-substituted aromatic group. The bands at about 2900, 1450, and 1350 cm^{-1} are also noted in the alcohol spectrum; the 1060 cm^{-1} shoulder is due to a P—O—C (alkyl) vibration; the 1430 cm^{-1} band is probably attributable to an aromatic type vibration.

C. *Di-sec-butylphenylphosphonate.* The spectrum of di-*sec*-butylphenylphosphonate,  is shown in Fig. 4. Several bands present are also noted in the spectra of 2-butanol given in the N.B.S. catalogue, Serial Nos. 431 and 750,[36] as well as bands typical of mono-substituted aromatic compounds. Such common bands are: the 2950, 1670, 1460, 1385, and 1250 cm^{-1} bands of the alcohol, the 3000 cm^{-1} region $\rangle$CH band, 4 typical mono-substituted aromatic bands in the 1600–2000 cm^{-1} region, and 5 more at 1460, 1175, 1130, 1070, and 1040 cm^{-1}. The bands of less definite assignment are: ~2600 cm^{-1}, R—O or P—OH; 2400–2200, phenyl or P—H impurities; ~1000 P—O—R (alkyl); 1327 or 1310 cm^{-1} P → O, calculated to be 1307 cm^{-1}.[8] The band at 3470 cm^{-1}, a hydrogen-bonded OH vibration, is probably due to alcohol, an impurity, and was more prominent in other samples. The bands in the 1650 to 2000 cm^{-1} and 2750 cm^{-1} regions also indicate traces of unreacted alcohol are present. The 690 cm^{-1} band is typical of mono-substituted aromatics.

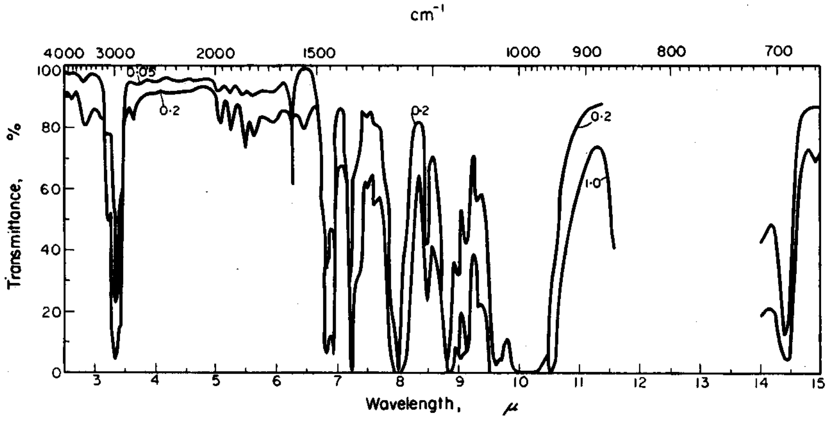
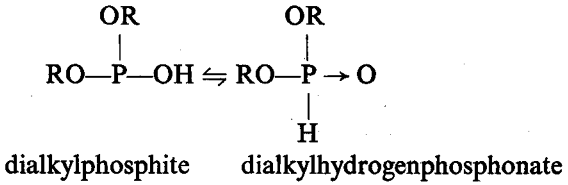


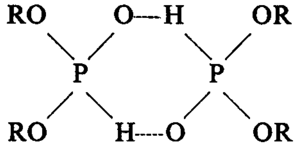
FIG. 4.—Di-*sec*-butylphenylphosphonate

D. *Dibutylhydrogenphosphonate.* The spectrum of a sample submitted as dibutylphosphite, of empirical formula $C_8H_{19}O_3P$, is presented in Fig. 5. Examination of the absorption peaks indicates the presence of a P—H grouping at 2428 cm^{-1}, and a probable P → O phosphoryl grouping at 1247 cm^{-1}, with only a weak broad shoulder in the 2800 cm^{-1} region where P—OH bands normally occur. Thus the indicated structure approaches that of the dibutylphosphite keto isomer, dibutylhydrogenphosphonate, as shown below.



$$\begin{array}{ccc} \text{OR} & & \text{OR} \\ | & & | \\ \text{RO—P—OH} & \leftrightharpoons & \text{RO—P} \rightarrow \text{O} \\ & & | \\ & & \text{H} \\ \text{dialkylphosphite} & & \text{dialkylhydrogenphosphonate} \end{array}$$

As prior discussions[39] have indicated, the actual structure of the compound submitted may be dimeric:



This structure would account for, at least in part, the hydrogen-bonded hydroxy vibration noted at 3500 cm^{-1}.

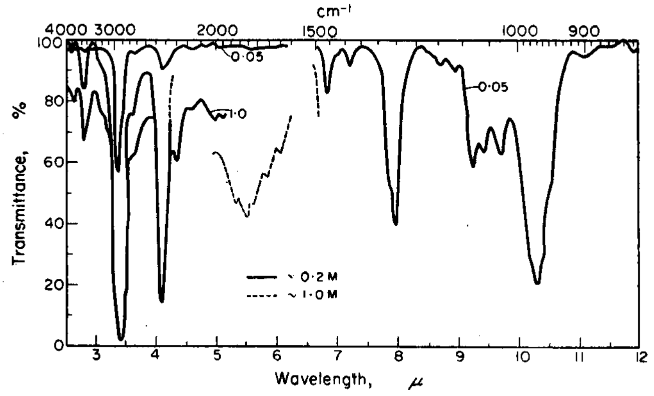


FIG. 5.—Di-*n*-butylhydrogenphosphonate

The experimental spectrum can be compared to spectra reported by others, including: Sadtler No. 9041,[40] Fox,[22] Bellamy-Beecher,[11] and also the typical bands for phosphorus compounds containing butoxy groups according to McIvor and co-workers.[33] Many bands are at about the same positions as expected and of appropriate intensity. The bands noted between 1615 and 2185 cm^{-1} (4·55 to 6·2 μ) for the 1·0-mm path spectrum were not noted in the prior studies with shorter path lengths. The band at 1375 cm^{-1} attributable to an R—O—P vibration is stronger than noted by McIvor's group. The band at 1248 or that at 1137 cm^{-1} may be the phosphoryl vibration, calculated to appear at 1254 cm^{-1}.[8] The 980 cm^{-1} band of the Sadtler spectrum was not noted in our scan, but other bands at 968 and 952 cm^{-1} in Fig. 5 were not in the Sadtler spectrum. The low frequency vibrations below 850 cm^{-1} anticipated from McIvor's work could not be observed in a carbon tetrachloride solution.

The bands in the 4·55 to 6·2 μ region cannot be assigned, owing to lack of correlations for this region. They may be harmonics, combination, or difference bands of fundamentals in lower frequency regions. Alternatively, they may be attributed in part to minor impurities. Similar bands appear in Fox's spectrum.[22]

The spectrum of Fig. 5 can also be compared to Daasch's most recent spectrum of this compound[20] which is likewise similar in most respects. However, the band at 1080 cm^{-1} in Fig. 5 is stronger than that at 1020 cm^{-1} whereas the situation is reversed in Daasch's spectrum. The bands for the Sadtler spectrum in this region are too intense for comparison. The intensity ratio for these bands in Fig. 5 is similar to that observed by Bellamy and Beecher.[12]

E. *Trialkylphosphites.* The spectra of samples of tri-*n*-butyl- and tris-*iso*propyl-phosphites, respectively, are presented in Figs. 6 and 7. The spectrum of the former can be compared to a spectrum published previously by Daasch and Smith,[19] and butoxy group positions indicated by McIvor and coworkers.[33] The bands of Fig. 7 can be compared with other isopropoxy group assignments.[33] Each spectrum can be also compared with the other and the general organo-phosphorus group vibrational correlations. Both of these phosphite samples show slight absorption in the 3400–3550 cm^{-1} region typical of hydrogen-bonded OH. This absorption is assumed to be due to impurities in the samples.

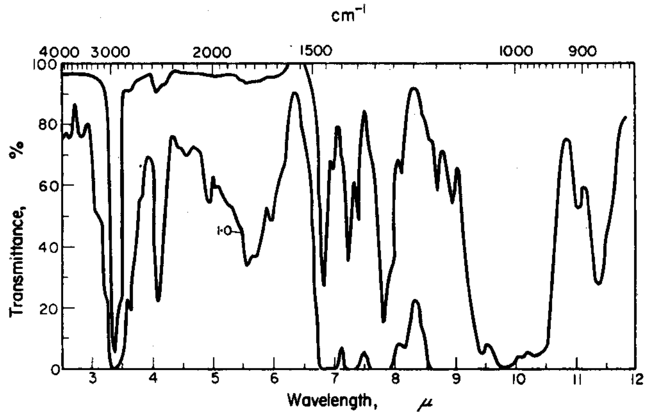


FIG. 6.—Tri-*n*-butylphosphite

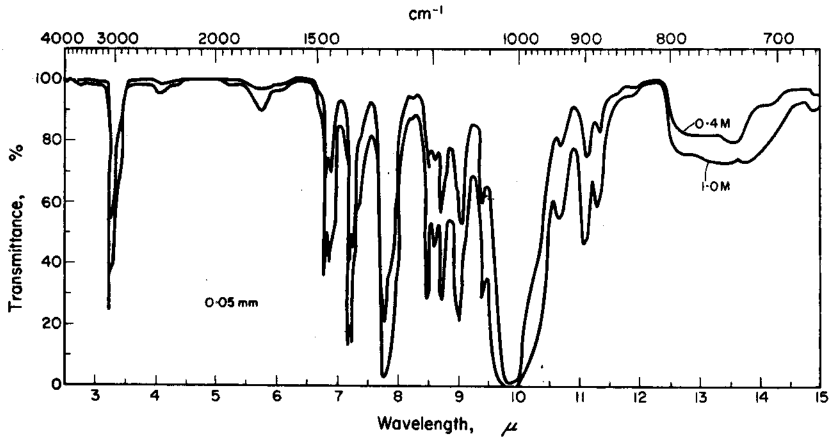


FIG. 7.—Tri-*iso*propylphosphite

For the tributyl phosphite, Fig. 6, the C—H stretching vibration is at 2950 cm^{-1} compared to 2940 cm^{-1} estimated from the literature.[20] Bands occur at 2910, 2750, 2440, 1990, 1905, 1795, 1685, 1625, 1430, 1265, and 880 cm^{-1} which were not observed in the spectrum reported previously, while the early spectrum has bands at 2780, 2380, 2335, 1490, and 955 cm^{-1} not noted in our spectrum. All the bands typical of butoxy groups[33] are apparent in both spectra.

For the tris-*iso*propylphosphite, Fig. 7, bands are noted at approximately all the positions typical of the *iso*propoxy, $(CH_3)_2CHO$, group[33] except that the weak band at 1184 cm^{-1} was not noted and the 1108 to 1114 cm^{-1} band is replaced by either the 1136 or 1096 cm^{-1} bands.

The 1·0-mm spectrum of the tributyl compound has a band shoulder near 2750 cm^{-1} typical of P—OH bands, probably indicating the presence of some type of impurity in the sample.

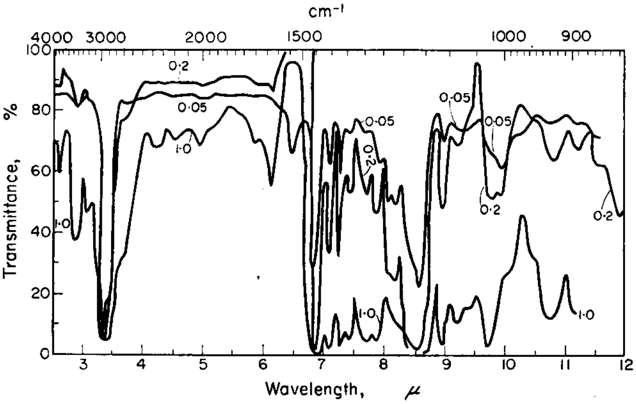


FIG. 8.—Tri-*n*-octylphosphine oxide

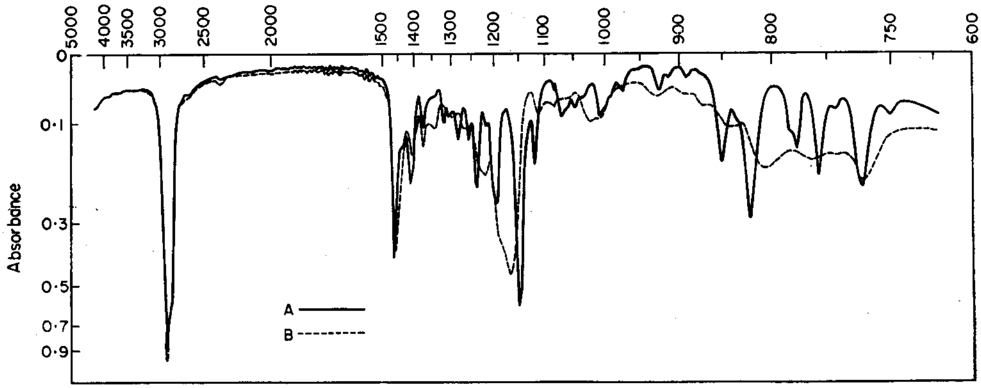


FIG. 9.—Tri-*n*-octylphosphine oxide A: solid (film) B: Liquid (film)

It is somewhat surprising how weak the absorption is near 2400 cm^{-1} due to the P—H grouping in both phosphites.

F. *Tri-n-octylphosphine oxide.* The spectrum of tri-*n*-octylphosphine oxide (TOPO) is shown in Figs. 8 and 9. This compound now has wide use as an analytical extractant. The complete spectrum has not previously been published. One study[34] reports that the phosphoryl stretching frequency occurs at 1142 cm^{-1} as a solid and at 1170 cm^{-1} in carbon disulphide solution. From our studies the frequencies for this $P \rightarrow O$ grouping are as shown in Table II.

This band is calculated to appear at 1177 cm^{-1},[8] or 1167 cm^{-1}.[43]

The spectrum was compared to the spectra given in the literature for *n*-octane and octanol-1. Several of the bands noted for the phosphine oxide occur at the same position as in the comparison spectra. Others appear which are typical of organophosphorus compounds.

The ~2900 cm^{-1}, 1460, 1140, 1116, 821, 760, and 720 cm^{-1} bands in the TOPO spectra correspond to similar bands in the hydrocarbon, alcohol, or both. The first three of these are the C—H stretching, bending, and skeletal frequencies; while the last, 720 cm^{-1}, is the CH_2 rocking vibration which appears in linear hydrocarbon derivatives containing 4 or more methylene groups.

TABLE II. PHOSPHORYL VIBRATION POSITIONS FOR TOPO

State	$P \rightarrow 0$, *cm*$^{-1}$
Solid film	1143
Liquid film	1165
CCl_4 solution	1154
Cyclohexane solution	1192 or 1171

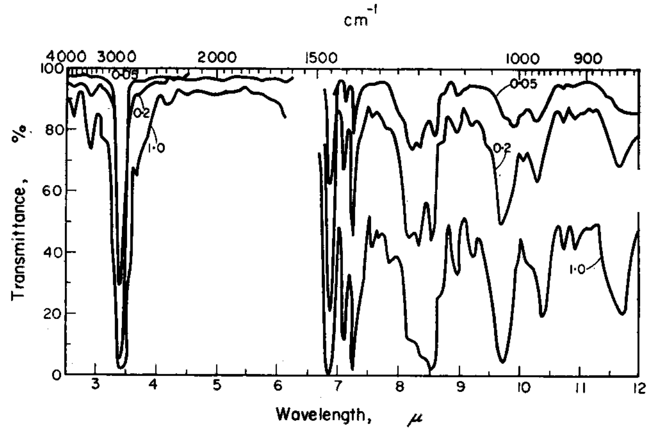


FIG. 10.—Tris-(2-ethylhexyl)-phosphine oxide (purified) (in CCl_4)

Unfortunately, no good correlation occurs for P—C compounds in the literature. Although bands in the 715 to 770 cm^{-1} region have been attributed to this vibration,[42] other work,[11,12] as well as the similar bands of hydrocarbon derivatives noted in the previous paragraph, indicate a band in this region may be due to other types of vibrations.

G. *Tris-(2-ethylhexyl)-phosphine oxide.* The spectrum of a sample of tris-(2-ethylhexyl)-phosphine oxide in carbon tetrachloride is displayed in Fig. 10. In the spectrum several absorption bands can be identified. These include: 3345 cm^{-1} H-bonded OH impurity, 2915 and 2865 C—H stretching, 1447 CH_3 deformation and $C—H_2$ scissor, 1390 CH_3 sym. deformation, 1155 phosphoryl stretching (1160 in CS_2, 1150 as solid film) and, not shown, the ~720 cm^{-1} CH_2 rocking vibrations. The band at 2780 cm^{-1} may be a tertiary carbon stretching vibration. The phosphoryl frequency tris-(*iso*-octyl)-thiophosphate is calculated to appear at 1177 cm^{-1}. [8]

H. *Tris-(iso-octyl)-thiophosphate.* The spectrum of a commercial sample of tris-*iso*-octylthiophosphate, $(C_8H_{15}O)_3\ P \rightarrow (S)$, is presented in Fig. 11. Hooge and Cristen[28] cite bands in the 550 to 750 cm^{-1} regions as due to the P → S group; Nyquist,[37] 715 to 760 cm^{-1}; and Bellamy,[10] 850 to 600 cm^{-1}. Bellamy remarks that this absorption usually is weak. Thomas, as cited by Bellamy, assigns a narrower range of 800 to 845 cm^{-1} for trialkylthiophosphates. In Fig. 11 a very broad absorption band is shown with maximum intensity at 820 cm^{-1}, probably due to the P → S group. Other bands identifiable are the CH bands at ~2900 and 1450, and the 1000 cm^{-1} P—O—C (alkyl) bands. The shoulder near 2650 cm^{-1} indicates the presence of P—OH as an impurity; the band at 2350 cm^{-1}, P—H as an impurity; and the band near 1870 cm^{-1}, an unidentified impurity.

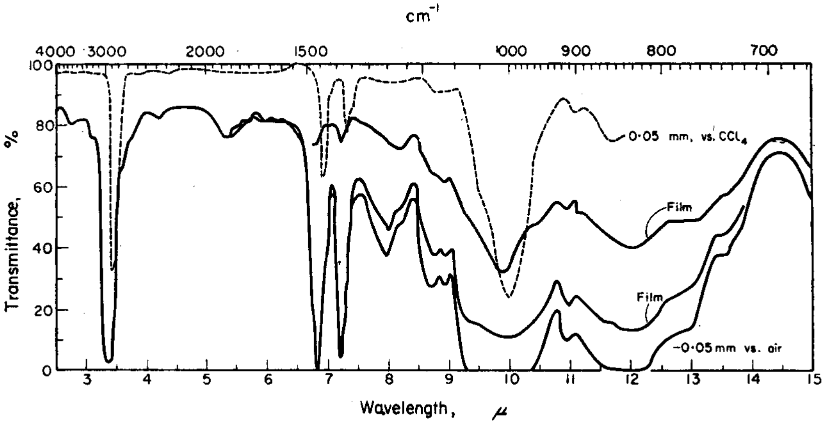


FIG. 11.—Tris-(*iso*-octyl)-thiophosphate

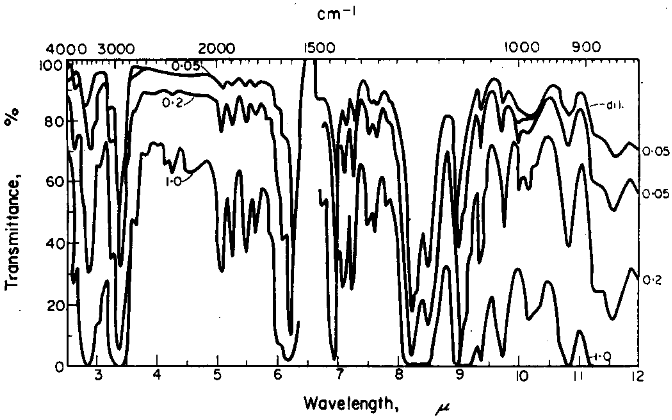
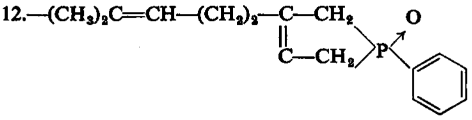
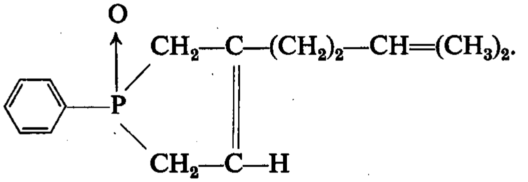


FIG. 12.—



I. 1-*Phenyl*-3-*isohexenyl*-1-*phospha*-3-*cyclopentene-P-oxide.* The spectrum of an unsaturated cyclic phenyl-substituted phosphine oxide is shown in Fig. 12. The structure of this compound is:



Perhaps one of the most complicated of the spectra recorded, it is nevertheless possible

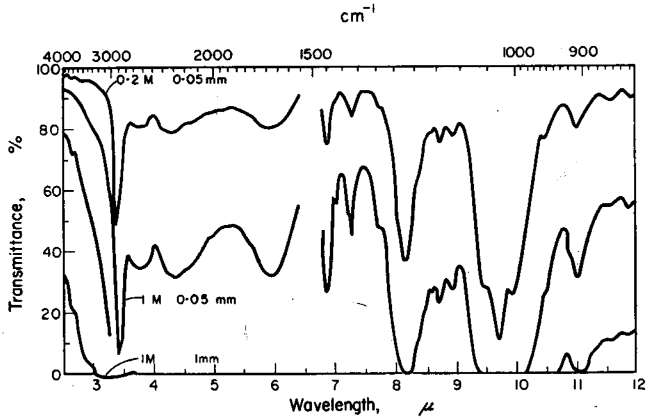


Fig. 13.—Di-*n*-butylphosphoric acid

to assign many of the observed bands to certain groupings of this compound, or possible impurities, as listed in Table III.

Impurities indicated are hydrogen-bonded types containing an OH group and lesser amounts of phosphine P—H and P—OH acidic impurities. The assignment of the phosphoryl frequency, calculated as 1183 cm^{-1} without consideration of the ring, is somewhat in doubt because of the strong doublet at 1215 and 1205 cm^{-1}. Tertiary phosphine oxides sometimes have a doublet phosphoryl vibration. The 1165 cm^{-1} band assigned to a phenyl vibration or the 1107 cm^{-1} band could also be due to the phosphoryl group. The 926 cm^{-1} band is assigned to the P-cyclic grouping by analogy to the observation of Cason and co-workers[16] who investigated some cyclic phosphorus esters.

J. *Dibutylphosphoric acid.* The spectrum of a sample of dibutylphosphoric acid is displayed in Fig. 13. This spectrum can be compared to the published spectra of this compound: Sadtler No. 9041,[40] and Peppard and co-workers.[38] In general, all three spectra are quite similar; however, the ~1230 cm^{-1} band of the Sadtler spectrum is less intense than in the other two. In our spectra, bands are resolved at 1058, 1030, and 1005 cm^{-1} whereas the spectrum reported by Sadtler has a shoulder at ~1060 and a broad band centred at 1030 and the 1030 cm^{-1} band is observed only in the spectrum presented by Peppard.

Gaunt and Meaburn[23] also show a spectrum of dibutylphosphoric acid which is very similar to all of the other spectra below 1450 cm^{-1} but differs slightly above this frequency.

TABLE III. BAND ASSIGNMENTS FOR UNSATURATED CYCLIC PHOSPHINE OXIDE

Band, approx.		Intensity*	Assignment
μ	cm^{-1}		
2·62	3815	mw sh	
2·88	3470	s	—OH polymer
3·04	3290	m sh	—OH polymer
3·22	3105	ms	$\mathrm{CH{=}C}<$ olefin
3·41	2930	vs	CH stretch
3·45	2900	ms sh	CH stretch
3·62	2760	w	P—OH
4·27	2340	w	P—H
4·49	2230	w	
4·65	2150	w	
5·06	1975	w	
5·24	1910	w	
5·47	1830	w	
5·61	1785	w	
5·83	1715	w	
5·99	1670	mw sh	$\mathrm{HC{=}C}<$ olefin
6·09	1640	m	$\mathrm{HC{=}C}<$ olefin
6·22	1605	s	Phenyl
6·77	1475	mw	Phenyl
6·91	1445	m sh	CH_3—C bend
6·96–8	1435	vs	CH_3—C bend, P—ø
7·10	1410	sh	
7·12	1405	m	CH_3—C bend
7·27	1375	m	CH_3—C bend
7·51	1330	mw	
7·64	1310	m	HC=C olefin
8·22	1215	vs	P → 0 stretch
8·30	1205		P → 0 stretch
8·59	1165	vs	Phenyl
9·02	1108	vs	—M bonded P → 0 stretch
9·36–9	1070	m	Phenyl
9·72	1030	mw	Phenyl
10·0	1000	m	
10·17	982	mw sh	
10·26	974	mw sh	
10·80	926	m	P—cyclic ring
11·3	885	ms	
11·55	866	ms	$>\mathrm{C{=}CH}$ olefin
12·2	820	m	
13·1	764	ms sh	
13·5	740	vs	Phenyl
14·48	690	vs	Phenyl

* w = weak, m = medium, s = strong, v = very, sh = shoulder.

K. *Tributylphosphate.* The infrared spectra of tributylphosphate available in the published literature, reports, and infrared catalogues are rather sparse. This is somewhat surprising since the compound is widely used as an extractant in atomic energy work. Reports have shown that the extraction of uranium and of other undesired elements by tributylphosphate is often affected by the presence of small proportions of impurities. The nature of the separation processes tends to promote the accumulation of degradation products of both the organo-phosphorus ester extractant and the diluent.

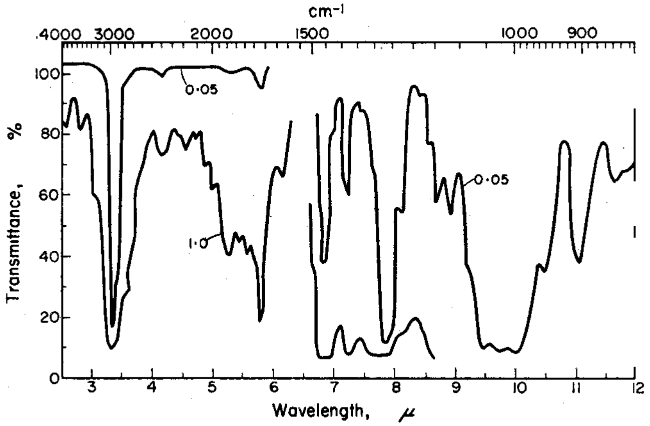


FIG. 14.—Tri-*n*-butylphosphate distillation residue

The approximate positions of the infrared absorptions bands of tributylphosphate as reported by various investigators are shown on Fig. 16.

Examination of these compiled spectra of tributylphosphate show there are many discrepancies in the position and relative intensity of some of the bands.

In the Kendall,[30] Daasch and Smith,[19] Gaunt and Meaburn, crude,[23] and, perhaps, in the Sadtler[40] spectra, bands occur in the 1550 to 2000 cm^{-1} region, which, with one exception, are absent in the Gaunt-Meaburn spectrum of a sample of purified material. Unfortunately, the path length used in most cases was insufficient to reveal bands due to weak absorbing overtone, combination vibrations or the absorption due to minor impurities. Our spectra, discussed later, show that many of these bands are noted only if samples in cells of longer path length are used in the absorbance measurement.

The purified sample studied by Gaunt, the Sadtler spectrum for a longer path length, and the Kendall spectra have too great an absorption in the 975 to 1100 cm^{-1} region for resolution of the individual absorption vibrational modes. Several differences in the spectra are also noted in the 700 to 920 cm^{-1} region.

Besides these spectra, several individual absorption bands for tributylphosphate have been reported as listed in Table IV.

Some of the typical positions for bands expected for various possible impurities are listed in Table V.

Figures to be published in a separate report show the spectra of varied samples of tributylphosphate investigated during this work. Shown here are Fig. 14, the spectrum

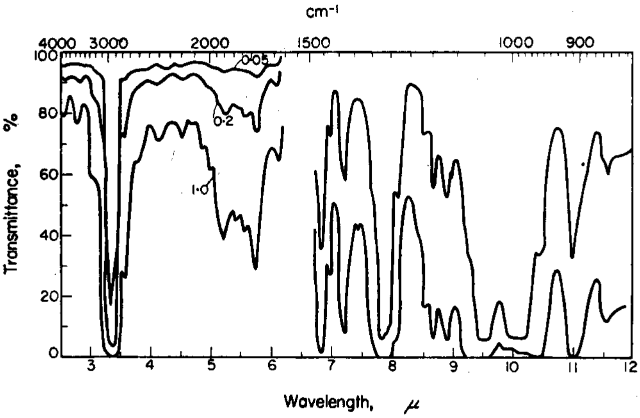


FIG. 15.—Tri-*n*-butylphosphate

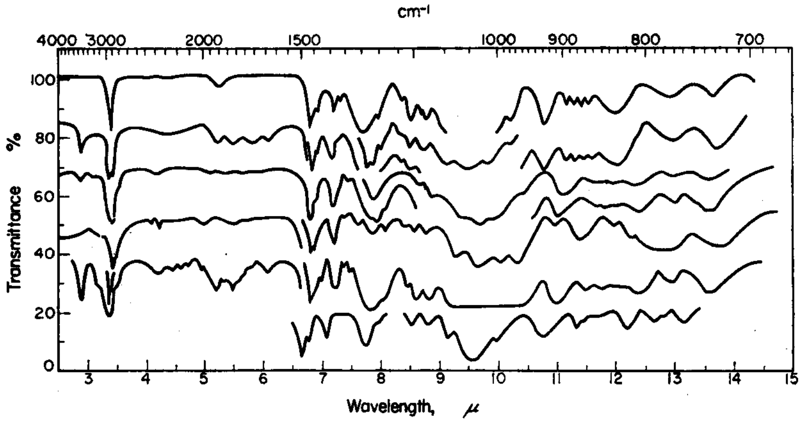


FIG. 16.—Literature spectra of tri-*n*-butylphosphate

TABLE IV. SELECTED ABSORPTION PEAKS REPORTED FOR TRIBUTYLPHOSPHATE

Bands, *cm*$^{-1}$	Reference
1233, 1275, 1290	5
931, 991, 1026	14
1269 (P → 0)	15
1015, 1031, 1061, 1129, 1157, 1280	35
989–93, 1250, 1290	24

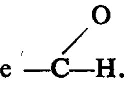
of a very impure compound, and Fig. 15, the spectrum of fairly pure tributylphosphate. By use of thicker cells and up to 27% of the compound in the carbon tetrachloride diluent, many bands appear in the 2·7 to 6·3 μ (1600 to 3700 cm^{-1}) region which are often absent in the spectra of films or those for solutions in 0·05-mm cells or at lower concentrations. The use of thin cells or lower concentrations or both is necessary, however, to determine the location of absorption peaks beyond 6·5 μ (under 1540 cm^{-1}).

From a study of the absorbancies of both major and minor infrared absorption peaks using cells of three different path lengths and two or three concentrations of tributylphosphate, it was shown that, in general, both Beer's and Lambert's laws apply to all absorption peaks investigated. It was also indicated that the intensity of bands in the 2·7 to 6·3-μ region are rather sensitive to the concentration of tributylphosphate. Consequently, for comparison of the intensities of peaks in this region all absorbancies were adjusted numerically to that expected for 25% (w/v) solutions, based on Beer's law.

TABLE V. EXPECTED IMPURITY BAND POSITIONS

Group	Bands, *cm*$^{-1}$
P—OH	2500–2640
C—O—C	1145
(C)—NO	1645
(C)—NO$_2$	1550, 1355
$-\overset{\overset{\text{O}}{\nearrow}}{\text{C}}-\text{OH}$	1695–1725, 2500–3450
C═C	1740–55
(R)—OH	3200–3550
$-\overset{\overset{\text{O}}{\nearrow}}{\text{C}}-\text{H}$	1720–40, 2720, 825–975 (w-m)
H—O—H	3095, 1715, 673
P—H	2350–2450

The residue from the flask following a vacuum distillation of commercial tributylphosphate was used in recording the spectrum shown in Fig. 14. The functional groups responsible for some of the bands can be identified as follows: 3500 hydrogen-bonded hydroxy; 2950 C—H stretching; 2600 (shoulder) acidic P—OH-type impurity; 2400 phosphine P—H-type impurity; 1900 to 1700, due partly to unidentified impurities; 1270 phosphoryl stretching mode; 1145 and 1110 cm^{-1} typical for several butyl-substituted compounds.

The spectrum of the purer sample, Fig. 15, can be discussed and compared to that of the impure sample. The 2950 cm^{-1} band due to a C—H stretching mode is expected; the $\sim$2600 partially resolved shoulder attributable to —P—O-type impurities is less pronounced than in Fig. 14; the $\sim$2600 band attributed to phosphine-type impurities is of about the same intensity as in the less pure product; the 1900 to 1700 cm^{-1} bands are of far lesser intensity than in the impure tributylphosphate, especially the unidentified 1725 cm^{-1} band. These changes on purification indicate that at least a portion of the absorbancy of the bands, in all but the first case, are due to impurities not removed during purification. The unexplained bands could not be confidently assigned from examination of the spectra of mixtures of a purer tributylphosphate with known amounts of butanol, mono- or dibutyl-phosphoric acids, nor tributylphosphine. Among the types of groups which can have bands in the 1900 to 1700 cm^{-1} region are: carboxylic acid —C(O)OH, olefin C=C, and aldehyde  $-\overset{O}{\overset{/}{C}}-H$.

The spectrum of the purer sample of tributylphosphate compares fairly well with some of the spectral bands shown in the literature, especially where varied authors agree as to the position and intensity of the infrared absorption bands,.

Acknowledgements—The authors are indebted to W. J. Ross and R. E. Feathers for synthesis or purification of some of the organo-phosphorus compounds, J. M. Schreyer for the loan of an Infracord, and T. G. Burke for assistance in obtaining some of the spectra.

Zusammenfassung—Die IR-Spektren von einigen für die Extraktion von Metallionen wichtigen organischen Phosphorverbindungen werden mitgeteilt und diskutiert. Spektra einiger wichtiger Abbauprodukte und Verunreinigungen sind ebenfalls gezeigt. Viele der für die Absorbtionsbanden verantwortlichen organischen Gruppen werden identifiziert.

Résumé—Les auteurs présentent et discutent les spectres infra-rouges d'un groupe de composés organiques du phosphore utilisés pour l'extraction des métaux en solutions aqueuses acides. Les spectres de quelques produits de dégradation organiques du phosphore ou des impuretés probables sont aussi présentés. Plusieurs groupes organiques responsables de certaines vandes d'absorption sont identifiés.

REFERENCES

[1] K. Alcock, *Trans. Faraday Soc.*, 1939, **52**, 39.
[2] J. F. Allen, *et al.*, *J. Amer. Chem. Soc.*, 1956, **78**, 3715.
[3] American Petroleum Institute, Proj. 44, Infrared Spectra.
[4] S. Anderson, *Correlation Chart*, Anderson Physical Lab., 1958.
[5] H. T. Baker and C. F. Baes, Jr., *U.S. Atomic Energy Comm.*, *ORNL*-2443, 29, 1958.
[6] M. Baudler, *Z. Elektrochem.*, 1955, **59**, 173.
[7] H. C. Beachell and B. Katlafsky, *J. Chem. Phys.*, 1957, **27**, 182.
[8] J. V. Bell, *et al.*, *J. Amer. Chem. Soc.* 1954, **76**, 5185.
[9] L. J. Bellamy, *J. Chem. Soc.*, 1952, 475; *Research*, 1956, **9**, 147.
[10] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*. John Wiley and Sons, Inc., N.Y., 2nd Ed., 1958, p. 5–8, 311–327.
[11] L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 1952, 1701; *ibid.*, 1953, 728.
[12] L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.*, 1959, **55**, 220.
[13] F. W. Bennett, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 3598.
[14] E. D. Bergmann, *et al.*, *ibid.*, 1952, 847.
[15] L. L. Burger, *J. Phys. Chem.*, 1958, **62**, 590; *U.S. Atomic Energy Comm.*, *HW*-44888, 1957.
[16] J. Cason, W. N. Baxter and W. DeAcetis, *J. Org. Chem.*, 1959, **23**, 247.
[17] D. E. C. Corbridge, *J. Appl. Chem.*, 1956, **6**, 456.
[18] D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 1954 4555.
[19] L. W. Daasch and D. C. Smith, *Analyt. Chem.*, 1951, **23**, 853; *J. Chem. Phys.*, 1951, **19**, 22.
[20] L. W. Daasch, *J. Amer. Chem. Soc.*, 1958, **80**, 5301.
[21] J. R. Ferraro, *J. Inorg. Nuclear Chem.*, 1959, **10**, 319.
[22] R. B. Fox, *U.S. Naval Research Lab.*, *NRL*-5242, 1959.
[23] J. Gaunt and G. M. Meaburn, *Atomic Energy Research Establ.*, *G. Brit.*, *A.E.R.E.-C/R*-785, 1951.
[24] A. L. Geddes, *J. Phys. Chem.*, 1954, **58**, 1062.
[25] E. Halpern, *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 4472.
[26] M. W. Hanson and J. B. Bouck, *ibid.*, 1957, **79**, 5631.
[27] B. Holmstedt and L. Larsson, *Acta Chem. Scand.*, 1951, **5**, 1179.
[28] F. N. Hooge and P. J. Cristen, *Rec. Trav. chim.*, 1958, **77**, 911.
[29] R. N. Jones and C. Sandorfy, *Technique of Organic Chemistry*, A. Weissberger, ed. Interscience, N.Y., 1956, Vol. IX, p. 247–680.
[30] J. K. Kendall, *Appl. Spectroscopy*, 1953, **7**, 179.
[31] J. A. A. Ketelaar and H. R. Gersmann, *Rec. Trav. chim.*, 1959, **78**, 190.

[32] R. L. McConnell and H. W. Coover, *J. Amer. Chem. Soc.*, 1956, **78**, 4450.

[33] R. A. McIvor, G. A. Grant and C. E. Hubley, *Canad. J. Chem.*, 1956, **34**, 1611; *ibid.*, 1959, **37**, 869.

[34] C. D. Miller, R. C. Miller and W. Rodgers, Jr., *J. Amer. Chem., Soc.* 1958, **80**, 1562.

[35] R. H. Moore, *U.S. Atomic. Energy Comm.*, *HW*-24502 *Rev.*, 1955.

[36] Natl. Res. Council, Natl. Bur. Standards Committee on Spectral Absorption Data, Spectra.

[37] R. A. Nyquist, *Appl. Spectroscopy*, 1957, **11**, 161.

[38] D. F. Peppard and J. R. Ferraro, *J. Inorg. Nuclear Chem.*, 1959, **10**, 225.

[39] D. F. Peppard, J. R. Ferraro and G. W. Mason, *ibid.*, 1958, **7**, 231.

[40] S. P. Sadtler, *Infrared Spectra*, Sadtler and Sons, Philadelphia.

[41] J. C. Sheldon and S. Y. Tyree, Jr., *J. Amer. Chem. Soc.*, 1958, **80**, 4775; *ibid.*, 1959, **81**, 2290.

[42] L. C. Thomas, *Applications of Infrared Spectroscopy*, *Chem. & Ind.*, 1957.

[43] L. C. Thomas and R. A. Chittenden, *Porton (England) Tech. Paper No.* 634 1958, (ASTIA-AD-211229), 1958.

Talanta, 1961, Vol. 7, pp. 232 to 236. Pergamon Press Ltd. Printed in Northern Ireland

THE QUANTITATIVE DETERMINATION OF URANYL ION BY MEANS OF THE URANYL-SENSITISED PHOTODECOMPOSITION OF OXALIC ACID

A. E. TAYLOR,® G. E. HECKLER and DONALD R. PERCIVAL
Idaho State College, Pocatello, Idaho, U.S.A.

(*Received* 16 *July* 1960)

Summary—The uranyl-sensitised photodecomposition of oxalic acid is followed by the use of a modified Warburg constant-volume micro-manometric apparatus. The minimum concentration of uranyl ion determined was 100 μM.

INTRODUCTION

OXALIC acid, in aqueous solution, decomposes very slightly when irradiated with ultraviolet light to give at least one gaseous product.[1,2,3] Uranyl ion sensitises this photodecomposition.[1] Furthermore, the rate of gas production for a solution of given oxalic acid concentration is a function of the uranyl ion concentration of the solution.[4] The amount of gas produced from an oxalic acid solution also containing uranyl ions, during an irradiation of time t, may, therefore, be used to determine the amount of uranyl ion present. However, the actual amount of gas may be determined by means of the change of pressure in a system of given volume.[5]

An apparatus well suited to the measurement of small pressure changes in systems of given volumes at constant temperature is the Warburg constant-volume respirometer.[6] By placing properly prepared samples containing oxalic acid and uranyl ion in Warburg flasks, irradiating the samples for a time t, and measuring the change in pressure, it is possible to determine from a previously prepared standard curve and the measured pressure changes, the concentrations of uranyl ion in the samples.

EXPERIMENTAL

Apparatus

A rectangular Warburg apparatus, model USL, accommodating fourteen flask-manometer assemblies was used. The necessary modification required instalment of two General Electric G 36 T 6 germicidal lamps in place of the fluorescent lamps supplied with the apparatus. General Electric 89 G 693 ballasts were used externally in place of the original ones. The G 36 T 6 lamps are instant starting and, according to the manufacturer's specifications, emit 11·6 W of power at 2537 Å at a lamp voltage of 105 V and a current of 420 mA. Quartz Warburg vessels with centre cups and single side arms were substituted for the ordinary Pyrex vessels. A shield for protecting the eyes of workers from ultraviolet radiation was constructed and placed over the top of the constant temperature water bath of the Warburg during operation. A Beckman Model G pH meter was used for all pH measurements.

Reagents

"Baker's Analysed" $H_2C_2O_4 . 2H_2O$, $UO_2(NO_3)_2 . 6H_2O$, hydrochloric acid and sodium hydroxide were used in the investigation. A master solution of uranyl chloride was prepared in the following manner: $UO_2(NO_3)_2 . 6H_2O$ was carefully heated to give UO_3 which was washed and digested in water at 70–80°, then dried at 110° for several hr.[7,8] The molecular weight of the UO_3 hydrate was determined by igniting weighed samples at 800° to U_3O_8.[8] After determining the molecular weight of the UO_3 hydrate, the amount necessary to give the desired uranyl chloride concentration was weighed out and dissolved in dilute hydrochloric acid.

Procedure

Standard solutions of uranyl chloride were prepared by diluting appropriate volumes of the master uranyl chloride solution. Standard solutions of oxalic acid, hydrochloric acid and sodium hydroxide were also prepared. The pH of the oxalic acid solution was adjusted to 2·75 with sodium hydroxide. This oxalic acid-binoxalate mixture was 0·025*M* in oxalate.

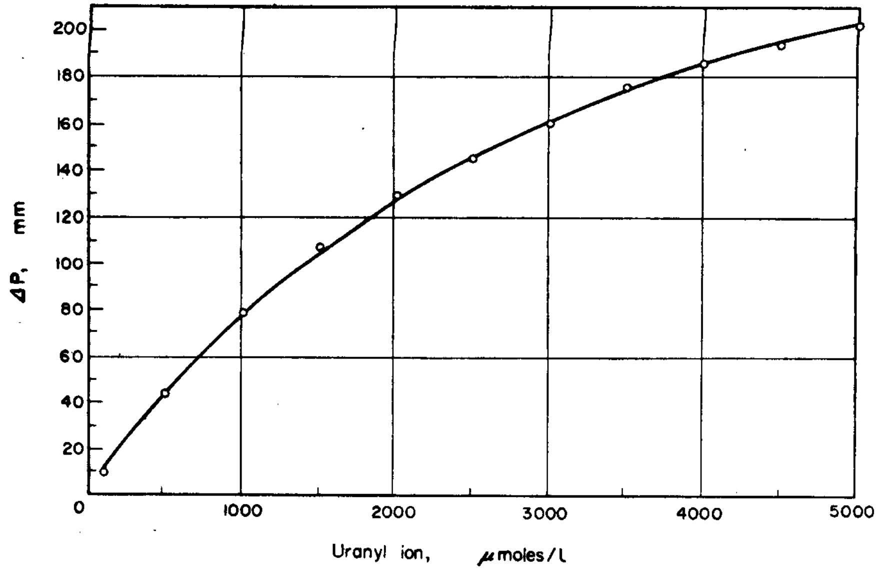


Fig. 1.—Standard curve for pressure change *vs.* uranyl concentration

In preparing the samples for analysis, the pH of each standard uranyl chloride solution was measured. Five ml of the standard solution were then diluted to 10 ml with dilute hydrochloric acid (or sodium hydroxide) and water; the amount of acid or base added being such that the pH of the diluted sample was 2·75 ± 0·25. Ten ml of the oxalic acid-binoxalate mixture (pH 2·75) were placed in a 25-ml volumetric flask and to this were added 5 ml of the prepared uranyl chloride sample. This was then diluted to volume with $1{\cdot}78 \times 10^{-3}M$ hydrochloric acid (pH 2·75). Three ml of the samples, as prepared in the foregoing manner, were then placed in each of five Warburg flasks. After introduction of the sample, each numbered flask was attached to the manometer of corresponding number. The ground glass joints of the flasks and manometers were sealed first with a water seal, then by coating with a paraffin-vaseline mixture. The ground glass joints of the side arms and side arm stoppers were sealed with a thin film of vaseline. The flask-manometer assemblies were then placed in position on the Warburg apparatus. The protective shield was placed over the top of the water bath and the pressure in the flasks was reduced by decreasing the compression on the manometer reservoirs. The shaking motor was started (frequency-75) and the flask-manometer assemblies were allowed to come to equilibrium at the temperature of the water bath (30°). After equilibrium had been reached, as indicated by relatively constant Brodie solution levels in the manometers, the flasks were irradiated for 2 min. Ten min were allowed to pass after irradiation before the final manometer readings were made. The average of the corrected pressure changes in the five flasks for a 2-min irradiation period was plotted against the concentration of uranyl ion in the original standard sample. Fig. 1 shows the curve obtained when various uranyl ion concentrations are plotted against Δp in 2 min. The standard curve may be used to determine the concentration of uranyl ion in solutions of unknown uranyl chloride concentrations provided that the compositions of the standard and unknown match in other respects.

DISCUSSION

Three factors affect the pressure changes observed in flasks containing equal volumes of an identical solution. These factors are:

(1) slight changes in the temperature of the water bath and in atmospheric pressure,

(2) small differences in the free volumes of the various flask-manometer assemblies,

(3) differences in the amount of ultraviolet radiation actually entering the solutions in the flasks.

The first factor is compensated for by means of thermobarometers as described by Umbreit *et al.*[5] The second and third factors may be accounted for by what have been termed pressure constants. From a theoretical standpoint, all flask-manometer assemblies of equal free volume containing equal volumes of identical oxalic acid-uranyl solutions into which is passing an equal amount of ultraviolet light should exhibit equal pressure changes for an irradiation of time t. Since not all flask-manometer assemblies have identical free volumes and the amount of light entering each flask is slightly different, pressure changes (after having been corrected for thermobarometer fluctuations) are not the same for all flasks containing equal volumes of identical solutions. For this reason a reference flask-manometer assembly was chosen to which pressure changes in other flask-manometer assemblies could be related in order to obtain corresponding results from all flasks. An empirical constant was obtained for each of the other flasks which, when multiplied by the pressure change in each such flask, gave a result equal to the pressure change in the reference flask. Solutions of identical composition were irradiated for a specific time interval in determining these constants for each cell in a definite position above the light source.

In addition to the thermal barometers, two standard flask-manometer assemblies were chosen for the purpose of maintaining a check on the reproducibility of the system. Before each experiment, equal volumes of a freshly prepared oxalic acid-uranyl solution were placed in the two flasks. The standard manometers were read along with the other manometers during the course of an experiment. These readings were compared from one experiment to the next and were generally found to agree to within 6 mm. The two thermobarometers were placed at diagonally opposite corners of the water bath, the standard flask-manometer assemblies occupying the two remaining corners.

As shown in Fig. 2, the change of pressure for a given irradiation period is dependent upon the pH of the system; the effect of pH being much more pronounced for the $0{\cdot}1M$ than for the $0{\cdot}01M$ oxalic-uranyl systems. In the range 2·5 to 3·0, pH has little effect on the pressure changes exhibited by $0{\cdot}01M$ oxalic acid-uranyl systems. Furthermore, the pressure change in this pH range is not greatly different from the maximum which occurs at pH 1·2–1·3. The points of Fig. 2 represent the average experimental results. The standard error for the upper portion of the curve for $0{\cdot}01\ M$ oxalic acid is ± 2 mm.

The points of Fig. 1 were found to be reproducible to within 4 mm at the lower and 8 mm at the upper uranyl ion concentration limits. In the determination of uranyl ion concentration these variations cause a relative error of 25% and 6% respectively. However, in the range $400\mu M$ to $5000\mu M$ uranyl ion the maximum relative error to be expected is 6%.

Increasing the irradiation period might make possible the determination of uranyl ion below a concentration of 100 μM. It is advisable, however, to limit irradiation periods to those which do not cause pressure changes greater than 250 mm of Brodie solution at the highest uranyl ion concentration since this is approximately the maximum pressure change which can be measured by one reading of a manometer. Thus, an increase of irradiation period would require a corresponding decrease in the upper concentration limit of uranyl ion.

Any ion which is capable of complexing with uranyl ion, sensitising the oxalic acid photodecomposition, or altering the over-all photolysis reaction in any way will, of course, be a source of interference to the method. Of the common ions studied, K^+, Na^+ and Cl^- have been found to have no observable effect on the rate of gas production. Sulphate causes a slight reduction while PO_4^{3-}, F^- and Al^{3+} greatly reduce the rate. Nitrate interferes by oxidation of organic materials. Iron^{III} sensitises the oxalic acid photodecomposition, thus increasing the rate. Any organic acid such as malonic, tartaric, lactic, succinic, glutaric, valeric and propionic, whose anions complex with uranyl ion, interferes.

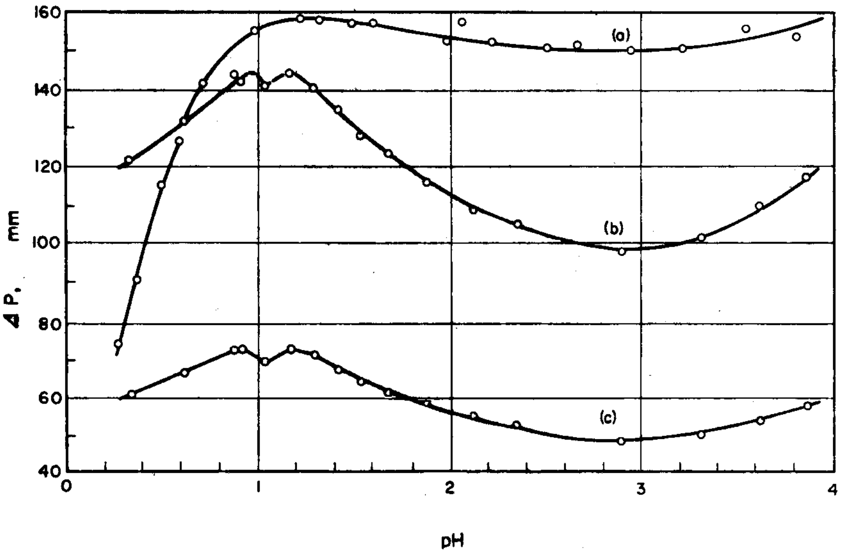


FIG. 2.—A, B and C—2500 μM uryanl ion.
A—0.01 M oxalic acid; 2 min irradiation
B—0.1 M oxalic acid; 4 min irradiation
C—0.1 M oxalic acid; 2 min irradiation

It is important that the amount of light entering the solutions in each Warburg flask be kept constant. It is necessary, therefore, to make certain that the flasks, surfaces of the ultraviolet lamps, and water in the water bath are kept clean. Several methods for cleaning the flasks are discussed by Umbreit *et al.*[5] An efficient method of removing the paraffin-vaseline sealing mixture from the flasks consists of soaking them in white gasoline followed by several rinsings in ethyl alcohol. The surfaces of the ultraviolet lamps were washed with a mild detergent solution before each run. After thorough rinsing of the lamp and water bath surfaces, the water bath was filled with distilled water to a point such that the water level was within 1/8 to 1/4 in. of the tops of the side arms on the flasks.

CONCLUSION

This method is new and its practical application requires considerable care. Further investigation is necessary for the application of the method to a specific problem. The fact that many common ions interfere restricts its use at the present time to the determination of uranyl ion in solutions of known composition. The shape of the standard curve (Fig. 1) is not ideal for the purpose of making quantitative determinations. Furthermore, the cost of the equipment involved is a deterrent.

Despite the limitations of the method, it illustrates what the authors believe to be a new analytical technique for the quantitative determination of uranyl ion.

Acknowledgement—This investigation represents a part of the research performed under contract No. AT(10–1)–310 between the United States Atomic Energy Commission and Idaho State College. Acknowledgement is made to Phillip Fung and Ronald Jensen, student assistants.

Zusammenfassung—Die durch Uranlyionen sensitivierte Photozersetzung von Oxalsäure wird mittels eines Modifizierten Warburgschen Mikromanometrischen Apparates (Konstantes Volum) verfolgt. Die bestimmte Mindestkonzentration an Uranyl war 100 Mikromolar.

Résumé—La photodécomposition de l'acide oxalique excitée par l'uranyle est suive par l'utilisation d'un appareil micro-manométrique de Warburg modifié à volume constant. La concentration minimale d'uranyle dosé était 100 micro-molaire.

REFERENCES

[1] L. Bruner and J. Kozak, *Z. Elektrochem.*, 1911, **17**, 354.
[2] P. F. Buchi, *Z. Physik*, 1924, Chem. **111**, 269.
[3] E. Baur, *ibid.*, 1924, Chem. **111**, 315.
[4] H. H. Paige, A. E. Taylor and R. B. Schneider, *Science*, 1954, **120**, 347.
[5] W. W. Umbreit, R. H. Burris and J. F. Stauffer, *Manometric Techniques and Tissue Metabolism.* Burgess Publishing Co., Minneapolis, 1949. Chap 1.
[6] O. Warburg, *Biochem. Z.*, 1923, **142**, 317.
[7] E. L. Nichols and H. L. Howes, *Fluorescence of the Uranyl Salts.* Carnegie Institution of Washington, Publication No. 298. 1919, 207.
[8] J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium.* McGraw-Hill, New York, 1951. National Nuclear Energy Series, Division VIII-Vol. 5, Part 1, pp. 310 and 319.

Talanta, 1961, Vol. 7, pp. 237 to 247. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF COPPER, NICKEL, COBALT, IRON AND MANGANESE AS THEIR PYRIDINE THIOCYANATES

SIMULTANEOUS DETERMINATION IN MIXTURES*

GILBERT H. AYRES and STEPHEN S. BAIRD†
Department of Chemistry, The University of Texas, Austin, Texas, U.S.A.

(*Received* 23 *May* 1960)

Summary—Spectrophotometric determinations of copper, nickel, cobalt, iron, and manganese, based on the chloroform extraction of the metal pyridine thiocyanates, have been investigated. Optimum conditions require the pH of the aqueous solution to be in the range about 5–8; tartaric acid is used to prevent precipitation of hydrous oxides. An excess of pyridine must be used because chloroform readily extracts pyridine from the aqueous solution. Results are improved by making the extraction from a solution of high ionic strength (2 or above), which is provided by magnesium nitrate. Perchlorate decreases the absorbance, but the effect is essentially constant over a perchlorate concentration range of 0·8 to 2*M*. Although the metal pyridine thiocyanates are extracted by benzene, substituted benzenes, and halogenated hydrocarbons, chloroform is superior to other solvents in extraction efficiency and in colour stability of the extracted species. An example is given of the simultaneous determination of copper, nickel, cobalt, and iron in the same solution. Anions that also form metal pyridine compounds must be absent.

INTRODUCTION

IN 1922 Spacu[1] reported a "sensitive reaction for copper, thiocyanates and pyridine" based upon the formation of an insoluble product by reaction of the three substances in neutral solution. For use in the detection of copper, Spacu warned against the addition of an excess of pyridine, in which the precipitate is soluble. He also reported that the sensitivity for the detection of copper could be increased by shaking the mixed solutions with chloroform, which acquires an emerald green colour. The reaction was later reported[2] as a microchemical method for copper, in which the chloroform extract was evaporated to dryness and the copper was weighed as $Cu(C_5H_5N)_2(CNS)_2$, or converted to CuS for weighing. Spacu and coworkers applied the pyridine thiocyanate reaction to the gravimetric determination of copper,[3–5] nickel,[6] cobalt,[7] cadmium,[8] mercury,[9] and zinc.[10] Cuny[11] first applied the reaction to the determination of thiocyanate. Cuny, and later Golse[12] devised indirect titrimetric methods for copper, based upon the titrimetric determination of the excess of thiocyanate in the filtrate after precipitation and filtration of the copper pyridine thiocyanate.

The precipitates formed by reaction with thiocyanate and pyridine were used by Martini[13] for the microchemical detection of nickel, copper, cobalt, cadmium, and zinc; similar precipitates were obtained by the use of aniline instead of pyridine. The

---

* Condensed from a dissertation submitted by Stephen S. Baird to the faculty of the Graduate School of The University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1958. Part of the work on copper pyridine thiocyanate was presented at a joint meeting of the Southeast and Southwest Regions, American Chemical Society, in New Orleans, Louisiana, December, 1953.

† Present address: Texas Instruments, Inc., Dallas, Texas, U.S.A.

pyridine thiocyanate reaction has been widely used for the determination of copper in organic materials.[14–22]

There are but few literature references to the instrumental measurement of the chloroform extract of copper pyridine thiocyanate. Jean[23] used the method for the determination of copper, cobalt, and nickel, although the instrumental details (including any optical filters used) were not given. Moeller and Zogg[24] recorded the spectrum of the chloroform extract of copper pyridine thiocyanate, and reported an absorption maximum at 415 mμ. They claimed that so long as stoichiometric quantities of pyridine and thiocyanate were present, the coloured compound was extracted by chloroform; on the contrary, we have found that an excess of pyridine is essential for the extraction.

Kruse and Mellon[25] used the chloroform extract of copper pyridine thiocyanate for the determination of thiocyanate; the absorbance was measured at 410 mμ. They reported that the colour was found to vary with the volume of aqueous phase in the extraction, and claimed that the colour "does not follow Beer's law." Only solvents "with some dipole" were reported to extract the coloured species.

Recently, Forsythe, Magee and Wilson[26] have fractionally precipitated nickel and cobalt as their pyridine thiocyanates by pH control. The nickel precipitate was extracted into chloroform and the cobalt precipitate was extracted into methyl *iso*butyl ketone for spectrophotometric determination.

The pyridine thiocyanates of twelve bivalent cations have been prepared in this laboratory, and many of their properties have been measured.[27] The present report deals with the spectrophotometric determination of copper, nickel, cobalt, iron, and manganese. Because these elements are frequently found together in various alloys, simultaneous spectrophotometric determination can prove to be useful. An illustration is given of the simultaneous determination of copper, nickel, cobalt, and iron.

EXPERIMENTAL

Apparatus

A Beckman Model DK-2 Recording Spectrophotometer was used for scanning to obtain the absorption spectra. A Beckman Model DU Spectrophotometer was used for quantitative absorbance measurements. Silica cells of 1·00-cm optical path were used with both instruments. A Leeds and Northrup Stabilised pH Indicator was used for the pH measurements, and a Beckman Model K Automatic Titrator was used for rapid adjustment of the pH of solutions before extraction.

Reagents

Unless otherwise specified, all reagents were of A.C.S. specification reagent purity. The water used was purified to a specific resistance of 200,000 Ω or more.

Standard solutions

Where convenient to do so, 0·10*M* stock solutions were prepared; solutions of lower concentration were prepared, as needed, by volumetric dilution of the stock.

Copper nitrate: 6·354 g of pure electrolytic copper were dissolved in nitric acid; the solution was evaporated nearly to dryness, then diluted to exactly 1 litre; concentration, 0·1000*M*.

Cobalt nitrate: approximately 30 g of cobalt nitrate hexahydrate were dissolved to make 1 litre of solution, which was standardised against standard EDTA and standard magnesium chloride solutions, using Eriochrome Black T indicator screened with methyl orange in the presence of diethanolamine.

Nickel nitrate: 5·869 g of pure nickel foil were dissolved in nitric acid; the solution was evaporated nearly to dryness, then diluted to exactly 1 litre; concentration, 0·1000*M*.

Iron^{II} chloride: 0·0559 g of pure iron wire for standardising was dissolved in iron-free hydrochloric acid; the solution was evaporated to about 5 ml, then diluted with water, and 10 ml of 20% hydroxylamine hydrochloride were added. Dilution to exactly 1 litre gave a 0·00100*M* solution. Solutions prepared in this way were stable for several months.

Manganese sulphate: 16·90 g of manganese sulphate monohydrate were made to 1 litre; concentration, 0·100*M*.

Buffer solutions

These were prepared to contain, per litre, 50 ml of pyridine, 2·0 g of potassium thiocyanate, and 30 g of magnesium nitrate, along with the buffer constituent. Hydrochloric acid or sodium hydroxide, as appropriate, was added to give the desired pH, which was measured with a pH meter. Buffer constituents for the various pH regions were as follows: pH about 2, saturated potassium chloride and hydrochloric acid; pH 3 to 6, potassium acid phthalate; pH 7 to 8, pyridine; pH 9 to 11, borate.

Other reagents and solvents

Percentage composition of solutions is given on a weight/volume basis.

Acetic acid: 1*M*.
Chloroform: reagent grade.
Citric acid: 1%.
Hydroxylamine hydrochloride: 20%.
Magnesium nitrate hexahydrate: 50%.
Potassium thiocyanate: 10%
Pyridine: clear, water-white; Coleman and Bell or J. T. Baker.
Tartaric acid: 10% and 20%.

Determination of Copper

Procedure

To approximately 100 ml of solution, containing about 0·2 to 0·5 mg of copper, add 25 ml of 10% tartaric acid (or 25 ml of 1% citric acid), 6 ml of 50% magnesium nitrate, 8 ml of pyridine, 8 ml of 10% potassium thiocyanate, and adjust the solution to pH 5–7 with sodium hydroxide. Extract with three 10-ml portions of chloroform. Drain the extracts into a 50-ml volumetric flask and dilute to about 40 ml with fresh chloroform. Add 1 ml (or more if necessary) of acetone to clear the extract, and complete the dilution to volume with fresh chloroform. Measure the absorbance, against a reagent blank, at 405 mμ in a 1·00-cm cell. (Obviously, the concentration range can be proportionately decreased by the use of cells of longer optical path.)

The absorption spectrum of the chloroform extract of copper pyridine thiocyanate is shown in Fig. 1, Curve A. A plot of absorbance against copper concentration is a straight line, the slope of which corresponds to a specific absorptivity of 27·4 ml per mg-cm.

If perchlorate is present in the original copper solution, adjust the perchlorate concentration to 0·8 to 2*M* (using sodium perchlorate), and proceed as described above. In this case the specific absorptivity is 22·8 ml per mg-cm.

Effect of variables

Effect of pH. A series of buffer solutions covering the pH range 2 to 11 was prepared; the buffers contained the pyridine and potassium thiocyanate reagents to develop the copper product, and magnesium nitrate to increase the ionic strength. Equal volumes of buffer solution and a standard copper solution were mixed, and the pH was measured. The mixture was transferred to a separatory funnel, and extracted with one 5-ml portion of chloroform. (A single extraction was used so as not to "smear out" the pH effect.) The extract was diluted to 10 ml with chloroform, and its absorption spectrum determined. The spectral curves are shown in Fig. 2. Fig. 3, in which absorbance (at 405 mμ) is plotted against pH of the aqueous solution before extraction, shows that there is a considerable pH range over which extraction is nearly constant.

The pH of the residual aqueous layer, after extraction with chloroform, was measured. Results are shown in Table I. The change in pH was always in the direction towards the neutral point (pH 7) which suggests that the change in pH was due to extraction of the buffer components by chloroform. The change of pH in the region used in the standard procedure (pH 5–7) is not significant. If ammonium thiocyanate is used as reagent, the decline in extractability begins at pH about 7, instead of 8, and

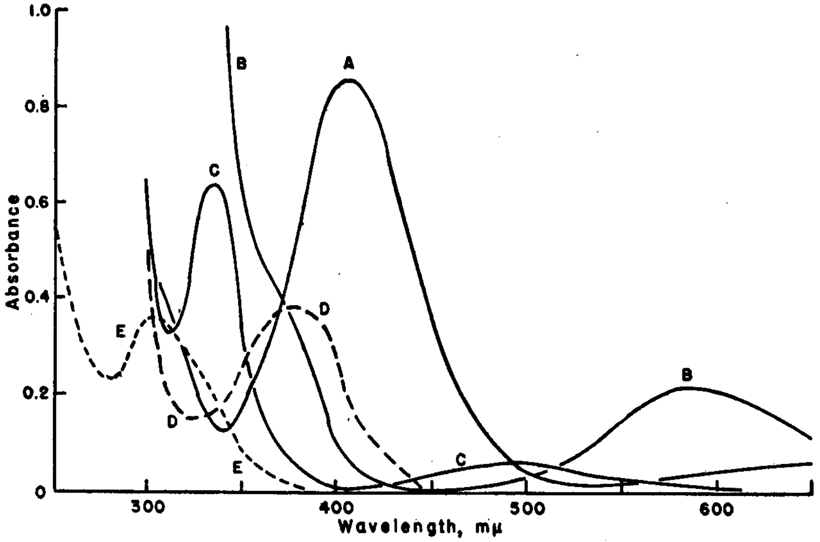


FIG. 1.—Spectral curves for chloroform solutions of metal pryidine thiocyanates. A: Copper, 31 μg/ml. B: Nickel, 1·1 mg/ml. C: Cobalt, 11·9 μg/ml. D: Iron^{II}, 11·2 μg/ml. E: Manganese, 0·30 mg/ml.

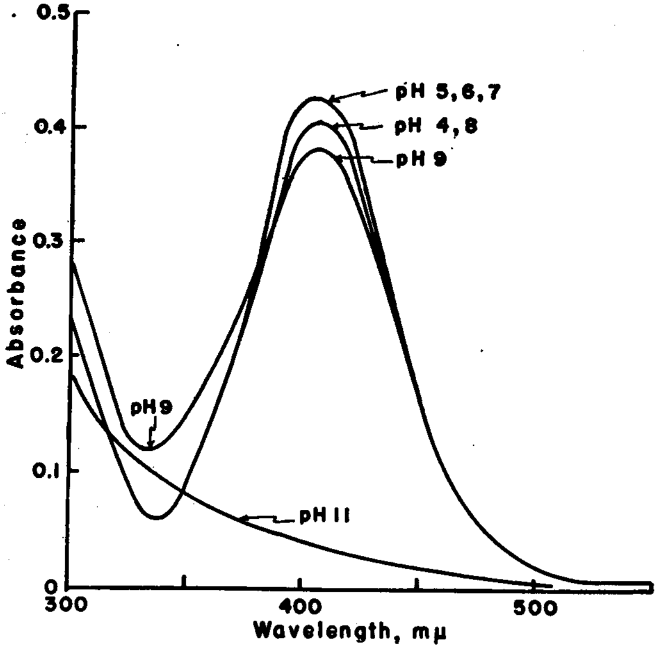


FIG. 2.—Absorption spectra of chloroform extract of copper pyridine thiocyanate as a function of initial pH of aqueous solution.

for a given pH above 7 the extractability is much less than when potassium thiocyanate is used. This difference is probably due to the competition between pyridine and ammonia in the solution for the complexation of the copper. It should be remarked that at high pH (above 11), different solute species are present; the aqueous solution and the chloroform extract are yellow-brown.

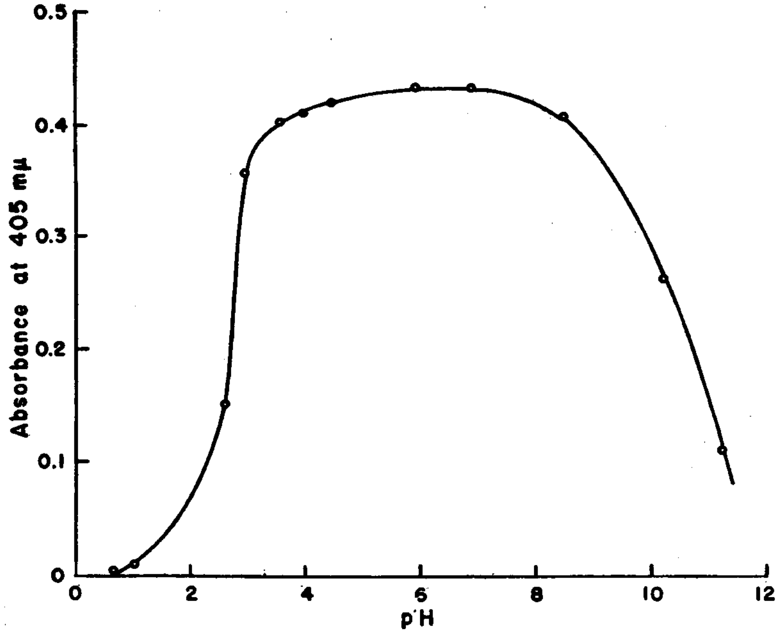


Fig. 3.—Effect of pH on chloroform extraction of copper pyridine thiocyanate. Copper, 16 μg/ml.

Table I.—Change of pH of aqueous solution due to extraction of copper pyridine thiocyanate with chloroform.

Initial pH	Final pH
3·30	3·95
3·52	4·15
4·03	4·92
5·00	5·08
5·98	6·30
6·67	6·98
6·88	7·12
7·88	7·70
8·88	8·52
10·04	9·25
10·9	9·6

Effect of tartaric acid. With a view to the possible use of tartaric acid as a sequestering agent to prevent the precipitation of various hydroxides, a study was made of the effect of tartaric acid on the extraction of the copper pyridine thiocyanate. When sufficient magnesium nitrate is added to give an ionic strength of 2 or greater, the colour (absorbance) of the extract, for a given amount of copper, is independent of the concentration of tartaric acid.

Effect of ionic strength. Magnesium nitrate was used to vary the ionic strength of the solutions. To 25·0 ml of copper solution (60 μg per ml) were added, in order, 10 ml of 20% tartaric acid, 2 ml of

10% potassium thiocyanate, 2 ml of pyridine, and various volumes of 50% magnesium nitrate. The mixture was adjusted to pH 5 with sodium hydroxide; all solutions were brought to the same volume, then extracted twice with 10-ml portions of chloroform. The extracts were diluted to 25·0 ml in volumetric flasks, and cleared by shaking with about 50 mg of ammonium chloride. The absorbance was measured at 405 mμ. A plot of absorbance against ionic strength of the solution is shown in Fig. 4. The initial point represents the ionic strength of the solution used in the pH studies. The conditions chosen for the standardised procedure are such that the ionic strength will always exceed 2.

Jean[23] reported that acetate is necessary for adequate extraction of copper pyridine thiocyanate from solutions containing iron^{III}. The effect observed by Jean may be an ionic strength effect. Chalk[28] states that acetate must be absent. When the ionic strength and the concentrations of pyridine and thiocyanate are adequate, no detrimental effect of acetate has been observed.

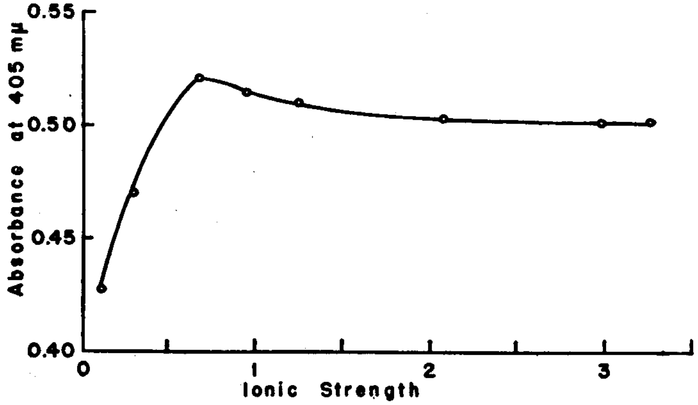


FIG. 4.—Effect of ionic strength on extraction of copper pyridine thiocyanate.

Effect of perchlorate. Fixed amounts of copper (10·0 ml of solution containing 60 μg per ml) were treated with various volumes of 8*M* perchloric acid, and tartaric acid, pyridine, and potassium thiocyanate as in the standard procedure. After adjustment to pH 5, the mixtures were extracted with two 10-ml portions of chloroform; the extracts were cleared with a small amount of solid ammonium chloride, diluted to 25·0 ml, and the absorbance measured at 405 mμ. A plot of absorbance against concentration of perchlorate is shown in Fig. 5. It was determined that perchlorate adversely affected the distribution of pyridine between the aqueous and the chloroform phases. If perchlorate is present, its concentration should be adjusted to 0·8–2*M* (the plateau region in Fig. 5) before proceeding with the analysis. Because of the lower absorptivity in the presence of perchlorate, the standardisation of the photometric method would, of course, have to be made under the same conditions.

Solvent effects. It was found that aliphatic hydrocarbons, alicyclic hydrocarbons, aliphatic ethers and esters did not extract copper pyridine thiocyanate. This was believed to be due to the unfavourable distribution of pyridine between water and the organic solvent under the conditions of formation of copper pyridine thiocyanate. In order to test this point, aqueous solutions of pyridine (1*M*) were adjusted to ionic strength 2 and pH 7, and extracted with an equal volume of organic solvent: chloroform, carbon tetrachloride, or di-*iso*propyl ether. Pyridine in the chloroform extract was determined spectrophotometrically by its absorbance at the 10·09 μ peak in the infrared. Pyridine in the aqueous layer was determined by adding water to about a volume of 125 ml, followed by 20 ml of 6*M* sodium hydroxide and distillation until 80 ml had passed over; the distillate was titrated with hydrochloric acid (about 0·1*N*) to a pH of 4·0. The distribution ratio found for pyridine between the organic and the aqueous phase was as follows: chloroform, 10·7; carbon tetrachloride, 3·8; di-*iso*propyl ether, 0·1.

Table II shows some spectral data for a chloroform and for a carbon tetrachloride extract of copper pyridine thiocyanate, under identical conditions of preparation.

Benzene and substituted benzenes extracted the copper pyridine thiocyanate. The time-stability of the colour decreased with increase in complexity and number of substituents; as judged visually, the colour-stability decreased in the order: benzene $\geqq$ toluene > xylene > bromobenzene, chlorobenzene, ethylbenzene > diethylbenzene $\gg$ cumene (*iso*propylbenzene) > triethylbenzene. In the latter two cases the colour was obviously changed within 1 hr, and had completely disappeared in 24 hr. By contrast, the colour in chloroform was stable indefinitely. The reason for the fading was not investigated. All of the tested halogenated hydrocarbons extracted copper pyridine thiocyanate to a greater or lesser extent; chloroform was superior to carbon tetrachloride, 1:1:2:2-tetrachlorethane (perchloroethylene), and 1:1:2-trichloroethane (trichloroethylene), in absorbance of the copper complex and in colour stability. Although the absorption curves in the various solvents were all of the same general shape, the absorption maximum occurred at somewhat different wavelengths; in chloroform, benzene, and bromobenzene, maximum absorption occurred at 405–410 mμ; in carbon tetrachloride, toluene, xylene, ethylbenzene and diethylbenzene, maximum absorption occurred at 425–430 mμ. This effect is possibly due to some interaction of the solvent with the pyridine of the complex.

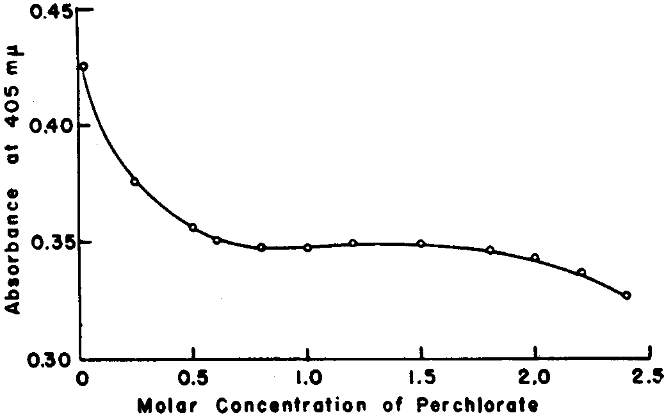


FIG. 5.—Effect of perchlorate concentration on the absorbance of chloroform extract of copper pyridine thiocyanate.

TABLE II.—RESULTS FOR COPPER PYRIDINE THIOCYANATE EXTRACTED INTO CHLOROFORM AND INTO CARBON TETRACHLORIDE

Wavelength, mμ	Absorbance in $CHCl_3$	Absorbance in CCl_4
350	0·197	0·013
375	0·503	0·051
400	0·835	0·143
410	0·835	0·177
425	0·722	0·209
440	0·501	0·199
475	0·113	0·072
500	0·034	0·025

A disadvantage in the use of chloroform is that below 400 mμ the absorbance of the pyridine-chloroform mixture increases quite rapidly with time (approximately quadruples in the first 50 hr). For any system that is to be measured below 400 mμ, this would require making the absorbance measurement without undue delay after the extraction, and for measurements below about 320 mμ (*e.g.* manganese pyridine thiocyanate, with absorbance peak at 300 mμ) it may be impossible to balance the spectrophotometer for zero absorbance reading of the blank.

Determination of Nickel

For the pyridine thiocyanates of nickel and the other cations reported herein, the effect of the different variables was investigated and found to be essentially the same as for copper. The same general procedure can therefore be followed for the determination of these cations.

Procedure

To approximately 100 ml of solution, containing about 20 to 60 mg of nickel, add the reagents and carry out the extraction as described for copper. If necessary, adjust the pH of the aqueous layer, between extractions, by the addition of pyridine.

The spectral curve for the chloroform extract of nickel pyridine thiocyanate is shown in Fig. 1, Curve B. Measure the absorbance, against a reagent blank, at 360 mμ; care must be taken to set the wavelength accurately because the measurement is made on a shoulder band. The absorbance is linear with concentration of nickel; at 360 mμ the specific absorptivity is 0·408 ml per mg-cm. Reduced sensitivity is obtained by measurement at 580 mμ; at this wavelength the absorbance is also linear with concentration, the specific absorptivity is 0·185 ml per mg-cm., and the optimum range is about 50 to 170 mg of nickel in the original solution.

Determination of Cobalt

Procedure

With approximately 100 ml of solution, containing 0·2 to 0·65 mg of cobalt, proceed as in the determination of copper. The spectral curve for the chloroform extract of cobalt pyridine thiocyanate is shown in Fig. 1, Curve C. Measure the absorbance at 335 mμ. Absorbance is linear with concentration of cobalt, and the specific absorptivity is 53.8 ml per mg-cm. At the 492 mμ absorption peak, the specific absorptivity is 0·415 ml per mg-cm., the absorbance is linear with concentration, and the optimum range for cobalt is about 25 to 85 mg in the original solution.

Determination of Iron

Procedure

For the determination of total iron, use a solution containing about 0·3 to 1 mg of iron. Add 20 ml of 20% hydroxylamine hydrochloride, allow the solution to stand for about 1 min, then proceed as in the determination of copper. The spectral curve for the chloroform extract of iron^{II} pyridine thiocyanate is shown in Fig. 1, Curve D. Measure the absorbance at 375 mμ. Absorbance is linear with concentration of iron, and the specific absorptivity is 35·1 ml per mg-cm. The solution has two very weak absorption regions centring at 585 and at 850 mμ; the absorptivities (0·096 and 0·173 ml per mg-cm., respectively) at these wavelengths are so small as to make the classical oxidimetric titration preferred as a completion procedure for the amounts of iron that would be required for optimum results by the spectrophotometric method.

Determination of Manganese

Procedure

Treat a solution containing about 0·8 to 3 mg of manganese^{II} as described for the determination of copper. The spectral curve is shown in Fig. 1, Curve E. Measure the absorbance at 300 mμ. Absorbance is linear with concentration of manganese, and the specific absorptivity is 12·1 ml per mg-cm. If too long a time (more than about 1 hr) has elapsed after extraction, it may not be possible to balance the spectrophotometer due to the high opacity of the reagent blank at 300 mμ.

Simultaneous Determinations

In order to apply the spectrophotometric method (matrix calculations) to the simultaneous determination of two or more constituents, it is necessary for the absorbances of the constituents to be additive. The conditions of additive absorbances are satisfied for the chloroform extracts of the pyridine thiocyanates of bivalent copper, nickel, cobalt, and iron, if sufficient pyridine and potassium thiocyanate are added to give concentrations, in the aqueous layer after extraction, of at least 40 ml and 6 g, respectively, per litre. Because some pyridine is removed with each extraction, additional pyridine may have to be added between extractions.

Table III summarises the spectrophotometric information for the different cations. With the conditions of additive absorbances satisfied, as indicated above, the absorptivites shown in Table IV apply for the simultaneous determination of the cations. Obviously, if a certain cation is known to be absent, measurement at its analytical wavelength may be omitted. The determination of manganese cannot be performed in the presence of moderate amounts of nickel, cobalt, or iron because of the opacity of the solution of their pyridine thiocyanates at 300 mμ.

TABLE III.—SUMMARY OF SPECTRAL RESULTS.

Cation	Wavelength, *mμ*	Specific Absorptivity, *ml/mg-cm*	Optimum Range, *mg/ml* in Extract
Copper	405	27·4	0·003–0·01
	705	2·30	0·03–0·12
Nickel	360	0·408	0·4–1·5
	580	0·185	1–4
Cobalt	335	53·8	0·004–0·015
	492	0·415	0·5–2
Iron	375	35·1	0·006–0·02
	525	0·096	2–7
Manganese	300	12·1	0·02–0·06

TABLE IV.—ABSORPTIVITIES OF PYRIDINE THIOCYANATES.
Tabular values in ml per mg-cm.

Wavelength, *mμ*	Cu^{++}	Ni^{++}	Co^{++}	Fe^{++}	Mn^{++}
300	10·4	21·0	50·1	40·3	12·1
335*	2·36	1·27	53·8	16·2	0·660
360*	9·53	0·408	5·90	30·8	0·136
375*	17·5	0·306	0·143	35·1	0·004
405*	27·4	0·065	0·031	20·2	0·001
492	0·97	0·028	0·415	0·080	—
525	0·21	0·047	0·331	0·096	—
580	0·68	0·185	0·039	0·037	—
705	2·30	0·019	0·006	0·057	—

* These wavelengths used for the simultaneous determination of nickel, cobalt, iron, and copper.

The simultaneous determination was tested as follows: Approximately 500 ml of a solution containing copper, nickel, cobalt, and iron were acidified with hydrochloric acid and treated with 20 ml of 20% hydroxylamine hydrochloride. After allowing the solution to stand for about 1 min, 100 ml of 50% magnesium nitrate solution were added, followed by 80 ml each of pyridine and 10% potassium thiocyanate. The solution was adjusted to pH 6–7 by addition of 50% sodium hydroxide. The mixture was transferred to a 2-litre separatory funnel and diluted to about 1 litre with water. Five extractions with 10-ml portions of chloroform were necessary before the extracts were colourless; two additional extractions were made. The extracts, drained into a 100-ml volumetric flask, were cleared by the addition of 4 ml of acetone and the solution was diluted to the mark with fresh chloroform. The absorbances, measured at 335, 360, 375, and 405 mμ, were 0·845, 0·580, 0·597, and 0·385, respectively. The matrix solution of the four simultaneous equations gave the results shown in Table V. The calculations for the simultaneous determination of more than three components are laborious, even by the matrix method.

DISCUSSION

The optimum conditions for the extraction of the metal pyridine thiocyanates are high ionic strength of the aqueous solution, adjusted to pH 5–8, and containing an excess of pyridine. Because pyridine is much more soluble in chloroform than it is in water, when equilibrated between the two solvents, the extractions are made from a relatively large volume of aqueous solution. This condition, generally unfavourable for an extraction method, is required in these methods to hold some pyridine in the aqueous phase in order to obtain complete reaction and extraction. The various metal pyridine thiocyanates vary widely in extractability in chloroform. The distribution ratios of the pyridine thiocyanates between chloroform-pyridine and water-pyridine were found, in the cases of nickel, cobalt, and copper, to be approximately 10^2,10^3, and 10^4, respectively.

TABLE V.—RESULTS OF SIMULTANEOUS DETERMINATION OF COPPER, NICKEL, COBALT, AND IRON

Component	Taken, *mg*	Found, *mg*
Copper	0·55	0·50
Nickel	46	41
Cobalt	0·63	0·61
Iron	1·0	1·1

Phosphate must be absent on account of the high concentration of magnesium ion used to increase the ionic strength. Bromide, iodide, cyanate, cyanide, and peroxydisulphate should be absent, because they also give cation-pyridine reactions similar to thiocyanate.[29]

Acknowledgment—Thanks are hereby expressed to Columbia-Southern Chemical Corporation for use of facilities in the Research Department in Corpus Christi, Texas; most of the work reported was carried out in those laboratories.

Zusammenfassung—Die spektrophotometrische Bestimmung von Eisen, Kupfer, Nickel, Kobalt und Mangan, beruhend auf der Chloroformextraktion ihrer Pyridin-thiocynate-komplexe wurde untersucht. Optimale Bedingungen benötigen einen pH-Bereich von 5–8 (wässrige Phase) und die Anwesenheit von Tartrate zur Verhinderung von Hydroxydfällungen. Pyridin muss in Überschuss anwesend sein, da es von Chloroform sehr rasch extrahiert wird. Die Resultate können verbessert werden, wenn die Extraktion aus Medium mit hoher ionaler Stärke (2 und darüber) gemacht wird, was durch Zusatz von Magnesium-nitrate erzielt wird. Perchlorate reduzieren die Absorption jedoch ist der Effekt im wesentlichen konstant über einen Bereich von 0·8–2 m in Perchlorat. Die Pyridin-thiocyanat-komplexe können auch mittels Benzol, substituiertem Benzol oder halogenierten Kohlenasserstoffen ausgezogen werden, jedoch ist Chloroform deutlich überlegen in Hinblick auf Schnelligkeit, Wirkungsgrad und Stabilität der Färbung. Ein Beispiel der Simultanbestimmung von Kupfer, Nickel, Kobalt und Eisen in derselben Lösung wird beschrieben. Anionen die ebenfalls Metallpyridin-komplexe bilden müssen abwesend sein.

Résumé—Les auteurs ont étudié les dosages spectrophotométriques du cuivre, du nickel, du cobalt, du fer et du manganèse, basés sur l'extraction par le chloroforme des thiocyanates de métal-pyridine. Les conditions les meilleures nécessitent que le pH de la solution aqueuse soit à peu près dans le domaine 5–8, l'acide tartrique est utilisé pour empêcher la précipitation des hydroxydes. Un excès de pyridine doit être utilisé car le chloroforme extrait rapidement la pyridine de la solution aqueuse. Les résultats sont améliorés en faisant l'extraction d'une solution de force ionique élevée (2 ou plus)

qui est obtenue à l'aide du nitrate de magnésium. Le perchlorate diminue l'absorbance, mais l'effet ne varie pas dans le domaine de concentration du perchlorate de 0,8 à $2M$. Bien que les thiocyanates de métal-pyridine soient extraits par le benzène, les benzènes substitués et les hydrocarbures halogènés, le chloroforme est supérieur aux autres solvants pour l'efficacité de l'extraction et pour la stabilité de la couleur du composé extrait. Les auteurs donnent un exemple de dosage simultané du cuivre, du cobalt et du fer dans la même solution. Les anions qui forment aussi des complexes de métal-pyridine doivent être absents.

REFERENCES

[1] G. Spacu, *Bul. Soc. Stiinte Cluj*, 1922, **1**, 284.
[2] *Idem, ibid.*, 296.
[3] G. Spacu and J. Dick, *Z. analyt. Chem.*, 1927, **71**, 185.
[4] *Idem, Bul. Soc. Stiinte Cluj*, 1928, **4**, 23.
[5] P. Spacu, *Z. analyt. Chem.*, 1939, **115**, 423.
[6] G. Spacu and J. Dick, *ibid.*, 1927, **71**, 442.
[7] *Idem, ibid.*, 97.
[8] *Idem, Bul. Soc. Stiinte Cluj*, 1928, **4**, 241.
[9] *Idem, Z. analyt. Chem.*, 1929, **76**, 273.
[10] *Idem, Bul. Soc. Stiinte Cluj*, 1928, **4**, 177.
[11] L. Cuny, *J. Pharm. Chim.*, 1924, **30**, 240.
[12] J. Golse, *Bull. Soc. chim.*, 1931, **49**, 84.
[13] A. Martini, *Mikrochemie*, 1929, **7**, 30.
[14] R. Biazzo, *Ann. Chim. appl.*, 1926, **16**, 96.
[15] R. A. Bosee and P. Fehder, *J. Amer. Pharm. Assoc.*, 1940, **29**, 141.
[16] D. L. Drabkin and C. S. Waggoner, *J. Biol. Chem.*, 1930. **89**, 51.
[17] C. A. Elvehjem and C. W. Lindlow, *ibid.*, 1929, **81**, 435.
[18] C. A. Elvehjem and W. F. Hart, *ibid.*, 1931, **91**, 37.
[19] H. T. Gebhardt and H. H. Sommer, *Ind. Eng. Chem. Analyt.*, 1931, **3**, 24.
[20] J. B. Hester, *Chem. Analyst*, 1936, **25**, 78.
[21] R. Schonheimer and F. Oshima, *Z. physiol. Chem.*, 1929, **180**, 249.
[22] F. D. Snell and C. B. Snell, *Colorimetric Methods of Analysis*. D. Van Nostrand Co., New York, 3rd Ed., 1949. Vol. II, p. 125.
[23] M. Jean, *Bull. Soc. chim. France*, 1945, **12**, 437.
[24] T. Moeller and R. E. Zogg, *Analyt. Chem.*, 1950, **22**, 612.
[25] J. M. Cruse and M. G. Mellon, *ibid.*, 1953, **25**, 446.
[26] J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, 1958, **1**, 249.
[27] S. S. Baird, Ph.D. dissertation, The University of Texas, June 1958.
[28] L. J. Chalk, *Analyst*, 1930, **55**, 187.
[29] F. J. Welcher, *Organic Analytical Reagents*. D. Van Nostrand Co., New York, 1947. Vol. III, Chap. I.

Talanta, 1961, Vol. 7, pp. 248 to 252. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF CALCIUM IN BIOLOGICAL MATERIAL*

THE USE OF CALCEIN AS AN INDICATOR IN THE EDTA TITRATION

TAFT Y. TORIBARA and LARYSA KOVAL
Department of Radiation Biology, University of Rochester,
School of Medicine and Dentistry, Rochester, New York, U.S.A.

(*Received* 30 *July* 1960)

Summary—The EDTA titration of calcium using the change in fluorescence of Calcein indicator under ultraviolet illumination at the end-point was very satisfactory for essentially pure calcium chloride solutions. In order to use this method for biological samples, it was found best to separate the calcium by an oxalate precipitation at a pH of 4·7, convert the calcium oxalate to calcium carbonate, and dissolve the calcium carbonate in hydrochloric acid.

INTRODUCTION

IN our laboratory, the routine method for the determination of calcium is a flame photometric procedure following a separation as the oxalate. The method[1] involves careful standardisation of technique with a precision estimated to be 4 to 5%. In certain instances, however, greater precision is desired. This could be achieved with a titrimetric method, providing the end-point was sufficiently sharp. The EDTA titration of calcium at the microgram level has been made very attractive by the recent demonstration of Wilkins[2] that the indicator Calcein[3] gave a very sharp and easily detected end-point under ultraviolet illumination.

Mori[4] has described the use of Calcein for the titration of calcium using CDTA (a reagent similar to EDTA) and has reported success in the direct titration of diluted serum and other biological fluids. Our experience with EDTA titrations has not been equally successful. We have obtained erratic results whenever any direct titrations were attempted.

Because the fluorimetric end-point was so sharp in the titration of pure solutions of calcium, the present studies were undertaken to find the conditions necessary for the determination of calcium in biological samples. We have concluded that the best procedure was to use a separation of calcium, and the separation scheme has been re-investigated.

EXPERIMENTAL

Reagents

Potassium hydroxide, 4% *solution*: Prepared by dissolving 4 g of reagent-grade potassium hydroxide in 100 ml of distilled water. It was stored in a polyethylene bottle.

EDTA, 0·0005*M solution*: Prepared from the disodium salt of (ethylenedinitrilo)tetra-acetic acid (Eastman Kodak No. 6354), and standardised against a calcium solution prepared from calcite.

Calcein solution: Prepared by dissolving 4 mg of Calcein W (G. Frederick Smith Chem. Co.) in

---

* This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

100 ml of 0·25N potassium hydroxide solution. The solution was kept in a refrigerator, but it was found best to make fresh indicator every 3 days.

Apparatus

Illumination. A black light source (George W. Gates and Co. Mil 2F–E) giving radiation of 366.mμ was directed on the titration beaker from the side at right angles to the line of vision of the observer.

Procedure

Separation of calcium. Calcium was precipitated as the oxalate from an acetate buffered solution at a pH of 4·7. Solutions containing protein should first be acidified by the addition of glacial acetic acid. The following directions for serum may be appropriately modified for other solutions:

Dilute 0·5 ml of serum with about 4 ml of distilled water and add 4 drops of glacial acetic acid in a Vycor* centrifuge tube. Add 1 drop of bromocresol green indicator, 1 ml of 4% ammonium oxalate solution and concentrated ammonia solution until the indicator just turns blue-green. Allow the solution to stand overnight in a refrigerator. Centrifuge the solution to settle the precipitate; remove the supernatnat liquid. Place the centrifuge tube in a drying oven until dry, then transfer to a muffle furnace at 500° for 1 hr. Cool the centrifuge tube, add 1 drop of dilute hydrochloric acid (1 part of concentrated acid to 3 parts of water) to dissolve the calcium carbonate, and transfer to the titration beaker with distilled water.

Titration. The titration was carried out in a 20-ml Pyrex beaker placed on a magnetic stirrer with a 0·5 in. Teflon-covered magnet inserted in the solution to supply agitation. The calcium solution was transferred to the beaker in a final volume approximating 5 ml. Careful attention was taken not to use excessive acid to dissolve the calcium salts because the subsequent addition of 1 ml of 4% potassium hydroxide solution had been calculated to maintain the pH about 12. Five hundredths (0·05) ml of Calcein solution was added and the titration was carried out in a darkened room with ultraviolet light illuminating the solution. The blank indicator solution itself fluoresces, but the end-point could be easily detected as an appreciable change in intensity of fluorescence which was very sharp.

RESULTS

Because of interest in the determination of calcium in the serum of patients who had been treated with EDTA, recoveries of calcium under exaggerated conditions were made. The precipitations were carried out at pH 4·7, and the samples with EDTA carried a quantity equimolar with the calcium present. Table I shows a series of 40-μg samples of calcium in which the presence or absence of EDTA had no effect on the quantity precipitated.

TABLE I. PRECIPITATION OF CALCIUM WITH AND WITHOUT EDTA PRESENT

Calcium recovered, μg	
EDTA absent	EDTA present
40·0	40·0
40·0	40·0
40·2	39·8
40·0	

Recoveries on pure solutions precipitated at pH 4·7 were good, so a further comparison was made on a pooled serum sample from which one series was precipitated directly as described here, and the other series was precipitated after protein

---

* Vycor centrifuge tubes are not commercially available but may be made easily by drawing the end of a test tube (Corning 19800, 15 mm × 125 mm) to a point in an oxy-gas flame. While borosilicate glass will withstand the temperature of 500°, the Vycor tubes withstand much better the thermal shock of sudden insertion into and withdrawal from the muffle furnace.

removal. The deproteinised serum sample was prepared by treating 2 ml of serum with trichloroacetic acid with a final dilution to 10 ml. A 5-ml aliquot of the acid solution was taken for calcium precipitation. If the volume of the usual quantity of protein in serum were considered, the calcium content of the aliquot of the deproteinised solution would be expected to be about 1·5% higher than that of 1 ml of serum.

Table II shows that the deproteinised serum samples had, in fact, a slightly higher calcium content than the untreated serum samples.

TABLE II. COMPARISON BETWEEN PRECIPITATION FROM UNTREATED AND DEPROTEINISED SERUM

Calcium per 100 ml of serum, *mg*	
Untreated	Deproteinised
8·7	9·1
8·7	8·9
8·8	8·9
8·6	9·1
8·7	8·8
8·8	9·0
—	—
Average 8·7	9·0

Previous studies[5] had shown that a direct precipitation of calcium from aged sera or from sera of some diseased patients did not always result in complete recovery. Complete recovery from deproteinised samples was attributed to the release of calcium from proteins when the pH was lowered. In the present work, it was reasoned that acidification of the serum without precipitation of the protein could accomplish the same result. To check this supposition, a number of 1-ml portions were pipetted from a pooled serum sample on the same day and precipitation according to present directions was carried out on three successive days. The samples were kept in a refrigerator until utilised. The results are given in Table III and show that the process of acidification liberates all of the calcium from the protein. Therefore, complete precipitation was realised.

TABLE III. RECOVERY OF CALCIUM FROM AGED SERUM

Days before precipitation	Calcium per 100 ml of serum, *mg*			
	0	1	2	3
	8·6	8·6	8·5	8·5
	8·5	8·5	8·6	8·7
	8·5	8·5	8·6	8·7
	8·5	8·8		8·5

A comparison on a number of dog serum samples was made between analyses run in the usual method of this laboratory employing the flame photometer[1] and the titration method. The results in Table IV show good agreement between the two methods.

TABLE IV. COMPARISON BETWEEN FLAME PHOTOMETRIC METHOD AND TITRATION

Calcium per 100 ml of serum, *mg*	
Flame photometer	Titration
8·3	8·6
8·8	9·0
8·7	8·9
10·1	9·8
13·9	13·6
13·0	12·7

DISCUSSION

The separation of calcium as the oxalate was utilised after initial attempts to titrate diluted serum directly resulted in poor end-points. Even wet-ashed serum samples gave erratic results; some gave satisfactory end-points immediately while others took as long as 1 to 2 hr to complete because of the fleeting nature of the end-point. The same type of behaviour was observed when phosphate was added to pure calcium chloride samples, and the difficulty was attributed to the slow reaction of the calcium phosphate precipitated at the high pH necessary for the titration. Attempts to titrate a solution of calcium oxalate were likewise unsuccessful because the calcium oxalate precipitated at the high pH. By heating the calcium oxalate at 500° we converted it to calcium carbonate which dissolved in dilute hydrochloric acid to give a solution of calcium chloride for satisfactory titration.

For the EDTA titration used in this work, the oxalate separation of the calcium made possible a uniform treatment of all kinds of samples. Because of the subsequent heating at 500°, it was not necessary to wash the precipitate to get rid of excess oxalate. Small amounts of sodium or phosphate did not interfere with the titration.

Previous work[5] had shown that all of the calcium could not be precipitated in the conventional Clark-Collip[6] manner from aged sera or in the case of some diseased states. The non-availability of some of the calcium was attributed to some alteration in the protein, possibly denaturation, which prevented complete precipitation of calcium oxalate. The liberation of all of the calcium in a form which could be completely precipitated was accomplished by trichloroacetic removal of the protein. The trichloroacetic treatment served a dual purpose in releasing the protein-bound calcium by lowering the pH (Carr[7] has shown that bovine serum albumin binds no calcium below a pH of 4·5) and in removing the protein.

If the calcium were precipitated as the oxalate at a pH at which there is virtually no protein binding, the necessity for protein removal would be eliminated. In a study of the effect of pH on the precipitation of calcium oxalate in the presence of EDTA,[8] it was shown that essentially complete precipitation could be accomplished at a pH as low as 4·7 (EDTA does not complex calcium at such pH). An acetate buffer system was utilised because the phosphate and bicarbonate systems native to serum did not buffer in this pH range. The addition of the acetic acid before the addition of ammonium oxalate released all of the protein-bound calcium by reducing the pH. Precipitation of calcium oxalate at the lower pH also reduced the possibility of contamination by calcium phosphate and by precipitation of magnesium compounds.

The indicator used in this work had an appreciable fluorescence in the absence of calcium. Wallach and coworkers[9] prepared and studied 3:6′-dihydroxy-2:4-bis-[N:N′-di(carboxymethyl)aminomethyl]fluoran which gave very little fluorescence at the end-point of a calcium titration with EDTA. Körbl and coworkers[10] studied a fluorescein-complexone (bis-[N:N′-di(carboxymethyl)aminomethyl]fluorescein) and reported that their compound showed in alkaline solution only a small residual fluorescence. These compounds are undoubtedly the purer forms of the active components in Calcein and would be preferable in a fluorescence method for calcium. For the titration end-point, however, the change in intensity of the fluorescence of the commercially available Calcein was sharp and easily detected.

Zusammenfassung—Die EDTA-Titration von Calcium mittels fluorimetrischen Endpunkte unter Verwendung von UV-Licht und Calcein-indicator, verläuft in reinen Calciumlösungen sehr zufriedenstellend. Um diese Methode für biologische Proben heranzuziehen, wird Calcium erst als Oxalat gefällt, das Oxalat ins Karbonat übergeführt und letzteres in Salzsäure gelöst.

Résumé—Le titrage du calcium par L'EDTA utilisant la variation de fluorescence de l'indicateur, la calcéine, sous exposition ultra-violette au point équivalent, est tres satisfaisant pour des solutions de chlorure de calcium pures. Afin d'utiliser cette méthode pour des échantillons biologiques, les auteurs ont trouvé qu'il était préférable de séparer le calcium par précipitation de l'oxalate à pH 4,7, de transformer l'oxalate de calcium en carbonate de calcium et de dissoudre le carbonate de calcium dans l'acide chlorhydrique.

REFERENCES

[1] T. Y. Toribara, P. A. Dewey and H. Warner, *Analyt. Chem.*, 1957, **29**, 540.
[2] D. H. Wilkins, *ibid.*, 1960, **32**, 5.
[3] H. Diehl and J. H. Ellingboe, *ibid.*, 1956, **28**, 882.
[4] K. Mori, *Arch. Biochem. Biophys.*, 1959, **83**, 552.
[5] P. S. Chen, Jr. and T. Y. Toribara, *Analyt. Chem.*, 1954, **26**, 1967.
[6] E. P. Clark and J. B. Collip, *J. Biol. Chem.*, 1925, **63**, 461.
[7] C. W. Carr, *Arch. Biochem. Biophys.*, 1952, **43**, 147.
[8] T. Y. Toribara and L. Koval, Submitted to *J. Lab. Clin. Med.*
[9] D. F. H. Wallach, D. M. Surgenor, J. Soderberg and E. Delano, *Analyt. Chem.*, 1959, **31**, 456.
[10] J. Körbl, F. Vydra and R. Přibil, *Talanta*, 1958, **1**, 138.

Talanta, 1961, Vol. 7, pp. 253 to 263. Pergamon Press Ltd. Printed in Northern Ireland

PRECIPITATION AND DETERMINATION OF TANTALUM AND NIOBIUM FROM HOMOGENEOUS SOLUTION WITH 3:3′:4′:5:7-PENTAHYDROXYFLAVANONE

FRANK L. CHAN
Aeronautical Research Laboratories
Wright-Patterson Air Force Base, Ohio, U.S.A.

(*Received* 28 *July* 1960)

Summary—3:3′:4′:5:7-Pentahydroxyflavanone in fairly concentrated acidic solution (6–9*N*) does not precipitate tantalum and niobium; however, on heating or boiling, in the presence of air, this flavanone is transformed into 3:3′:4′:5:7-pentahydroxyflavone, which precipitates any tantalum and niobium present in the solution. Under the precipitation conditions, racemisation of the flavanone also takes place. The racemised flavanone which is less soluble than the original *d*-form may accompany the tantalum and niobium precipitates without affecting the quantitative determination of these elements.

The precipitation of the tantalum and niobium complexes can be controlled by regulating the acidity and the duration of boiling, as well as the concentration of the flavanone. Experimental data and procedures are given for the precipitation and determination from homogeneous solution of tantalum and niobium complexes. Zirconium and molybdenum do not interfere with the determination. Titanium must be absent or present only in minute quantity.

Since the generation of the precipitating reagent, flavone, from the flavanone is comparatively slow, the precipitation of tantalum and niobium is uniform throughout the solution. By this technique, adsorption and co-precipitation of potassium and sulphate ions in the solution are shown to be negligible. This is in contrast to the less effective dropwise addition of the flavone reported by earlier investigators, in which adsorption and co-precipitation were pronounced.

In the present study, tantalum and niobium oxides were fused with potassium bisulphate. There is no necessity using hydrofluoric acid to dissolve these oxides and therefore no polyethylene apparatus is required.

INTRODUCTION

ALL investigators and authors dealing with the chemical determination of tantalum and niobium have emphasised that it is a difficult undertaking.[6,10,16,17,19] Dupraw,[6] as late as 1953, commented that current methods for the separation and determination of the oxide combinations of titanium, tantalum, niobium and tungsten, failed to qualify as acceptable analytical procedures with respect to selectivity, accuracy, reproducibility, and ease of manipulation. Among the earlier methods for the determination of niobium and tantalum, Hoffman[10] has mentioned that Schoeller's tannin method[23] is satisfactory, though laborious. Besides the elaborate separations and operations, Schoeller's method has such undesirable features as the formation of colloidal solutions and precipitates, and absorption in solution due to hydrolysis.

Moshier and Schwarberg have used N-benzoyl-N-phenylhydroxylamine for the determination of tantalum in the presence of niobium.[20] Hiskey and his associates[9] reported the use of octochloropropane with chlorinated ores containing titanium, niobium, tantalum, and zirconium. Titanium is subsequently distilled off leaving the remaining three elements. Spectrophotometric determination of tantalum and niobium has also been reported by Klinger and Koch[11] and by Pallila, Adler, and Hiskey[21] using sulphuric acid and hydrogen peroxide.

Other approaches to the determination of tantalum and niobium have been reported.[8] Among them, the X-ray fluorescence method should be mentioned. Since the second order K-lines of niobium are difficult to resolve from the $L_{\alpha 1}$-line of tantalum, Birks and Brooks[1] have made measurements at several angles and compared the integrated intensity of the unresolved tantalum-niobium lines with that of a single niobium line. Carl and Campbell[2] adopted Birks and Brooks' procedure for the analysis of combined tantalum and niobium oxides separated chemically from ores. Mortimore, Romans, and Tews[19] made use of the internal standard principle to analyse ores containing tantalum and niobium. A more recent development in X-ray fluorescence analysis of tantalum and niobium has been the introduction of silicon and germanium crystals by Lablin.[15] By using these crystals, small amounts of tantalum can be determined in the presence of large amounts of niobium.

The method for the determination of tantalum and niobium described in this paper makes use of 3:3′:4′:5:7-pentahydroxyflavanone as a precursor of the precipitation agent. 3:3′:4′:5:7-Pentahydroxyflavanone is also known as dihydroquercetin (DHQ).

DHQ was first found in small quantity in Douglas-fir heartwood by Pew.[22] It was later discovered that this compound exists in large amounts in Douglas fir bark. Kurth and Chan[12] have made an extensive study of the extraction and isolation of this compound. Barks collected from New Mexico, California, Washington and Oregon have been analysed for DHQ, wax, and tannin. Properties such as the anti-oxidant activity of DHQ and its esters have also been investigated by Kurth and Chan.[13]

Exceptionally pure DHQ has been successfully used as a reagent for the spectrophotometric determination of molybdenum in steel and other substances.[4,5]

A large number of experiments has been carried out with the sole purpose of determining whether or not DHQ forms insoluble chelates with tantalum or niobium. Results showed that DHQ does not precipitate tantalum and niobium in acidic solution stabilised with ammonium oxalate, even after standing for a period of 3 weeks at room temperature. However, upon boiling in the presence of air, DHQ in acidic solution readily changes to quercetin which forms an insoluble chelate with tantalum and niobium. Since quercetin can thus be generated from DHQ at elevated temperatures, it provides a means for their precipitation and separation from homogeneous solution, a technique originated by Willard.[3,7] Advantages of precipitation from homogeneous solution are fully explained in a book recently published.[7]

Although the detailed mechanism involving precipitation of tantalum and niobium with DHQ is under investigation in the Aeronautical Research Laboratories, it is believed[18] that the reaction involved may take place according to the scheme shown in Fig. I.

Blank runs on DHQ, sulphuric acid, and ammonium oxalate in the same proportion and under identical conditions to those used for the determination of tantalum and of niobium have been made. Besides much unreacted DHQ, quercetin and some degradation products of DHQ were found in the precipitate.

The fact that the earth acids are readily hydrolysed and that it is difficult to keep tantalum and niobium in solution requires that the precipitation of these elements with DHQ must take place in strong acid solution and in the presence of oxalate. In $6N$ or more strongly acidic solution, DHQ is readily racemised and precipitates of tantalum and of niobium may be accompanied by the racemised DHQ, especially when filtration is performed at room temperature. The racemised material does not interfere with the determination of either tantalum or niobium when these chelates are ignited and weighed as oxides. Furthermore, elements such as zirconium, which do not precipitate with either DHQ or quercetin and which remain in 6*N* or more strongly acidic solution, can be separated quantitatively from tantalum or niobium by the technique of precipitation from homogeneous solution. Separation of tantalum oxide and niobium oxide from molybdenum is also possible. Titanium is only partially precipitated by this method and therefore separation is not possible unless only a trace of it is present.

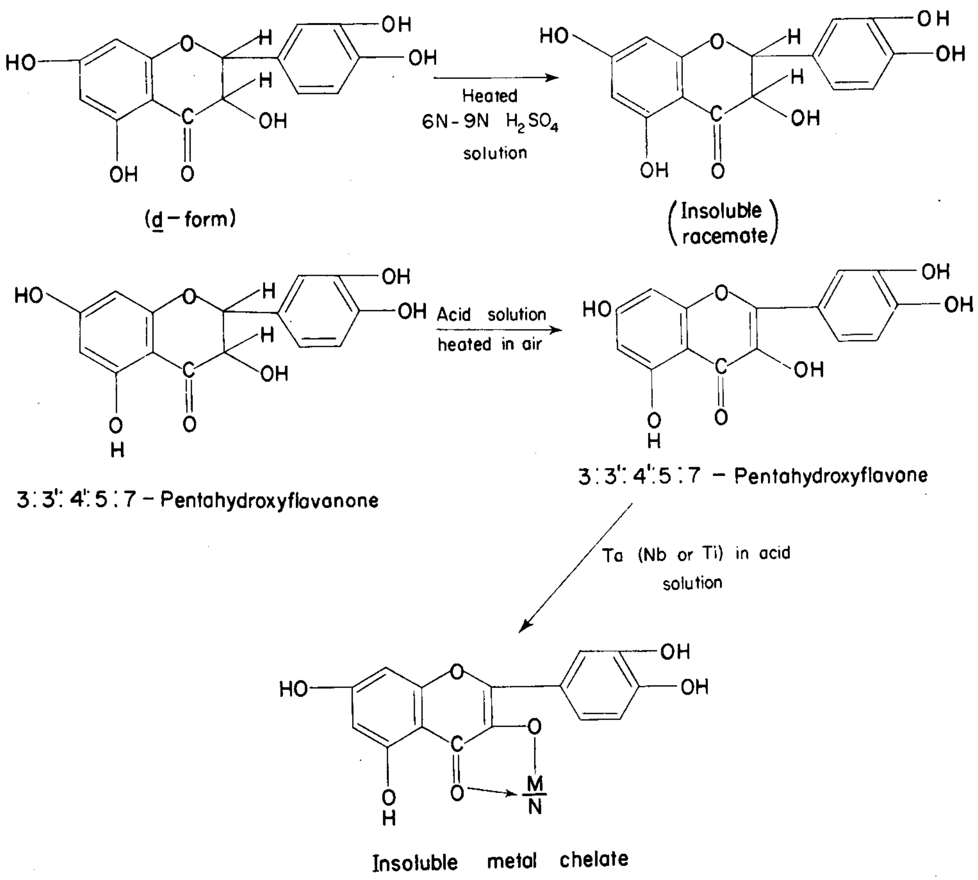


FIG. 1.—Transformation of flavanone to flavone and the formation of insoluble chelates.

EXPERIMENTAL

Reagents

DHQ: Prepared as described by Kurth and Chan.[12]

Molybdenum stock solution: To 4·9042 g of $(NH_4)_6MO_7O_{24}\cdot 4H_2O$ (analytical reagent, Merck & Co., Inc.) was added a small amount of water. The clear solution was diluted to 1000 ml (1 ml ≡ 4 mg of molybdenum oxide).

Tungsten stock solution: To 5·69 g of $Na_2WO_4\cdot 2H_2O$ (analytical reagent, J. T. Baker Chem. Co.) sufficient water was added to dissolve the solid, then the solution was diluted to 1000 ml (1 ml ≡ 4 mg of tungsten oxide).

Titanium stock solution: A mixture of 0·5000 g of titanium oxide (analytical reagent, J. T. Baker Chem. Co.) and 5 g of potassium bisulphate was fused until a clear mass resulted. The melt was cooled, then dissolved in concentrated sulphuric acid. More concentrated sulphuric acid was added until the final volume was 100 ml (1 ml ≡ 5 mg of titanium oxide).

Zirconium stock solution: To 3·2692 g of $ZrOCl_2 \cdot 8H_2O$ (analytical reagent, Fisher Scientific Co.) was added 10 ml of 18*N* sulphuric acid. The mixture was heated until fumes of sulphur trioxide appeared. Concentrated sulphuric acid (22 ml) was added. The mixture was cooled and carefully diluted to 250 ml (1 ml ≡ 5 mg of zirconium oxide).

Tantalum and niobium stock solutions: Tantalum pentoxide, reagent grade, was from Fisher Scientific Co. and niobium pentoxide, reagent grade, from A. D. Mackay Inc. Spectrographic determination indicated that only a trace of impurities such as Si, Fe, Mg, and Sn were present in these oxides. Fusion of niobium pentoxide with potassium bisulphate and solution of the melt in concentrated sulphuric acid and saturated ammonium oxalate solution was accomplished without difficulty. However, in the early stage of this study, fusion of tantalum pentoxide and potassium bisulphate always gave a cloudy sulphuric acid-saturated oxalate solution. After many trials, the following procedure worked well and a clear solution was obtained with a single fusion.

In a 20-ml silica crucible was placed 3 g of reagent-grade potassium bisulphate. A sample of 400 mg of tantalum (or niobium) pentoxide was weighed, placed in a 30-ml beaker (tall-form) and, with a stirring rod, mixed thoroughly with 13 g of potassium bisulphate. The mixture was transferred to the fusion crucible. The beaker and the stirring rod were cleaned twice with 2 g of potassium bisulphate and placed on top of the mixture in the crucible. Fusion was watched with great care so that no spattering took place. In this way, it was found that a single fusion will effect complete solution of the tantalum (or niobium) pentoxide. The melt was extracted with hot concentrated sulphuric acid, followed by cooling, then by the addition of saturated ammonium oxalate solution. The solution was made up to 500 ml, having a ratio of concentrated sulphuric acid to saturated ammonium oxalate of 0·825.

H_2SO_4-*DHQ-quercetin wash solution 1N:* Five g of DHQ were dissolved in 500 ml of 1*N* sulphuric acid and refluxed for 24 hr. The yellow wash solution was filtered after cooling to room temperature.

Saturated aqueous quercetin wash solution: Prepared by suspending 5 g of quercetin in 500 ml of distilled water. Any undissolved quercetin was filtered off. Quercetin can best be prepared by the method of Kurth and Chan,[13] using DHQ as the starting material. This is conveniently carried out by refluxing 200 ml of a solution containing 10 g of DHQ with 20 g of sodium bisulphite and filtering off any quercetin at intervals of 20 to 25 min. The yellow quercetin melts with sublimation at 316–317°.

Apparatus

Beckman DU Spectrophotometer

Procedure

1. *Precipitation and determination of tantalum and of niobium with DHQ*

A sample containing not more than 20 mg of tantalum oxide (or not more than 20 mg of niobium oxide) is fused in a 20-ml silica crucible with 1 g of potassium bisulphate until completely dissolved. The melt, after cooling to room temperature, is extracted with 25·0 ml of hot concentrated sulphuric acid in four to five portions. Each extract is cooled to room temperature and poured into a 250-ml beaker containing 30 ml of saturated ammonium oxalate. (If properly carried out the resulting solution is colourless and clear). To a 100-ml beaker containing 45 ml of hot water is added 0·5 g of DHQ (1·5 g in the case of the niobium determination) and heated to dissolve. Add, with stirring, the DHQ solution to the covered beaker containing the hot solution of tantalum and boil* for 1 hr (in the case of the niobium determination 15 hr†). To avoid excessive reduction of the volume of solution during boiling, cold distilled water is placed on the concave side of the watch-glass cover.

Add to the reacting solution, after removal from the hot-plate, 50 ml of cold water. Let stand 1 hr.

---

* To avoid bumping due to superheating, it is advisable to heat only part of the bottom of the beaker so that boiling takes place on one side of the beaker.

† The duration of boiling depends on the amount of tantalum and of niobium present, and on the manner in which the DHQ is prepared.

Filter through a Whatman No. 40 filter paper and wash four times with 5-ml portions of 1*N* sulphuric acid-DHQ-quercetin solution and 6 times with 5-ml portions of saturated quercetin solution. Place the filter with its contents in a weighed platinum crucible, dry in an oven at 105°, then ignite to constant weight in an electric muffle furnace heated to 950° (or in a Meker burner having the same temperature, as determined by an optical pyrometer).

Evaporate the filtrate and washings to 140 ml. If precipitation is complete, no more insoluble chelate will appear.

2. *Separation of tantalum from niobium*

A. *Determination of tantalum:* The oxide sample (containing not more than 20 mg of tantalum oxide and not more than 20 mg of niobium oxide) is fused with potassium bisulphate as in 1. The melt, cooled to room temperature, is extracted with 16·8 ml of hot concentrated sulphuric acid in four to five portions. Each extract is cooled to room temperature and poured into a 250-ml beaker containing 30 ml of saturated ammonium oxalate. Heat the clear liquid to 70° and add 1·0 g of DHQ dissolved in 53 ml of hot water. Boil the solution until it turns to brown. Add 20 ml of water and decant through a Whatman No. 40 filter paper. Wash and ignite the precipitate as in 1. Reserve the last 20 ml of the washings for dissolving the DHQ to be used in the niobium determination under B. Evaporate the filtrate to 100 ml for the determination of niobium. A yellow precipitate which appears during the course of the evaporation is filtered through a Whatman No. 40 filter paper and ignited together with the main precipitate.

Determine the amount of niobium in the tantalum precipitate by fusing the entire or a part of the ignited oxide with 0·3–1·0 g of potassium bisulphate. Dissolve the melt with concentrated sulphuric acid. Add 0·1 ml of 30% hydrogen peroxide and make up to 10 ml in a volumetric flask. Compare the solution with standards similarly prepared in a Beckman spectrophotometer at 365 mμ.[21] Reprecipitate tantalum if necessary by adding sufficient concentrated sulphuric acid and saturated ammonium oxalate and by following the procedure given above.

B. *Determination of niobium.* Evaporate the filtrate and the first 30 ml of the washings from the tantalum precipitation until the volume is about 75 ml. Cool the solution and add 7·6 ml of concentrated sulphuric acid. Dissolve 1–1·5 g of DHQ in the 20 ml of filtrate reserved from A and add it to the hot solution. Boil from 1–1·5 hr. Remove from the hot-plate and add 50 ml of water. Let stand for 1 hr. Decant the liquid through a Whatman No. 40 filter paper. Wash and ignite the precipitate as in 1. Evaporate the filtrate and washings to the same volume before filtration to ensure complete precipitation.

RESULTS AND DISCUSSION

The knowledge gained from the many experiments performed elsewhere[11,12] on the air oxidation of DHQ reduced the effort and time on this phase of the present experimental work. Nevertheless, a series of experiments has been conducted here to determine the optimum conditions consistent with good analytical procedures. Only a limited number of the experiments are given in this paper. A number of variables may be cited as follows:

1. Concentration of DHQ in solution.
2. Source and method of extraction of DHQ and its effects on the precipitation.
3. Concentration of sulphuric acid for the reaction between DHQ and tantalum or niobium.
4. Quantity of saturated ammonium oxalate solution added to prevent hydrolysis of the earth acids.
5. Time of boiling the reacting solution.
6. Time of standing after boiling for complete precipitation.
7. Nature of wash solutions.
8. Titanium, molybdenum, and zirconium contamination of the tantalum and niobium precipitate.

Some of the experiments on the precipitation of tantalum and niobium with DHQ are shown in Table I. These results firmly establish that, although tantalum and niobium solutions containing DHQ, sulphuric acid, and ammonium oxalate will remain clear at room temperature for many days, DHQ, under optimum conditions, can be made to react to form the corresponding flavone and thus quantitatively precipitate tantalum or niobium. A detailed study of these results has revealed that for complete precipitation under identical experimental conditions, a greater excess of DHQ is needed to precipitate niobium than to precipitate tantalum. Because tantalum is the first to precipitate from solutions of tantalum and niobium and its precipitation is accomplished with relative ease, attempts have been made to effect a quantitative separation of these two elements, with some success as shown in Table IV. This indicates an improvement over previous results obtained by other investigators, who used an acetone solution of quercetin, added by the dropwise technique.[24]

TABLE I.—STUDY OF VARIABLES ON THE DETERMINATION OF TANTALUM AND NIOBIUM WITH DHQ

Experimental conditions: Sat. $(NH_4)_2C_2O_4$, 30 ml; total volume, 100 ml.

Normality of H_2SO_4	Boiling		Water added after cooling, *ml*	Time of standing, *hr*	DHQ		Ta_2O_5		Nb_2O_5	
	Time, *hr*	Temp, °*C*			Lot no.	Amount used, *g*	Added, *mg*	Found, *mg*	Added, *mg*	Found, *mg*
7	3	100	None	None	1	1	21·4	21·7	—	—
1st–10 2nd–6	1	100	67	1	1	1	21·4	21·3	—	—
1st–10 2nd–6	0·75	100	67	1	1	0·5	21·4	20·2	—	—
6	1·5	94	—	0·5	1	0·5	20·0	18·7	—	—
9	0·25	100	50	None	1	0·5	20·0	15·1	—	—
9	1	100	50	1	6	0·5	20·0	19·8	—	—
9	1	100	50	1	1	0·30	20·0	19·7	—	—
6	None	Room	50	72 (after mixing hot. soln.)	1	0·10	20·0	1·6*	—	—
15	1	100	50	1	1	0·5	20·0	20·0	—	—
18	1	100	50	1	1	0·5	20·2	20·2	—	—
7	6	100	None	None	1	1	—	—	20·0	17·3
7	1	100	None	None	1	0·5	—	—	20·0	3·8
1st–9 2nd–6	0·75	100	50	1	1	0·5	—	—	20·0	11·2
9	0·75	100	50	1	1	0·5	—	—	20·0	15·4

* This amount was due probably to mixing the two solutions at an elevated temperature.

Acid concentration plays an important role in the quantitative precipitation of tantalum and of niobium. Present experiments have shown that precipitation is less complete at lower acidity than at higher acidity. This is a phenomenon which may be considered noteworthy for the separation of elements in general. It is an established fact that if precipitation is attempted in highly acidic solution, a separation from impurities is more likely. With 4*N* sulphuric acid solution, almost no niobium precipitated even after prolonged boiling. However, with 9*N* or higher acidities, both tantalum and niobium were found to precipitate quantitatively. The optimum acid concentration for the separation of tantalum from niobium is between 4·5 and 6·5*N*. In the present study 6*N* sulphuric concentration is used for this separation.

Tantalum and niobium oxides shown in Table I were determined semi-quantitatively for the presence of any potassium adsorbed or co-precipitated with the chelates by using an emission spectrographic method. For a 20-mg sample, the amount of potassium in the oxides varies from 0·01 to 0·2 mg and is 0·1 mg on average. A number of oxides also were used for the determination of sulphate adsorbed or co-precipitated during the precipitation procedure. The amount of sulphate found in the precipitate is of the same order of magnitude as that of potassium present in these oxides.

In Table II, methods of extraction and preparation of the different lots of DHQ are shown. Lot 1 in Table II was prepared by aqueous extraction of the cork portion of Douglas fir bark, converted to alkali salt of DHQ, filtered, then acidified with hydrochloric acid. The material was crystallised once from water. For the method of preparation, see the work of Kurth, Hergert and Ross[14]. The cork portion of the bark was purchased from Weyerhaueser Timber Company, Longview, Washington. Lot 2 was prepared in the same way as Lot 1 with the exception that it was crystallised twice. Lot 3 is a mixture of both the *d*-form and the *l*-form of DHQ. Lot 4 was prepared in the same as was Lot 1 but the material showed a slight yellow discoloration. Lot 5 was prepared by aqueous extraction of Douglas fir cork followed by separation from tannin with ether and crystallised from water twice using activated charcoal. Lot 6 was prepared by ether extraction of Douglas fir cork after wax had been removed, then crystallised from water. For methods of extraction and purification of DHQ, see Kurth and Chan.[12] All of the DHQ in these lots with the exception of Lot 4 is colourless. Regardless of methods and procedures of extraction and preparation, DHQ precipitates tantalum and niobium quantitatively. It was noted that the colour and the rate of precipitation are, however, different with the different lots. For instance, in Lot 4, precipitation of tantalum commenced immediately when a hot solution of DHQ was added to a hot solution consisting of tantalum, 6*N* or 9*N* sulphuric acid, and ammonium oxalate. On the other hand, precipitation of tantalum by DHQ from Lot 5 and Lot 6 will not take place in a solution of 9*N* sulphuric acid and saturated oxalate until 15 min of boiling has elapsed. Quantitative results are shown in Table II. The precipitate of tantalum chelate from DHQ is yellowish or

TABLE II.—METHOD OF EXTRACTION OF DHQ AND ITS EFFECTS ON THE PRECIPITATION OF TANTALUM AND NIOBIUM

Experimental conditions: H_2SO_4, 9*N*; sat. $(NH_4)_2C_2O_4$, 30 ml; total volume 100 ml; water added after boiling, 50 ml; standing time 1 hr.

DHQ		First appearance of precipitate after boiling, *min*	Boiling time, *hr*	Ta_2O_5		Nb_2O_5	
Lot no.	Used, *g*			Added, *mg*	Found, *mg*	Added, *mg*	Found, *mg*
1	0·5	5	1	20·0	20·0	—	—
2	0·5	5	1	20·0	20·3	—	—
3	0·5	5	1	20·0	19·9	—	—
4	0·5	0	1	20·0	20·0	—	—
5	0·5	15	1	20·0	20·2	—	—
6	0·5	15	1	20·0	19·8	—	—
2	1·0	5	1	—	—	20·0	20·4
3	1·0	5	1	—	—	20·0	20·0
5	1·0	20	2·5	—	—	20·0	20·3
6	1·0	20	2·5	—	—	20·0	19·9
6	1·5	25	1·5	—	—	20·0	20·0

light orange in colour. The precipitate of niobium, on the other hand, is deep red or maroon. These precipitates settle readily; they can be filtered without difficulty. Normally the precipitate is fairly yellow at the start and as the reaction progresses, the colour changes slightly to yellowish-orange and sometimes a brownish tint appears when the acid concentration is high. This discoloration is probably due to the presence of niobium or unreacted quercetin.

In spite of the fact that the precipitation of tantalum or of niobium is quantitative under the conditions tried, it is essential that the DHQ used be specified. For the purpose of reproducibility the DHQ must have the following characteristics: crystallised DHQ has 2·5 moles of water, m.p. 241–242° and optical rotation $[\alpha]_D^{25}$ $+39$ (4 g in 100 ml of equal volumes of acetone and water). The DHQ meeting these specifications was prepared by the method described by Kurth and Chan.[12]

Methods of X-ray diffraction and photomicrography are used to identify the transformation of DHQ to quercetin under the conditions used for the precipitation of tantalum and niobium. Figs. 2 and 3 show the different diffraction patterns which serve to distinguish these compounds.

Table III shows that zirconium and molybdenum can be separated from tantalum and from niobium. On the other hand, as much as 3·6 mg of titanium oxide was found in a 20-mg sample of tantalum oxide when 5·0 mg of it was added to the solution before precipitating tantalum with DHQ. The results indicate that the greater the amount of titanium in the mixture, the greater will be the contamination. In 9*N* sulphuric acid, the presence of tungsten to the extent of 24 mg of tungsten oxide gave a cloudy solution even though 3 g of tartaric acid is present.

TABLE III.—DETERMINATION OF TANTALUM AND OF NIOBIUM IN THE PRESENCE OF ZIRCONIUM, MOLYBDENUM, AND TITANIUM

Experimental conditions: H_2SO_4, 9*N*; sat. $(NH_4)_2C_2O_4$, 30 ml; DHQ (Lot 1) for Ta determination 0·5 g, for Nb determination 1 g; total volume, 100 ml; boiling time for Ta determination, 1 hr for Nb determination, 1·5 hr; water added after boiling, 50 ml; standing time, 1 hr.

Zirconium oxide added, *mg*	Molybdenum oxide added, *mg*	Titanium oxide added, *mg*	Ta_2O_5		Nb_2O_5	
			Added, *mg*	Found, *mg*	Added, *mg*	Found, *mg*
30·0	—	—	20·0	20·0	—	—
60·0	—	—	20·0	20·0	—	—
120·0	—	—	20·0	30·0	—	—
15·0	—	—	—	—	20·0	19·7
30·0	—	—	—	—	20·0	20·0
60·0	—	—	—	—	20·0	20·3
—	24·0	—	20·0	20·4	—	—
—	48·0	—	20·0	21·2	—	—
—	—	5·0	20·0	23·6	—	—
—	—	10·0	20·0	25·5	—	—
—	—	20·0	20·0	28·7	—	—

By the dropwise addition of quercetin reagent to a 50:50 mixture of tantalum and

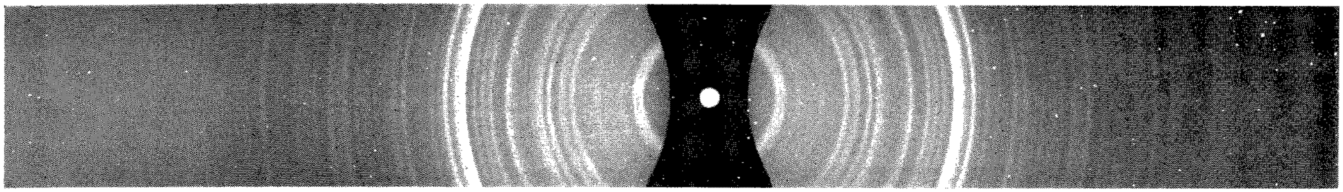


FIG. 2.—X-ray diffraction pattern of DHQ extracted from Douglas fir bark by the method of Kurth and Chan.[12]

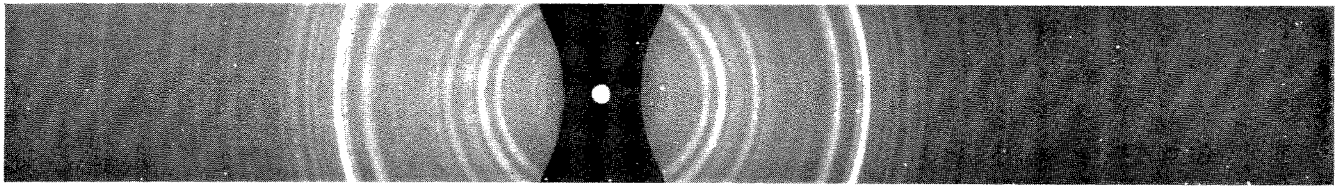


FIG. 3.—X-ray diffraction pattern of quercetin prepared by the method of Kurth and Chan.[13]

niobium, earlier investigators[24] have found that 22–35% of niobium oxide is present in the tantalum precipitate. Thus these investigators concluded that no separation of tantalum from niobium can be achieved by the use of quercetin or morin.

Attempts have been made to separate tantalum from niobium by regulating the acidity and the amount of DHQ in the boiling mixture. It was found that, in 4–6*N* sulphuric acid solution, the precipitation of tantalum will take place first in the homogeneous solution. As long as tantalum is present in the mixture, the flavone, slowly generated from DHQ, will precipitate it and practically no niobium will be precipitated. After all of the tantalum has been precipitated, the flavone from DHQ will then precipitate the niobium. The two stages of precipitation can be observed by the change in colour of the precipitate.

In the present study many attempts were made to effect a sharp separation, but with only partial success. It was finally discovered that in order to precipitate all of the tantalum from a solution, a small amount of niobium accompanied the tantalum. A correction was then made on the niobium precipitated. The small amount of niobium oxide in the tantalum oxide can be quickly and reliably determined spectrophotometrically using concentrated sulphuric acid and hydrogen peroxide. The results are shown in Table IV.

TABLE IV.—SEPARATION OF TANTALUM FROM NIOBIUM USING THE METHOD OF PRECIPITATION FROM HOMOGENEOUS SOLUTION WITH DHQ

Experimental conditions: H_2SO_4, 6*N*; sat. $(NH_4)_2C_2O_4$, 30 ml; total volume, 100 ml; DHQ for Ta determination, 1·0 g, for Nb determination, 1·5 g (1–5), 1·0 g (6); boiling time for Ta determination, 70 min (5), 100 min (4), 130 min (3), 160 min (1, 2, 6), for Nb determination, 150 min; standing time for Nb determination, 60 min, for Ta determination, none; water added after boiling for Nb determination, 50 ml, for Ta determination, none.

	$Ta_2O_5 + Nb_2O_5$ found, *mg*	Nb_2O_5 found spectrophotometrically, *mg*	Ta_2O_5			Nb_2O_5			$Ta_2O_5 + Nb_2O_5$		Diff, *mg*
			Present, *mg*	Found, *mg*	Diff, *mg*	Present, *mg*	Found, *mg*	Diff, *mg*	Present, *mg*	Found gravimetrically + spectrophotometrically, *mg*	
1.	21·1	1·26	20·0	19·8	−0·2	20·0	20·5	+0·5	40·0	40·3	+0·3
2.	21·2	1·08	20·0	20·1	+0·1	13·3	13·8	+0·5	33·3	33·9	+0·1
3.	17·0	1·66	16·0	15·3	—0·7	20·0	20·5	+0·4	36·0	35·8	−0·2
4.	12·9	1·98	11·2	10·9	−0·3	20·0	20·2	+0·2	31·2	31·1	−0·1
5.	5·8	1·04	5·6	4·8	−0·8	20·0	20·6	+0·6	25·6	25·4	−0·2
6.	20·7	0·72	20·0	20·0	0·0	4·0	3·9	−0·1	24·0	23·9	−0·1

Acknowledgement—The author wishes to thank Captain S. F. Brokeshoulder, USAF, and his assistant, Mr. W. H. Jones, of Materials Central, WADD, W-PAFB, Ohio, for emission spectroscopic determinations of the trace of potassium adsorbed or coprecipitated with tantalum and niobium by precipitation from the homogeneous solution. Acknowledgment is also due to Mr. C. D. Houston of the same organisation for the determination of sulphur in the ignited oxides.

Zusammenfassung—3:3′:4′:5:7-Pentaoxyflavanon in stark saurer Lösung (6–9*N*) gibt keine Fällung mit Niob und Tantal. Wird die Lösung jedoch in Gegenwart von Luft gekocht, so oxydiert das Flavanon zu 3:3′:4′:5:7-Pentaoxyflavon, welches die genannten Metall fällt. Unter den Fällungsbedingungen racemisiert das Flavanon. Das Racemat ist schwer löslich, sodass es im Metallniederschlag gefunden werden kann, was jedoch die quantitative Fällung nicht beeinflusst.

Die Fällung kann durch Regulieren der Acidität, Dauer des Kochens und Konzentration des Flavanons kontrolliert werden. Experimentelle Ergebnisse werden mitgeteilt. Zirkon und Molybdän stören nicht, Titan jedoch muss abwesend sein.

Da die Bildung des Flavons langsam ist, findet eine gleichmässige Fällung durch die gesamte Lösung statt. Daher ist die Absorption von Kalium und Sulfat äuasserst gering und praktisch vernachlässigbar. Das steht in vorteilhaftem Gegensatz zu der tropfenweisen Zugabe von Flavone in früher beschriebenen Methoden, die stark nuter Mitfällungserscheinungen leiden.

Tantal- und Nioboxyd werden mit Kaliumbisulfat aufgeschlossen. Flussäure wird nicht verwendet, weshalb sich der Gebrauch von Polyäthylenapparaturen erübrigt.

Résumé—La 3:3′:4′:5:7-pentahydroxyflavanone en solution acide moyennement concentrée (6*N*–9*N*) ne précipite pas le tantale et le niobium; cependant, en chauffant ou en portant à l'ébullition, en présence d'air, cette flavanone est transformée en 3:3′:4′:5:7-pentahydroxyflavone, qui précipite le tantale et le niobium en solution. Dans les conditions de précipitation utilisées, il se produit une racémisation de la flavanone. La flavanone racémisée, qui est moins soluble que la forme D originale, peut accompagner les précipités de tantale et de niobium sans gêner le dosage quantitatif de ces éléments.

La précipitation des complexes du tantale et du niobium peut être controlée par le réglage de l'acidité, la durée de l'ébullition, ainsi que la concentration de la flavanone. L'auteur donne les résultats expérimentaux et les processus de précipitation et de dosage en solution homogène des complexes du tantale et du niobium. Le zirconium et le molybdène ne gênent pas le dosage. Le titane doit être absent ou présent seulement en très faible quantité.

Comme le formation du réactif précipitant, la flavone, à partir de la flavanone est comparativement lente, la précipitation du tantale et du niobium est uniforme dans toute la solution. Par cette technique, l'auteur montre que l'adsorption et la coprécipitation des ions potassium et sulfate dans la solution sont négligeables. Cela est à l'opposé de l'addition goutte à goutte, moins efficace, de flavone, mentionnée par des chercheurs plus anciens; dans cette méthode, l'adsorption et la coprécipitation sont marquées.

Dans cette étude, les oxydes de tantale et de niobium ont été fondus avec du bisulfate de potassium. Il n'est pas nécessaire d'utiliser d'acide fluorhydrique pour dissoudre ces oxydes, et c'est pourquoi un appareillage en polyéthylène n'est pas exigé.

REFERENCES

[1] L. S. Birks and E. J. Brooks, *Analyt. Chem.*, 1950 **22,** 1017.

[2] H. F. Carl and W. J. Campbell, *Symposium on Fluorescent X-ray Spectrographic Analysis.* ASTM Special Tech. Publication No. 157, Feb., 1954.

[3] F. L. Chan, Ph.D. Dissertation, University of Michigan, 1932.

[4] F. L. Chan and R. W. Moshier, *Talanta,* 1960, **3,** 272–6.

[5] *Idem,* WADC, 1959, TN 59–265, 6 pp.

[6] W. A. Dupraw, *Separation and Determination of Silicon, Tungsten, Titanium, Niobium and Tantalum in Oxide Mixtures,* Final Report for Proj. No. CO20-5 (90-996C), AMC, W-PAFB, by Armour Research Foundation, October, 1953.

[7] L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution.* John Wiley and Sons, Inc., New York, 1959.

[8] J. L. Hague and L. A. Machlan, *Bur. Stand. J. Res.*, 1959, **62,** 53–7.

[9] C. F. Hiskey, L. Newman and R. H. Atkinson, *Analyt. Chem.* 1952, **24,** 1988–91.

[10] J. I. Hoffman, *ibid.*, 1959, **31,** 1934–40.

[11] P. Klinger and W. Koch, *Tech. Mitt. Krupp Forchungsber,* 1939, **14,** 179.

[12] E. F. Kurth and F. L. Chan, *J. Amer. Leather Chemists Assoc.*, 1953, **XLVIII,** 20–32.

[13] *Idem, J. Amer. Oil Chemists' Soc.*, 1951, **XXVIII,** 433–6.

[14] E. F. Kurth, H. L. Hergert and J. D. Ross, *J. Amer. Chem. Soc.* 1955, **77,** 1621–1622.

[15] P. Lablin, Proceedings, 7th Annual Conference on Industrial Applications of X-ray Analysis, 1958, University of Denver, Denver, Colo.

[16] G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis.* John Wiley and Sons, Inc., 2nd Ed., 1953.

[17] G. E. F. Lundell, J. I. Hoffman and H. A. Bright, *Chemical Analysis of Iron and Steel.* John Wiley and Sons, Inc., New York, 1932.

[18] A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds.* Prentice-Hall, Inc., New York, 1952.

[19] D. M. Mortimore, P. A. Romans and J. L. Tews, *Appl. Spectroscopy*, 1954, **8**, 107–10.
[20] R. W. Moshier and J. E. Schwarberg, *Analyt. Chem.*, 1957, **29**, 947–51.
[21] F. C. Palilla, N. Adler and C. F. Hiskey, *ibid.*, 1953, **25**, 926–31.
[22] J. C. Pew, *J. Amer. Chem. Soc.*, 1948, **70**, 3031–34.
[23] W. R. Schoeller and A. R. Powell, *Analysis of Minerals and Ores of the Rarer Elements.* Hafner Publishing Co., New York, 1955.
[24] O. Tomicek and V. Holocek, *Chem. Listy*, 1952, **46**, 11–4.

Talanta, 1961, Vol. 7, pp. 264 to 268. Pergamon Press Ltd. Printed in Northern Ireland

SOME PHYSICAL AND CHEMICAL PROPERTIES OF VANADIUM DI- AND TRI-CHLORIDES

HEADLEE LAMPREY® and PAUL F. FORSYTH
Metals Research Laboratories, Union Carbide Metals Company,
Niagara Falls, New York, U.S.A.

(*Received* 5 *August* 1960)

Summary—New physical property data are reported for the compounds VCl_2 and VCl_3. Both compounds hydrolyse and oxidise in acidic aqueous solution, the former rapidly and the latter slowly. They are slightly soluble in organic solvents and the solutions are stable when protected from moisture and oxygen of the air. Heated in air, VCl_2 begins to oxidise to V_2O_5 around 300°, but some formation and volatilisation of $VOCl_3$ occurs; under similar conditions VCl_3 is converted to volatile $VOCl_3$ around 250°. Heated in argon, VCl_2 volatilises at 1000°, whereas VCl_3 first disproportionates at 600° to volatile VCl_4 and solid VCl_2, and the latter volatilises as the temperature is raised to 1000°. X-ray diffraction data are given for VCl_2.

THE lower chlorides of vanadium, VCl_2 and VCl_3, have been known since the time of Berzelius. They have never been commercially available and as a result their properties are, even today, not too well known. About the only use to which they have been put is as titrimetric agents in analytical chemistry.[1] Recently, these compounds have been offered for sale, particularly as catalysts for olefin polymerisations. Because of their impending industrial utility, it is timely to study the physical and chemical properties of the commercial materials in greater detail. In this paper the results of recent studies on their solubilities and their hydrolytic and thermal stabilities are given. Powder X-ray diffraction analysis is also given for vanadium dichloride; corresponding data for vanadium trichloride have already been published.[2]

EXPERIMENTAL

Preparation of materials

Fifty-one lb of vanadium tetrachloride, made by direct chlorination of scrap vanadium or vanadium carbide, were refluxed in a 5-gal, glass-lined vessel and the liberated chlorine allowed to escape:

$$2VCl_4 \rightarrow 2VCl_3 + Cl_2 \uparrow .$$

Thirty-three lb of vanadium trichloride were obtained, *i.e.* a 70% yield based on vanadium. Analysis of the product showed 94·6% VCl_3 and 5·4% VCl_4 for a gross composition of approximately $VCl_{3\cdot04}$.

Vanadium dichloride was prepared by reducing this vanadium trichloride with hydrogen at 750°. Ninety-two per cent conversions to material consisting of 99·57% VCl_2 and 0·25% VCl_3 were obtained. The iron content of the product was less than 0·10%.

These products are, therefore, technical-grade compounds rather than ultrapure chemicals. Some of their known properties, as reported in the literature, are as shown in Table I.

Solubilities

The organic solvents used were reagent quality in all cases. The benzene, ethyl ether, and carbon tetrachloride were dried by storing in contact with sodium, then distilled. The tetrahydrofuran was refluxed over and distilled from caustic soda to remove peroxide contamination, then dried over Linde Molecular Sieves. The ethanol was slurried with Molecular Sieves, refluxed over freshly prepared calcium oxide and finally distilled from additional lime. The acetone was dried over Molecular Sieves and distilled from anhydrous potassium carbonate.

The water remaining in the solvents was determined with Karl Fischer reagent. Values obtained are given in Table II.

TABLE I

	VCl_2	VCl_3
Melting point	Sublimes at dull red heat, in H_2 or CO_2	Non-volatile; forms red $VOCl_3$ when heated in air[3]
Colour and form	Hygroscopic, apple-green hexagonal plates	Hygroscopic, peach to purple coloured plates
Sp. gr.	3·09[4,5]	2·82[5]

TABLE II

Solvent	Water, %
Carbon tetrachloride	0·004
Benzene	0·004
Ethyl ether	0·017
Tetrahydrofuran	0·001
Ethanol	0·040

The solubilities of the vanadium chlorides were determined by adding excess solids to the solvents in an argon atmosphere, agitating the mixtures in a constant temperature bath at 25° for 18 hr, and analysing filtered aliquots of the solutions for the total metal contents. These values were then calculated to the weights of metal chlorides in the solutions. Values obtained are shown in Table III, with the colours of the solutions indicated parenthetically.

TABLE III. SOLUBILITIES IN g/100 ML AT 25°

	VCl_2	VCl_3
Acetone	0·07 (blue)	2·47 (red)
Benzene	insoluble	insoluble
Carbon tetrachloride	insoluble	insoluble
Ethanol	0·06 (blue)	3·20 (green)
Ethyl ether	0·04 (blue)	0·09 (blue)
Tetrahydrofuran	0·04 (blue)	0·04 (colourless)

Stability in aqueous solutions

The literature contains conflicting statements as to the stability of vanadium di- and tri-chlorides in water. Vanadium dichloride, in particular, has been variously reported as stable in 0·5*N* hydrochloric acid solution[6] and as soluble with decomposition.[7] Both of these phenomena have been observed in our work. One sample of crystals was found to be very slowly wetted by water, but eventually to dissolve giving solutions which were fairly stable at room temperatures; another batch dissolved immediately in water or dilute hydrochloric acid giving solutions which decomposed rapidly. The difference undoubtedly lay in the way the compound was prepared and perhaps in the presence of traces of catalytic materials. The vanadium dichloride product studied in this investigation was the form that is reactive to water; it decomposes rapidly in hydrochloric acid solutions and much more slowly in dilute sulphuric acid solutions.

In order to study this behaviour in greater detail, solutions containing 0·2% of metal chloride were prepared in de-aerated water containing 5% sulphuric acid. Some of the solutions were exposed to air and some were kept under argon for the duration of the test. The solutions were not shaken. Fig. 1 shows the rate of oxidation of the vanadium di- and tri-chlorides in the solutions under these conditions. Clearly vanadium dichloride begins to decompose rapidly and immediately, and vanadium trichloride much more slowly. Over a period of 12 hr less than 5% of the vanadium trichloride, and 50 to 60% of the vanadium dichloride, is oxidised.

Thermal stability

Little information is contained in the literature concerning the stability[3,8] of vanadium di- and tri-chlorides. The thermal results reported here were measured on an automatic recording Stanton Thermobalance. This apparatus permits continuous weighing on an analytical balance while the sample is being heated in a controlled atmosphere. Furnace temperature and sample weight are followed simultaneously and automatically recorded on a twin-pen electronic recorder. The results here presented were obtained using a heating programme of 4 hr from room temperature to 1400°, *i.e.* a temperature rise of approximately 6° per min. Some tests were made in a flowing argon atmosphere (3 litres of argon per min through the furnace tube) and some in an ordinary air stream. Since the chlorides are hygroscopic all transfers were made in a dry box containing argon and all weighings were made using argon-filled weighing bottles. The weighed test samples were heated in a platinum crucible. The sample weight taken was approximately 500 mg and for convenience all changes in weight were recalculated to a 1-g sample basis before plotting as a function of the change in temperature.

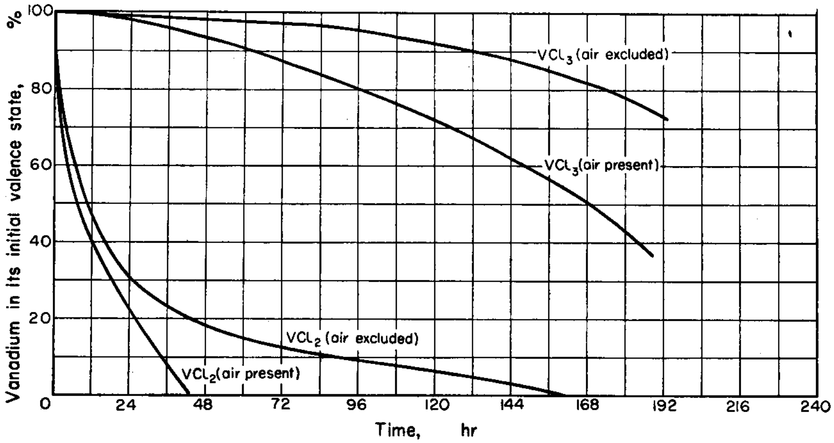


Fig. 1.—Stability of VCl_2 and VCl_3 in 5% sulphuric acid.

The results obtained are shown in Fig. 2. It must be remembered that these curves are the results of heating the samples to 1400° in 4 hr. Somewhat differently shaped curves would be obtained by holding the furnace temperature constant for a period of time at any temperature where a weight change is in progress. A descending slope indicates a weight loss. A horizontal line indicates a stable composition to be present.

The upper curves show that vanadium di- and tri-chloride both decompose in the temperature range between 250 and 350° when heated in air, vanadium dichloride being slightly more stable. From the measured weight losses it can be shown by calculation that vanadium dichloride does not convert quantitatively to vanadium pentoxide. The recorded loss in weight is greater than that necessary for conversion to the oxide, indicating that some of the vanadium volatilised. Thus, it is very probable that some volatile oxychloride is formed simultaneously with the oxidation to vanadium pentoxide. The small increase in weight occurring above 350° corresponds to oxidation of lower oxide states to pentoxide.

When vanadium trichloride is heated in air it forms mainly vanadium oxytrichloride,[3] which immediately boils off. The reaction proceeds rapidly above 250°, as shown by the curve in the figure:

$$VCl_3 + O_2 \rightarrow VOCl_3 \uparrow .$$

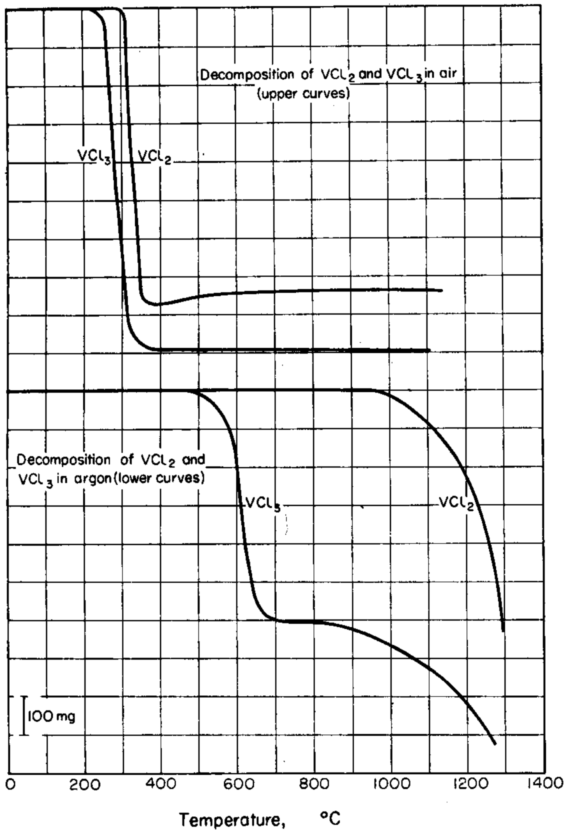


FIG. 2.—Thermal decomposition of vanadium chlorides.

TABLE IV

d (observed)	I (relative)	d (observed)	I (relative)
6·311	1	1·645	6
4·042	10	1·529	2
2·906	5	1·503	3
2·750	6	1·454	7
2·122	7	1·372	2
2·016	3	1·341	2
1·978	0·5	1·319	0·5
1·938	0·5	1·243	3
1·797	5	1·215	5
1·699	1		

In an inert atmosphere (lower curves) vanadium dichloride is seen to sublime at temperatures above 1000°. Vanadium trichloride first disproportionates at 600° to give vanadium tetrachloride, which boils off, and vanadium dichloride, which remains behind. At 1000° this vanadium dichloride then volatilises away.

X-ray diffraction

Powder X-ray diffraction analysis of vanadium dichloride was carried out. Table IV gives the "d" lines and relative intensities on a scale of ten units from unfiltered chromium radiation.

Zusammenfassung—Neue physikalische Daten für die Verbindungen VCl_2 und VCl_3 werden mitgeteilt. Beide Verbindungen hydrolysieren und oxydieren in Wàssriger Lösung, die erstere viel schneller als die letztere. Beide Verbindungen sind sehr wenig löslich in organischen Solventien. Die Lösungen sind stabil, wenn Zutritt von Feuchtigkeit und Luftsauerstoff ausgeschlossen wird. Wenn in Luft erhitzt, beginnt bei etwa 300°C das VCl_2 zu V_2O_5 zu oxydieren, wobei jedoch zu einem kleinen Teil Vanadin-oxychlorid gebildet wird, welches sich verflüchtigt. Unter den gleichen Bedingungen geht VCl_3 bei 250° in fluchtiges $VOCl_3$ über. Wenn unter Argon erhitzt verflüchtigt sich VCl_2 bei 1000°. VCl_3 disproportioniert bei 600° zu flüchtigem VCl_4 und festem VCl_2 welch letzteres bei höherer Temperatur verflüchtigt. Röntgenstrahlungsdaten werden für VCl_2 mitgeteilt.

Résumé—Les auteurs donnent de nouveaux résultats sur les propriétés physiques des composés VCl_2 et VCl_3. Ces deux composés s'hydrolysent et s'oxydent en solution aqueuse, le premier rapidement et le dernier lentement. Ils sont faiblement solubles dans les solvants organiques, et les solutions sont stables quand elles sont protégées de l'humidité et de l'oxygène atmosphérique. Chauffé à l'air, VCl_2 commence à s'oxyder en V_2O_5 vers 300°, mais il y a formation et volatilisation d'oxychlorure de vanadium; dans des conditions semblables VCl_3 se transforme en $VOCl_3$ volatile vers 250°. Chauffé sous argon, VCl_2 se volatilise à 1000°, alors que VCl_3 se dismute à 600° en VCl_4 volatile et VCl_2 solide, et ce dernier se volatilise quand la température atteint 1000°. Des résultats de diffraction des rayons X sont donnés pour VCl_2.

REFERENCES

[1] K. Maass, *Z. analyt. Chem.*, 1934, **97**, 241.
[2] W. Klemm and E. Krose, *Z. anorg. Chem.*, 1947, **253**, 218.
[3] O. Ruff and H. Lickfett, *Ber.*, 1911, **44**, 506.
[4] W. Klemm and L. Grimm, *Z. anorg. Chem.*, 1941, **249**, 198.
[5] F. Ephraim and E. Ammann, *Helv. Chim. Acta*, 1933, **16**, 1273.
[6] W. R. King and C. S. Garner, *J. Phys. Chem.*, 1954, **58**, 29.
[7] *Handbook of Chemistry and Physics*, Chem. Rubber Publ. Co., 32nd Ed.
[8] W. Biltz, *Z. anorg. Chem.*, 1919, **109**, 132.

Talanta, 1961, Vol. 7, pp. 269 to 275. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM WITH 4-METHYLNIOXIME*†

JAMES L. KASSNER, SHIH-FAN TING and E. L. GROVE‡
School of Chemistry, University of Alabama, University, Alabama, U.S.A.

(*Received* 29 *July* 1960)

Summary—A simple method applicable to the spectrophotometric determination of less than 0·001% to more than 1·0% of rhenium in molybdenite concentrate and in "molybdenite roaster flue dust" has been developed. Interfering elements commonly found in these materials are removed in three operations: evaporation with hydrochloric acid, precipitation of hydrous oxides with ammonia, and formation of organometallic compounds with ethyl xanthate and chloroform extraction. The method is based on the formation of a soluble, stable, yellow-green rhenium-4-methylnioxime chelate where rhenium^{VII} is reduced by tin^{II} chloride in a dilute hydrochloric acid solution in the presence of 4-methylnioxime (4-methyl-1:2-cyclohexanedionedioxime). The colour develops in less than 5 min and the chloroform extract shows a maximum absorption at 436 mμ. The calibration curve conforms to Beer's law. The molar extinction coefficient for rhenium-4-methylnioxime is about 6·89 × 10^4 as compared to less than 4·5 × 10^4 reported for other methods for rhenium.

VOTER and Banks[15] pointed out that six- or seven-membered alicyclic *vic*-dioximes with oxime groups attached to adjacent carbon atoms have a much higher molar solubility in water than straight chain aliphatic *vic*-dioximes and that they are more sensitive reagents for the detection of submicrogram amounts of nickel and palladium. Banks and Hooker[2] reported the use of 4-methylnioxime as an excellent gravimetric reagent for both nickel and palladium. Banks and Smith[3] used palladium 4-methylnioxime chelate to develop a spectrophotometric method that had several advantages over other methods.

A similarity of the chemical reactions of nickel, palladium and rhenium with straight-chain aliphatic *vic*-dioximes suggested the possibility of using 4-methylnioxime as a chelating reagent for rhenium.

The method described in this paper is based on the formation of a soluble, stable, yellow-green rhenium-4-methylnioxime chelate, where rhenium^{VII} is reduced by tin^{II} chloride in a dilute hydrochloric acid solution in the presence of 4-methylnioxime.

The colour develops almost immediately and the absorbancy of the chloroform extract of the chelate and the blank remain almost constant for 24 hr or more when room temperature is about 25° and the complex is formed and extracted under optimum conditions.

The calculated molar extinction coefficient for rhenium-4-methylnioxime is about 6·89 × 10^4, compared to less than 4·5 × 10^4 reported for other methods for rhenium.

This method is applicable to the spectrophotometric determination of less than 0·001% to more than 1·0% of rhenium in molybdenite concentrate and in "molybdenite roaster flue dust". Interfering elements[11]—molybdenum, iron, copper, selenium,

---

* This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)-1567.

† Submitted by Shih-Fan Ting in partial fulfillment for the degree of Doctor of Philosophy. Present address, Fisk University, Nashville, Tennessee, U.S.A.

‡ Present address, Armour Research Institute, Chicago, Illinois, U.S.A.

nickel, gold, and silica—commonly found in these materials are removed in three operations: evaporation with hydrochloric acid, hydrous oxide precipitation with ammonia and organometallic compound formation with ethyl xanthate[6,7,8,10,12] and extraction from a dilute hydrochloric acid solution with chloroform.

EXPERIMENTAL

Apparatus

Beckman Model D.U. Spectrophotometer equipped with ultraviolet attachment, matched 1·000-cm silica cells and matched 1·000-cm stoppered Corex cells.

Leeds and Northrup Model 7664 pH Meter (line operated).

Reagents

Standard rhenium stock solution: Prepared from potassium perrhenate with a 99·5% assay obtained from A. D. Mackay, Inc. A solution containing 1·0 mg of rhenium per ml was prepared by dissolving 0·3883 g of the potassium perrhenate in de-ionised water and diluting to 250 ml in a volumetric flask.

Standard rhenium working solutions: Prepared by diluting appropriate aliquots of the stock solution.

4-*Methylnioxime solution:* A 0·34% aqueous solution was used. This approximately saturated solution is stable indefinitely.[1]

Tin^{II} chloride stock solution: Dissolve 3 g of Mallinckrodt analytical reagent tin^{II} chloride dihydrate in 40 ml of concentrated hydrochloric acid and dilute to 100 ml in a volumetric flask with water. This gives a solution approximately 2·5% in tin^{II} chloride.

Ammonium molybdate: Mallinckrodt analytical reagent.

Liquid bromine: Baker & Adamson reagent-grade.

Potassium ethyl xanthate solution: Dissolve 27 g of the salt in water, filter and dilute to 50 ml. Highest purity potassium ethyl xanthate obtained from Eastman Kodak Company was used without purification. Prepare this solution fresh daily.

Chloroform: Baker and Adamson reagent-grade.

All other chemicals used were of analytical reagent quality.

Procedure

Standardisation curve. A calibration curve was prepared by running 6 or more samples ranging from 20 to 160 μg of rhenium, and by plotting micrograms of rhenium versus absorbance at 436 mμ. The straight-line relationship extrapolates through the origin when the extractions are made under optimum conditions.

No interfering elements present. Transfer a nearly neutral solution, containing not more than 160 μg of rhenium as perrhenate, to a 50-ml glass-stoppered volumetric flask. Add 25 ml of 4-methylnioxime solution, 5 ml of tin^{II} chloride solution, dilute to the mark with water and mix. Let stand 5 min, then transfer the solution quantitatively to a 125-ml glass-stoppered separatory funnel. Extract the aqueous phase at room temperature (20–30°) with three portions (4, 3 and 3 ml) of chloroform.[5] Drain the chloroform layers into a 10-ml volumetric flask, and dilute to volume with chloroform. Measure the absorbance of the chloroform phase of the chelate at 436 mμ in a 1-cm stoppered Corex cell versus the chloroform extract of a blank solution prepared in the same manner except for the exclusion of the perrhenate. Convert the absorbance to micrograms of rhenium with the aid of a calibration curve. The range of application can be controlled by varying the size of sample or by diluting to volume and taking an aliquot.

Interfering elements present. Cautiously decompose a sample, containing 160 to 50 μg of rhenium and less than 200 mg of molybdenum, with dilute nitric acid on a steam bath until red fumes have cleared from the beaker. Add concentrated hydrochloric acid and digest the mixture below 100° to a volume of not less than 3 ml to remove nitrate ions. Add hydrochloric acid repeatedly in 5- to 25-ml increments depending on the amount of nitric acid used until all of the nitrate is removed. Usually five or six additions of the hydrochloric acid are required.

After all of the nitrate has been removed from the sample, add 20 ml of water and filter to remove the silica.

Removal of interfering ions. Adjust the silica-free filtrate to a pH of about 9 to 10 with concentrated ammonia. Heat the solution to near boiling for 1–2 min, add filter paper pulp and let stand until the hydrous oxide colloidal particles agglomerate and settle out. Filter and wash the precipitate with 1% ammonium chloride solution. Neutralise the filtrate with sulphuric acid, then add 2 drops of sulphuric acid (sp. gr. 1·84) in excess. Add 10 drops of liquid bromine to ensure that all of the molybdenum in the sample is in the highest valency state. Heat the sample on a low-temperature hot plate, without boiling, to remove the excess bromine. Dilute to volume samples containing more than 160 μg of rhenium and/or about 200 mg of molybdenum and take a suitable aliquot.

Adjust the pH of the solution within the range of 9 to 11 with approximately 5N sodium hydroxide solution. Concentrate the solution on a low-temperature hot plate to a volume of 20 to 25 ml, cool to room temperature and transfer to a glass-stoppered 250-ml separatory funnel, add 10 ml of xanthate solution and mix. Add 6 ml of hydrochloric acid (sp. gr. about 1·36), shake for 5 sec and finally add 50 ml of chloroform. Shake vigorously for 1 min and let stand until separation of the two layers is complete. The aqueous layer should be colourless or very pale pink. The chloroform layer should have an intense red-violet colour. Draw off the chloroform layer and discard it. Continue the extraction with three more 25-ml portions of chloroform to complete the removal of the xanthate complexes. Transfer the sample quantitatively to a 250-ml beaker, add approximately 0·3N potassium permanganate solution dropwise until the permanganate colour persists, then add a drop or two in excess. Destroy the permanganate colour in the sample with a drop of tin^{II} chloride colution. Add about 3 ml of concentrated ammonia and adjust the pH within the range of 8 to 9. Evaporate the sample on a hot plate to a volume of less than 100 ml. Add filter paper pulp, filter the manganese hydrous oxide precipitate and wash with hot 1% ammonium chloride solution.

Adjust the filtrate to a pH of 7 to 6 with dilute hydrochloric acid solution and evaporate on a low-temperature hot plate, without boiling, to a volume of about 20 ml. Continue the evaporation on a steam bath to a volume of about 5 ml. The salts which crystallise out during the evaporation dissolve when 25 ml of 4-methylnioxime solution is added. Quantitatively transfer the sample to a 50-ml glass-stoppered volumetric flask. Add 5 ml of tin^{II} chloride solution, dilute to the mark with water, mix and extract with chloroform.

DEVELOPMENT OF THE METHOD

Preparation of sample

Two methods have been used for the decomposition of molybdenite concentrate and "molybdenite roaster flue dust" samples—fusion with sodium peroxide[10] and treatment with nitric acid.[10]

Investigation in this laboratory showed that nitric acid treatment offered two advantages over sodium peroxide fusion: (1) the operation is simpler, and (2) later evaporation with hydrochloric acid to remove nitrate ions volatilises selenium[16] and dehydrates the silica, which can be removed by filtration. Hydrochloric acid should be added as soon as the initial reaction with nitric acid is complete, to avoid the separation of molybdenum^{VI} oxide.

Care should be taken during this and subsequent evaporations to avoid losing rhenium by volatilisation.[9,14] Rhenium is not volatilised by boiling alkaline solutions.[13]

Effect of foreign ions.

The effect of a number of ions on the 4-methylnioxime method for rhenium is illustrated in Table 1.

Ethyl xanthate extraction of interfering elements

The ethyl xanthate extraction technique for removing molybdenum[7] and selenium[10]

TABLE I. EFFECT OF FOREIGN IONS
(100 μg of rhenium present)

Ion	Added as	Amount of ion added, *mg*	Rhenium found, *μg*
Strontium^{II}	$SrCl_2$	100	95·0
Magnesium^{II}	$MgCl_2$	100	101·0
Barium^{II}	$BaCl_2$	100	97·0
Zinc^{II}	$ZnCl_2$	100	95·0
Cadmium^{II}	$CdCl_2$	100	97·0
Aluminium^{III}	$AlCl_3$	100	98·0
Manganese^{II}	$MnCl_2$	100	90·0
Nickel^{II}	$NiCl_2$	1	113·0
Cobalt^{II}	$CoCl_2$	1	143·0
Iron^{II}	$Fe(NH_4)_2(SO_4)_2$	1	165·0
Iron^{III}	$FeCl_3$	1	275·0
Copper^{I}	Cu_2Cl_2	1	122·0
Copper^{II}	$CuCl_2 2NH_4Cl$	1	132·0
Chromium^{III}	$CrCl_3$	1	82·5
Zirconium^{IV}	$ZrOCl_2$	1	87·0
Nitrate	NH_4NO_3	100	100·0
Nitrate	NH_4NO_3	200	92·0
Nitrate	NH_4NO_3	300	81·0
Bromide	KBr	100	104·5
Iodide	KI	100	111·5
Sulphate	Na_2SO_4	100	100·0
Perchlorate	$HClO_4$	100	105·0
Vanadate	$NaVO_3$	100	103·5
Thiocyanate	KCNS	100	100·0
Acetate	$NaC_2H_3O_2$	100	105·0
Citrate	$(NH_4)_2HC_6H_5O_7$	100	101·5
Tartrate	$(NH_4)_2C_4H_4O_6$	100	104·5
Oxalate	$(NH_4)_2C_2O_4$	100	104·0
Phosphate	H_3PO_4	100	Interference
Phosphate	K_2HPO_4	100	Interference

as modified by Meloche, Martin and Webb[12] was extended to the separation of iron,[6] gold, copper, nickel,[6] arsenic[8] and molybdenum from small amounts of rhenium.

The following amounts of these elements were separated by ethyl xanthate extraction from 100 μg of rhenium—4·658 g of gold as chlorauric acid, 100 mg of molybdenum as ammonium molybdate, 5 mg of iron as iron^{III} chloride, 1 mg of arsenic as sodium arsenate, 500 μg of copper as copper^{II} ammonium chloride—and the rhenium determined with a maximum absolute error of +0·004 μg of rhenium. This corresponds to an error of 0·004% rhenium when calculated on the basis of a 0·1-g sample.

Erratic results were sometimes obtained on synthetic samples when bromine oxidation of molybdenum[10] was omitted and also when oxidation with potassium permanganate[12] after xanthate extraction was omitted.

Absorption spectra of reagents

To determine the effect the reagents used in the procedure might have on the absorption spectra of rhenium 4-methylnioxime complex, the saturated aqueous solution of 4-methylnioxime, the chloroform extract of 4-methylnioxime, and the chloroform extract of tin-4-methylnioxime were prepared and their absorbancies were measured. Neither the aqueous solution nor the chloroform extract of 4-methylnioxime absorbs throughout the entire visible region. The chloroform extract of tin-4-methylnioxime absorbs at 436 mμ. However, this interference is cancelled in the determination of rhenium because the chloroform extract of a blank containing all of the reagents except rhenium is used in "zero-setting" the instrument.

Rhenium-4-methylnioxime complex

The yellow-green colour of the rhenium-4-methylnioxime compound used for the spectrophotometric determination of rhenium reached a maximum intensity in less than 5 min. The distribution ratio of the complex between chloroform and water is about 85. Thus it is necessary to extract with three portions of chloroform for quantitative extraction of the complex.[5] However, good results can be obtained by extracting with one 10-ml portion of chloroform provided the same technique is used to prepare the calibration curve (Table II). The change in absorbancy of the chloroform phase of the complex and blank was negligible for 24 hr or more when room temperature was about 25° and the complex was formed and extracted under optimum conditions.

Effect of reagent concentrations

The hydrochloric acid concentration at which the complex is formed and extracted is rather critical. The maximum colour intensity is developed with a hydrochloric acid concentration of 0·43 ± 0·05*N*. The absorbancy decreases and the rate of fading increases somewhat for higher and lower concentrations of acid. The optimum tin^{II} chloride concentration for maximum development and stability of colour was found to be 0·25%. A 20% increase or decrease in concentration of tin^{II} chloride only produced a 1 to 1·5% deviation respectively in the absorbancy. The optimum con-

TABLE II. RESULTS OBTAINED WITH U.S. BUREAU OF MINES SAMPLES

Sample	Certified value,* %	Experimental value, %	Difference	Other materials present as determined by U.S. Bureau of Mines, %						Other elements known
				Mo	Se	S	Cu	Fe	Au	
Molybdenite concentrate	0·12	0·130‡ 0·128‡ 0·132§ 0·131§	0·010 0·008 0·012 0·011	56·4	—	—	0·7	—	5·3†	
Low grade "molybdenite roaster flue dust"	0·48	0·488‡ 0·487‡ 0·477§ 0·486§	0·008 0·007 0·004 0·006	35·0	1·0	2·36	0·5	3·6	—	
High grade "molybdenite roaster flue dust"	0·96	1·010‡ 1·000‡ 0·956§ 0·959§	0·050 0·040 0·004 0·001	28·4	10·0	—	—	—	—	
Rhenium bearing synthetic samples	0·0050	0·0051‡ 0·0054‡	0·0001 0·0004	2·5						Si, Al, Mg, Ca, Na, K, Fe, Cl, As, Ba, & Cu.
	0·0012	0·0014§ 0·0012§ 0·0011§	0·0002 0·0000 0·0001	0·6						

* Figure given by the Salt Lake City Metallurgy Research Center, U.S. Bureau of Mines, Salt Lake City, Utah, U.S.A
† Ounces per ton.
‡ Single extraction.
§ Triple extraction.

concentration of hydrochloric acid and tin^{II} chloride is readily obtained by preparing the tin^{II} chloride reagent with the desired amount of each present, then measuring the reagent with a pipette.

Eighty-five mg of 4-methylnioxime (25 ml of the stock solution) are capable of converting 160 μg of rhenium in 50 ml of solution quantitatively to the rhenium-4-methylnioxime complex. Less than 1% deviation in the absorbancy is produced by varying the concentration of the 4-methylnioxime by $\pm 20\%$ from the optimum—85 mg per 50 ml of solution.

APPLICATION OF METHOD

This procedure has been successfully applied to the analyses of synthetic samples prepared in this laboratory containing arsenic, copper, gold, iron, and molybdenum and to three rhenium-containing materials and two synthetic samples[4] obtained from the Salt Lake City Metallurgy Research Center, U.S. Bureau of Mines, Salt Lake City, Utah, U.S.A. (Table II).

The proposed method makes possible the determination of rhenium in all rhenium-bearing materials found in U.S.A.

Zusammenfassung—Eine methode zur photometrischen Bestimmung von weniger als 0·001% bis über mehr als 1% Rhenium in Molybdenit und Flugstaub nach der Röstung von Molybdenit wurde entwickelt. Störelemente, die normalerwiese vorhanden sind, werden durch drei Operationen entwernt: Abrauchen mit Salzsäure, Hydroxydfällung mit wässrigem Ammoniak und Chloroformextraktion der Metalläthylxanthate. Die Bestimmung basiert auf der Bildung einer löslichen, stabilen, gelbgrünen Chelatverbindung mit 4-Methylnioxim. Rhenium(VII) wird in Gegenwart des Reagenses durch Zinn(II) in salzsaurer Lösung reduziert. Die Farbentwicklung findet in weniger als 5 Minuten statt. Das Absorptionsmaximum liegt bei 436 mμ; Beer's Gesetz wird befolgt. Der molare Extinktionskoeffizient beträgt $6{\cdot}89 \times 10^4$ im Vergleich zu unter $4{\cdot}5 \times 10^4$ fur andere Methoden zur Bestimmung von Rhenium.

Résumé—Les auteurs ont développé une méthode simple applicable au dosage spectrophotométrique de moins de 0,001 pour cent à plus de 1,0 pour cent de rhénium dans un concentré de molybdénite et dans "molybdenite roaster flue dust". Les éléments gênants couramment rencontrés dans ces produits sont éliminés en trois opérations, à savoir, évaporation avec de l'acide chlorhydrique, précipitation des hydroxydes par l'ammoniaque et formation de composés organométalliques avec le xanthate d'éthyle, et extraction par le chloroforme. La méthode est basée sur la formation d'un chelate rhénium-4-méthylnioxime jaune-vert, stable, soluble où le rhénium (VII) est réduit par le chlorure stanneux en solution acide chlorhydrique dilué en présence de 4-méthylnioxime. La couleur se développe en moins de cinq minutes, et le corps extrait par le chloroforme montre un maximum d'absorption à 436 mμ. La courbe de calibrage est conforme à la loi de Beer. Le coefficient d'extinction molaire du rhénium-4-méthylnioxime est environ $6{,}89 . 10^4$, alors qu'il est inférieur à $4{,}5 . 10^4$ pour les autres méthodes de dosage du rhénium.

REFERENCES

[1] Charles V. Banks, Donald T. Hooker and John J. Richard, *J. Org. Chem.*, 1956, **21**, 547; Donald T. Hooker, and Charles V. Banks, *Preparation, Properties and Analytical Applications of Substituted Alicyclic* Vic-*Dioximes* Ames Laboratory, Iowa State College, Ames, Iowa, ISC-597, U.S. Atomic Energy Commision, 1955. (March).

[2] Charles V. Banks and Donald T. Hooker, *Analyt. Chem.*, 1956, **28**, 79.

[3] Charles V. Banks and Ronnie V. Smith, *Analyt. Chim. Acta.*, 1959, **21**, 308.

[4] B. H. Clemmons, Salt Lake City Metallurgy Center, Bureau of Mines, Salt Lake City, Utah, Private communication.

[5] Arnold Weissberger, *Technique of Organic Chemistry*. Interscience Publishers, Inc., New York, 1950, Vol. III, p. 183.

[6] Dorothy Hall, *J. Amer. Chem. Soc.*, 1922, **44,** 1462.
[7] Loren C. Hurd, *Ind. Eng. Chem. Analyt.*, 1936, **8,** 11.
[8] A. K. Klein and F. A. Vorkes, *J. Assoc. Offic. Agric. Chemists,* 1939 **22,** 121.
[9] G. E. F. Lundell and James Irvin Hoffman, *Outlines of Methods of Chemical Analysis.* John Wiley & Sons, Inc., New York, 1951, p. 29.
[10] Emil E. Malouf and Merwin G. White, *Analyt. Chem.*, 1951, **23,** 947.
[11] A. D. Melaven, University of Tennessee, Knoxville, Tennessee, Private communication.
[12] Villiers W. Meloche, Ronald V. Martin and William H. Webb, *Analyt. Chem.*, 1957, **29,** 527.
[13] Robert J. Meyer and Charles L. Rulfs, *ibid.*, 1955, **37,** 1387.
[14] Wilfred W. Scott, *Standard Methods of Chemical Analysis,* N. Howell Furman. D. Van Nostrand Company, Inc., New York, 5th ed., 1939, I, p. 769.
[15] R. C. Voter and C. V. Banks, *Analyt. Chem.*, 1949, **21,** 1320.
[16] Don M. Yost and Horace Russell Jr., *Systematic Inorganic Chemistry.* Prentice-Hall, Inc. New York, 1946.

Talanta, 1961, Vol. 7, pp. 276 to 280. Pergamon Press Ltd Printed in Northern Ireland

A STUDY OF THE SEPARATION OF PHOSPHATE ION FROM ARSENATE ION BY SOLVENT EXTRACTION

HARLEY H. ROSS* and RICHARD B. HAHN
Department of Chemistry, Wayne State University, Detroit, Michigan, U.S.A.

(*Received* 8 *September* 1960)

Summary—The results presented confirm the postulate of Keggin that oxygen-containing materials are good solvents for heteropoly acids. The results also show that none of the solvents examined will completely separate phosphate ion from arsenate ion with a single extraction.

The butanol-chloroform system is studied extensively. The results show that as the percentage of butanol is increased in the mixed solvent, the percentage of phosphate and arsenate extracted also increases. Of the various concentrations of butanol studied, the 10% concentration shows the most promise as a selective extractant for phosphate consistant with a high yield. The results also show that the amount of arsenate ion extracted with any given concentration of butanol is relatively independent of the concentration of phosphate ion in the system.

INTRODUCTION

THE separation of phosphate ion from arsenate ion is an important problem in analytical chemistry. The separation is especially difficult when the amount of arsenate ion is large as compared to that of phosphate. Precipitation methods do not serve to separate phosphate from arsenate, as similar insoluble arsenate compounds are formed. The gathering of phosphate ion on a precipitate of aluminum or iron^{III} hydroxide has been used to separate phosphorus from other elements but, here again, arsenate interferes. Arsenate can be separated from phosphate by reducing the arsenic to the tervalent state, then boiling with either hydrochloric acid or hydrofluoric acid. In this process the arsenic is volatilised from solution but this method is quite long and is not suitable for removing microgram amounts of arsenate from solution. Of all the various methods solvent extraction procedures have shown the most promise. For this reason, this study has been limited to solvent extraction techniques.

There are many methods in which phosphate ion is separated from other elements by extracting phosphomolybdic acid with an organic solvent. Wu[19] and Copaux[4] used diethyl ether as the solvent for the heteropoly acid. Scroggie[14] found that esters, ketones, aldehydes, and ethers are good extractants but carbon disulphide, carbon tetrachloride, chloroform, benzene, and toluene are not. Keggin[8] postulated that oxygen-containing materials are good solvents for heteropoly acids. Other solvents that have been used to extract heteropoly acids include ethyl acetoacetate,[16] ethyl acetate,[7] butyl acetate,[9] 2-methyl-1-propanol,[2,3,15] 3-methyl-1-butanol,[11] 1-octanol,[13] and 1-butanol.[17] Mixtures of 1-butanol in chloroform have also been used to extract phosphomolybdic acid from arsenomolybdic acid.[1,5,6,10] In all of the above mentioned solvents, arsenic was extracted to some extent also and only a limited amount could be tolerated without interference. An article by Wadelin and Mellon[18] compares various solvents.

---

* Present address: Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee, U.S.A.

Rosenheim[12] gives a general equation for the formation of heteropolymolybdic acids:

$$X^{n}O_{a}^{(2a-n)-} + 12MoO_4^{-2} + (24 + 2a - n)H^{+} \rightarrow H_{(12-n)}X(Mo_2O_7)_6 + (6 + a)H_2O \qquad \text{(I)}$$

where X is P^{V}, As^{V}, Si^{IV}, or Ge^{IV}. Inspection of equation (I) shows that a large excess of molybdate ions or hydrogen ions will force the reaction to the right. Wadelin and Mellon, however, were unable to utilise a high concentration of molybdate ion to enhance the formation of the heteropoly acid because it exhibits strong absorption in the same region as the complexes they measured.

In the present work, various solvents were studied using radiochemical methods. The chloroform-butanol system was examined extensively. Unlike the spectrophotometric method, none of the solution variables affect the accuracy of the measurements made on the system.

EXPERIMENTAL

Reagents

In addition to standard laboratory reagents, the following solutions were used:

Phosphorus-32 and Arsenic-76 tracer solutions: Solutions of these isotopes, in the form of phosphate and arsenate, were diluted to the desired activity with $0{\cdot}01N$ hydrochloric acid.

Phosphorus carrier: Dissolve 2·8657 g of pure potassium dihydrogen phosphate (KH_2PO_4) in 100 ml of water and dilute to 1 litre. The resulting solution contains 2·00 mg of phosphate ion per ml.

Arsenic carrier: Dissolve about 4·5 g of disodium hydrogen arsenate ($Na_2HAsO_4{\cdot}7H_2O$) in 100 ml of water and dilute to 1 litre. The resulting solution contains about 2 mg of arsenate ion per ml.

Magnesia mixture: Dissolve 55 g of magnesium chloride ($MgCl_2{\cdot}6H_2O$) and 140 g of ammonium chloride in 500 ml of water. Add 130 ml of concentrated ammonium hydroxide and dilute to 1 litre.

Organic solvents: All organic solvents were chemically pure or reagent-grade. Mixed solvents were prepared on a volume percentage basis by adding the required volumes of each component using a pipette.

Apparatus

Various methods were used to detect and count the activities of the isotopes used in this work. Beta activity was measured with end-window Geiger tubes of both the halogen and organic quenched types. Gamma radiation was measured with a thallium-activated sodium iodide crystal in the form of a well-type scintillation detector. The counts were recorded with a variety of commercial scalers.

General procedure

Various concentrations of reagents are recommended in the literature for the extraction of heteropolymolybdic acids. The following concentrations were decided upon as being representative and consistent with a large molybdate and hydrogen ion concentration. The hydrochloric acid concentration was 50% (V/V) and the sodium molybdate was $0{\cdot}31M$ (15 ml of 20% sodium molybdate solution in 40 ml of final solution). All extractions were performed with 40 ml of solution in each phase. After preliminary experimentation, the following general procedure was developed to determine the amount of phosphate extracted.

Procedure

(1) Pipette exactly 5 ml of phosphate carrier into a 250-ml separatory funnel.

(2) Add an amount of ^{32}P tracer solution (10–50 μl) to give an activity of 10,000-15,000 cpm.

(3) Add 15 ml of 20% sodium molybdate solution.

(4) Add 50 ml of the solvent being examined.

(5) Add 20 ml of concentrated hydrochloric acid, stopper the funnel, shake for 2 min, and allow the phases to separate.

(6) Separate the layers, discard the aqueous phase, and add 50 ml of $3M$ ammonium hydroxide-$1M$ ammonium chloride buffer solution to the organic phase, shake 2 min, and allow the phases to separate.

(7) Drain the aqueous layer into a 150-ml beaker and heat to boiling.

(8) Add 10 ml of magnesia mixture and allow to stand until cool.

(9) Collect the precipitate of magnesium ammonium phosphate on a filter disc in a Hirsch funnel. Wash the precipitate with three 10-ml portions of buffer solution and three 5-ml portions of acetone.

(10) Air dry the precipitate and beta count.

(11) The percentage of phosphate extracted is found using the equation:

$$\%\ \text{extracted} = \frac{A_1 \times 100}{A_2}$$

where A_1 = the activity of the precipitate (cpm),
and A_2 = the activity of the original tracer solution (cpm).

A procedure similar to the above was used to determine the percentage of arsenate extracted with the same solvents. The numbered steps in the general procedure were replaced by the following:

(1a) Pipette exactly 5 ml of arsenate carrier into a 250-ml separatory funnel.

(2a) Add an amount of ^{76}As tracer solution (10–50 μl) having a total activity of 70,000–80,000 CPM.

Steps 3, 4, and 5 are the same as above.

(6a) Pippette a 5-ml portion of each layer into different test tubes suitable for use in a well-type scintillation counter.

(7a) Count each layer. The percentage of arsenate extracted is calculated by means of the following equation:

$$\%\ \text{extracted} = \frac{A_0 \times 100}{A_0 + A_a}$$

where A_0 = the activity of the organic phase (cpm),
and A_a = the activity of aqueous phase (cpm).

RESULTS

Using the above procedures, several solvents were examined to determine how much phosphate and arsenate was extracted by each. The results of these experiments are shown in Tables I and II.

The results obtained in the first two sets of experiments indicated that 20% butanol in chloroform was a promising solvent, in that a large percentage of phosphorus was extracted while only a small amount of arsenic was carried through. It was thought

TABLE I.—PERCENTAGE OF PHOSPHATE EXTRACTED USING VARIOUS ORGANIC SOLVENTS

Solvent	% Phosphate extracted ±5%*
Ethyl acetoacetate	100·00
20% Butanol in chloroform	94·97
Ethyl acetate	79·92
Butyl acetate	73·58
50% *Iso*butanol in benzene	72·63
*Iso*butanol	67·21
1-Butanol	60·63
1-Octanol	29·86
Chloroform	00·00
Benzene	00·00

* Average of two determinations

TABLE II.—PERCENTAGE OF ARSENATE EXTRACTED USING VARIOUS ORGANIC SOLVENTS

Solvent	% Arsenic extracted ±5%*
20% Butanol in chloroform	4·74
Butyl acetate	8·49
1-Octanol	14·39
Ethyl acetate	29·46
50% *Iso*butanol in benzene	36·76
*Iso*butanol	87·05
1-Butanol	87·91
Ethyl acetoacetate	96·67
Chloroform	00·00
Benzene	00·00

* Average of two determinations

that a more favourable mixture of 1-butanol might exist for this extraction. To this end, the same procedures were used to determine the percentage of phosphate and arsenate extracted with various concentrations of 1-butanol. The extractions of arsenate were made with three concentrations of this ion. Extractions were performed both in the presence and absence of phosphate ion to determine the effect of this variable. The experimental conditions and results are shown in Tables III, IV, and V.

TABLE III.—PERCENTAGE OF PHOSPHATE EXTRACTED USING VARIOUS CONCENTRATIONS OF 1-BUTANOL IN CHLOROFORM

% Butanol	% Phosphate extracted ±5%*
20	94·97
19	95·04
18	97·23
17	93·26
16	92·99
15	96·31
10	85·60
7·5	55·01
5·0	18·30

* Average of two determinations

TABLE IV.—PERCENTAGE OF ARSENATE EXTRACTED USING VARIOUS CONCENTRATIONS OF 1-BUTANOL IN CHLOROFORM

% Butanol	% Arsenic extracted at indicated level*		
	10-mg	100-μg	Tracer
5	0·20	0·27	0·076
10	0·36	1·42	0·78
15	1·56	2·45	1·99
20	5·16	4·58	4·17
30	13·57	13·15	13·06

* Average of two determinations

TABLE V.—PERCENTAGE OF ARSENATE EXTRACTED USING VARIOUS CONCENTRATIONS OF 1-BUTANOL IN CHLOROFORM WITH 10 mg OF ADDED PHOSPHATE

% Butanol	% Arsenic extracted at indicated level*		
	10-mg	100-μg	Tracer
5	0·073	0·14	0·12
10	0·69	0·88	0·80
15	2·30	1·61	1·77
20	4·32	3·62	4·50
30	12·12	12·38	12·38

* Average of two determinations

Zusammenfassung—Das Postulat von Keggin, wonach sauerstoffhaltige verbindungen gute Lösemittel für Heteropolysäuren sind, wird bestätigt. Keines der untersuchten Lösemittel kann eine völlige Trennung von Phosphat und Arsenat in einem Extraktionschritt bewirken. Das System Butanol-Chloroform wurde eingehend studiert. Mit ansteigender Butanolkonzentration steigen die extrahierten Phosphat und Arsenatmengen an. Eine Butanolkonzentration von 10% scheint meistversprechend für eine selektive Phosphatextraktion zu sein. Die extrahierte Arsenatmenge ist weitgehend unabhängig von der vorherrschenden Phosphatkonzentration.

Résumé—Le postulat de Keggin, à savoir que les substances contenant de l'oxygène sont de bons solvants des hétéropolyacides, est confirmé. Aucun des solvants étudiés ne sépare complètement l'ion phosphate de l'ion arséniate en une seule extraction. Le système butanol-chloroforme a été très étudié. Quand le pourcentage de butanol augmente dans le mélange de solvants, le pourcentage de phosphate et d'arséniate extraits augmente aussi. Parmi les concentrations variées de butanol étudiées, 10 pour cent offrent le plus de promesses comme produit extrayant sélectivement le phosphate, avec un rendement important. La quantité d'arséniate extraite par toute concentration de butanol est relativement indépendante de la concentration d'ion phosphate dans le système.

REFERENCES

[1] R. I. Akkseev, *Zavodskaya Lab.*, 1945, **11**, 122.
[2] R. J. L. Allen, *Biochem. J.*, 1940, **34**, 858.
[3] I. Berenblum and E. Chain, *ibid.*, 1938, **32**, 287.
[4] H. Copaux, *Compt. rend.*, 1921, **173**, 656.
[5] K. T. H. Farrer and S. J. Muir, *Austral. Chem. Inst. J., and Proc.*, 1944, **11**, 222.
[6] N. A. Filippova and L. I. Kuznetsova, *Zavodskaya Lab.*, 1950, **16**, 536.
[7] J. Hure and T. Ortis, *Bull. Soc. chim. France*, 1949, 834.
[8] J. F. Keggin, *Proc. Roy. Soc.*, 1934, **144**, 75.
[9] T. Koto, *et al.*, *Technol. Repts. Tôhoku Univ.*, 1950, **15**, 70.
[10] R. V. Mervel, *Zavodskaya Lab.*, 1945, **11**, 135.
[11] C. Rainbow, *Nature*, 1946, **157**, 268.
[12] A. Rosenheim, in Abegg and Auerbach's *Handbuch der anorganischen Chemie*, Leipzig S. Hirzel 1921, Bd. IV, 1 Abt., 2 Halfte, pp. 977–1065.
[13] F. L. Schaffer, *et al.*, *Analyt. Chem.*, 1953, **25**, 343.
[14] A. G. Scroggie, *J. Amer. Chem. Soc.*, 1929, **51**, 1057,
[15] C. Sideris, *Ind. Eng. Chem. Analyt.*, 1942, **14**, 762.
[16] K. Stoll, *Z. analyt. Chem.*, 1938, **112**, 81.
[17] C. Wadelin and M. G. Mellon, *Analyst*, 1952, **77**, 708.
[18] *Idem*, *Analyt. Chem.*, 1953, **25**, 1668.
[19] H. Wu, *J. Biol. Chem.*, 1920, **43**, 189.

Talanta, 1961, Vol. 7, pp. 281 to 287. Pergamon Press Ltd. Printed in Northern Ireland

THE PRECIPITATION OF HYDRATED COBALT 1-NITROSO-2-NAPHTHOLATE FROM HOMOGENEOUS SOLUTION*†

ARNO H. A. HEYN® and PHYLLIS A. BRAUNER‡
Department of Chemistry, Boston University, Boston, Massachusetts, U.S.A.

(*Received* 21 *September* 1960)

Summary—A method has been developed for determining cobalt by precipitating cobalt^{III} 1-nitroso-2-naphtholate from homogeneous solution. The reagent is synthesised within the reaction mixture by treating 2-naphthol with nitrous acid in the presence of cobalt^{II} ion. Thus nitrous acid serves the dual role as oxidant for the cobalt^{II} ion and also as a reactant in the synthesis of the reagent. Excess reagent precipitates after the cobalt nitroso-naphtholate has settled. A washing procedure has been developed to eliminate the excess reagent without affecting the cobalt nitroso-naphtholate. After washing to remove excess reagent and filtration, the precipitate is dried at 115° and weighed as $Co(C_{10}H_6O_2N)_3 \cdot H_2O$.

The presence of fluoride prevents the interference of iron, tungsten and other elements which form strong fluoride complexes.

The precision and accuracy is within 0·1 mg of cobalt at a 10-mg level and within 0·2 mg of cobalt at a 50-mg level.

INTRODUCTION

ALTHOUGH many precipitants have been used for the gravimetric determination of cobalt,[1-3] the one most often selected because of the extreme insolubility of its cobalt complex and its alleged ability to separate cobalt from nickel is 1-nitroso-2-naphthol.[4] The resulting 1-nitroso-2-naphtholate is bulky and, therefore, is filtered and washed with difficulty. The cobalt naphtholate is generally believed to be in the tervalent state and thus the cobalt^{II} ion in aqueous solution has been oxidised at the expense of the reagent. The reduction product of the reagent co-precipitates with the cobalt naphtholate. The precipitate is, therefore, not pure and cannot be weighed directly but must be converted into a suitable weighing form such as Co_3O_4, an oxide of variable composition, reduction of the oxide to the metal in a stream of hydrogen, or conversion to the sulphate.

The present investigation was initiated to develop a better gravimetric method for the separation and determination of cobalt. The problem was two-fold in nature: it was hoped to produce a precipitate with superior physical properties using 1-nitroso-2-naphthol on the one hand, and one which could be weighed directly without conversion into another form, on the other hand.

The method of precipitation from homogenous solution, by decreasing supersaturation, frequently has the effect of increasing particle size and decreasing contamination and coprecipitation.[5,6]

A pure precipitate of cobalt 1-nitroso-2-naphtholate can be weighed directly. This

---

* From a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1959.

† Presented in part at the 135th meeting of the American Chemical Society, Boston, Mass., April, 1959.

‡ Present address: Simmons College, Boston, Mass., U.S.A.

not only eliminates the conversion to another weighing form, but also has the advantage of a favourable gravimetric factor.[7] As mentioned above, the cobalt 1-nitroso-2-naphtholate formed from cobalt$^{\mathrm{II}}$ solutions is usually contaminated with the reduction products of the 1-nitroso-2-naphthol. Other investigators have attempted to pre-oxidise the cobalt$^{\mathrm{II}}$ ion before the precipitant was added by the formation of cobalt$^{\mathrm{III}}$ hydroxide which was subsequently dissolved in acetic acid.[8] Such a method suffered from the difficulty of redissolving the hydrous oxide. In fact, as a recent paper by Kolthoff and Jacobsen[9] points out, the precipitation probably took place from a cobalt$^{\mathrm{II}}$ solution rather than a cobalt$^{\mathrm{III}}$ solution, as claimed originally. Synthesis of the 1-nitroso-2-naphthol within the solution was found to be a workable approach to the cobalt precipitation.

EXPERIMENTAL

Reagents

2-naphthol solution: Prepared by dissolving 0·5 g of technical grade 2-naphthol in 100 ml of a warm 25% glacial acetic acid solution.

Hydrochloric acid, acetic acid and ammonia, 1:10 *solutions:* Prepared by diluting 10 ml of the respective concentrated reagent-grade solutions to 100 ml.

Hydrochloric acid, 1:20 *solution:* Prepared by diluting 5 ml of concentrated reagent-grade hydrochloric acid to 100 ml.

Ammonium fluoride solution, 25%: Prepared by dissolving 25 g of reagent-grade ammonium fluoride and diluting to 100 ml.

Apparatus

Crucibles: Selas porcelain filtering crucibles No. 3010 were used (medium porosity).

Radioactive tracer studies were made with a well-type γ-scintillation counter using the appropriate isotopes.

Procedure

To 10 ml of a neutral or slightly acid solution[*] containing from 1 to 90 mg of cobalt in a 600-ml beaker, add 10–15 drops of glacial acetic acid, 4 or 5 ice cubes (made from distilled water) and 1 g of sodium nitrite.[†] Stir and allow to stand for 10 min with occasional stirring, preferably by clean air or oxygen.

Add 100 ml of 25% ammonium fluoride solution, stir, then add the appropriate quantity of 2-naphthol solution[‡] rapidly and with vigorous stirring. Continue to stir for 1 min, add sufficient ice (2 or 3 more cubes) to keep the solution cold for the next 0·5 hr. Allow to stand for 0·5 hr or until the supernatant liquid is *clear yellow*.

Decant the clear liquid through an unweighed[§] porcelain filtering crucible, leaving as little of the filtrate as possible in the beaker. Wash any solid adhering to the crucible back into the beaker using water. Heat the contents of the beaker on a hot plate (temperature between 50° and 60°) for approximately 0·5 hr with occasional stirring at the beginning. Remove from the hot plate, allow to settle and decant through the crucible, again washing any adhering precipitate back into the beaker with water.

Add 100 ml of 1:20 hydrochloric acid and heat nearly to boiling, but do not boil. Allow to settle. Decant.

Add 1:10 ammonia solution, heat to boiling. Allow to settle. Decant.

Add 1:10 acetic acid, heat to boiling. Allow to settle. Decant.

---

[*] In the case of solutions containing vanadium, chromium, manganese, molybdenum, *etc.*, the solution should be treated with nitric acid or ammonium persulphate to be sure that these ions have been oxidised to vanadate, chromate, permanganate or molybdate, respectively.

[†] 90–150 mg of cobalt can be precipitated if 2 g of sodium nitrite are added.

[‡] The amount of 2-naphthol to be added is determined by the amount of cobalt in the sample. To find the correct number of ml of stock solution which must be added multiply the approximate number of mg of cobalt to be precipitated by 2 and add 10. For example, if the sample is known to contain approximately 15 mg of Co^{2+}, add $30 + 10 = 40$ ml of the 2-naphthol solution. This is not critical; 20 ml (0·1 g) of 2-naphthol in excess only prolongs the washing of the precipitate from the reagent.

[§] The crucible cannot be pre-weighed because of weight loss owing to the presence of fluoride.

Continue to wash with hot 1:10 hydrochloric acid until the wash water is colourless. Boiling in hydrochloric acid is not harmful after the first wash.

After the wash water is colourless, transfer quantitatively to the crucible. Dry the precipitate to constant weight at 115°.

Dissolve the precipitate by washing the crucible with chloroform until all of the red precipitate has been dissolved. Dry to constant weight at 115°.

The gravimetric factor for cobalt in the precipitate is

$$\frac{\mathrm{Co}}{\mathrm{Co(C_{10}H_6O_2N)_3 \cdot H_2O}} = 0{\cdot}0965.$$

DISCUSSION

Since iron which also forms an insoluble nitroso-naphtholate complex is often associated with cobalt, it is commonly removed by treatment with zinc oxide. Such a procedure, however, does not remove tungsten and certain other interfering ions. Tungsten and iron^{III} form stable fluoride complexes, and in consequence are prevented from precipitating. Cobalt, however, forms no such stable fluoride. The effect of the addition of ammonium fluoride to the reaction mixture was studied using radioactive iron-59 and cobalt-60 as tracers. This showed that the precipitation of cobalt 1-nitroso-2-naphtholate was as complete in the presence of fluoride ion as in the absence of this ion. In fact, in the presence of fluoride, the precipitate was more dense and settled more rapidly.

The presence of ammonium fluoride acts as an effective buffer, maintaining a pH of 3·8–4·0, a favourable range for two reasons: 1-nitroso-2-naphthol exists in two tautomeric forms, possibly only one of which precipitates the cobalt^{III} ion; some authors indicate that the precipitating tautomer exists only in mildly acidic solution.[10] The cobalt nitroso-naphtholate is not precipitated from strongly acidic solutions although it is insoluble in strong acids, once it is formed. Secondly, the oxidation of the cobalt^{II} ion must be carried out in weakly acidic solution because strong acids decompose the cobaltinitrite complex. Large quantities of acetic acid cause the precipitate to become bulky and colloidal, thus delaying the settling of the precipitate. The colloidal nature of the precipitate also causes low results. The correct acidity should be produced with as small a quantity of acetic acid as possible, thus the presence of ammonium fluoride is most beneficial.

TABLE I.—COMPLETENESS OF PRECIPITATION

Cobalt taken, *mg*	Cobalt found in filtrate, *mg*	
	Ammonium fluoride present	No ammonium fluoride present
10	0·005	0·03
15	0·003	
	0·008	
100	0·5	0·7
	0·1	

In an effort to avoid the use of low temperatures, several runs were made at an increased temperature of the precipitating mixture. In each case, however, some tarring occurred which gave rise to abnormally high results. This is probably due to the presence of excess nitrous acid in the precipitating mixture. In the recommended procedure, the filtrate containing nitrous acid is separated from the precipitate before the temperature is elevated.

The time needed for the settling of the precipitate varies somewhat. If the supernatant liquid is not a clear yellow the precipitate is probably colloidal. Vigorous stirring followed by settling of the precipitate a second time may clear the supernatant liquid. This difficulty is seldom encountered if sufficient 2-naphthol has been added.

TABLE II.—EFFECT OF VARIOUS WASH SOLUTIONS ON COBALT PRECIPITATE (15 mg of cobalt present)

Wash solution	Amount of cobalt removed, *mg/100 mp*
1:20 HCl boiled 5 min at the beginning of washing	0·002
1:20 NH_4OH boiled 10 min	0·0026
1:3 acetic acid boiled	0·0089
1:10 acetic acid	0·0014
1:20 HCl boiled 5 min at end of washing	0·00075

TABLE III.—INTERFERENCE OF OTHER IONS (10-MG SAMPLES OF COBALT)

Ion present	Added as	Amount found in precipitate	Weight of cobalt
Mo	$Na_2MoO_4 \cdot H_2O$ (50 mg of Mo)	None	Theoretical
	Steel sample	Less than 0·1% (spectrographic)	
V	Na_3VO_4(50 mg of V)	None	Theoretical
	Steel sample	Less than 0·01% (spectrographic)	
As	Na_3AsO_4 (50 mg of As)	None	Theoretical
	Steel sample	Not present (spectrographic)	
Ag	Interferes		
Cu	Interferes		
W	Steel sample	Not present (spectrographic)	
Mn	Steel	Not present (spectrographic)	
Cr	Steel	Not present (spectrographic)	
Fe	10 mg of Fe/1 mg of Co $Fe(NH_4)SO_4 \cdot 12H_2O$	0·007 mg (radioactive tracer study)	

To ascertain the completeness of the precipitation of cobalt by the proposed method, a series of studies was made using radioactive cobalt-60. Tests were run with 10 mg and 100 mg of cobalt per run. The results are shown in Table I.

The precipitate must be washed carefully to remove excess reagent. For this reason the nature of the wash solution was very important. In order to test the efficacy of wash solutions without redissolving the precipitate, tracer studies with cobalt-60 were conducted. Following the reaction the precipitate was subjected to a series of appropriate wash solutions, and from the amount of radioactivity in the filtrate the amount of cobalt that had been redissolved was determined. The results are shown in Table II.

The initial wash with mineral acid, which is the most critical step in the analysis, removed small amounts of nickel or other metal naphtholates. If too much filtrate has been retained by the precipitate, or if the wash solution is too hot or added too rapidly without adequate stirring, tarry matter may be formed. The reagent itself is not very soluble in mineral acids but soluble in a base, thus one basic wash is included. A second wash with a base should be avoided since such a wash tends to cause the precipitate to peptise.

TABLE IV.—INTERFERENCE OF NICKEL

Nickel taken, *mg*	Cobalt		Cobalt error, *mg*
	Taken, *mg*	Found, *mg*	
Fluoride absent			
10	10·3	10·9	+0·6
50	10·3	11·8	+1·5
100	10·3	13·7	+3·4
200	10·3	17·3	+7·0
25	25·7	26·7	+1·0
Fluoride present			
10	10·3	10·35	0·05
	10·3	10·2	−0·1

Ions that commonly occur in association with cobalt were tested for interference. The results of this study are shown in Table III. Nickel was tested at several levels. The results are shown in Table IV. Amounts of nickel in excess of 10 mg caused the formation of a grey precipitate resulting in weights well above the theoretical value for the known amount of cobalt added. Copper and silver were found to interfere to a marked extent. The initial precipitate was black, indicating contamination.

TABLE V.—ANALYSIS OF N.B.S. STEEL NO. 153

Cobalt taken, %	Cobalt found, %	Devn. from av., %	Std. devn., %
8·45	8·42	−0·03	0·054
	8·38	−0·07	
	8·52	+0·07	
	8·48	+0·03	
	8·46	+0·01	

A U.S. National Bureau of Standards steel sample was analysed for cobalt. The results of this analysis appear in Table V.

The cobalt 1-nitroso-2-naphtholate precipitate forms in a dense layer on the bottom of the beaker. Although it does not appear to be either granular or crystalline, it is easy to handle if the directions are followed carefully. The precision is within 0·1 mg of cobalt at a 10-mg level and within 0·5 mg of cobalt at the 50-mg level (see Table VI). The most time-consuming step in the analysis is the washing of the precipitate. The method is more rapid and less time-consuming than many other gravimetric

Table VI.—Determination of cobalt

Cobalt taken, *g*	Cobalt found, *g*	av.	Devn. from known val., *mg*	Devn. from av. val., *mg*	Std. devn., *mg*
0·0010	0·0011	0·0011	+0·1	0·0	0·07
	0·0010		0·0	−0·1	
	0·0011		+0·1	0·0	
0·0050	0·0050	0·0050	0·0	0·0	0·12
	0·0049		−0·1	−0·1	
	0·0049		−0·1	−0·1	
	0·0052		+0·2	+0·2	
0·0103	0·0102	0·0103	−0·1	−0·1	0·06
	0·0103		0·0	0·0	
	0·0103		0·0	0·0	
	0·0103		0·0	0·0	
	0·0104		+0·1	+0·1	
	0·0103		0·0	0·0	
0·0250	0·0250	0·0250	0·0	0·0	0·14
	0·0251		+0·1	+0·1	
	0·0248		−0·2	−0·2	
	0·0249		−0·1	−0·1	
0·0257	0·0257	0·0258	0·0	−0·1	0·23
	0·0261		+0·4	+0·3	
	0·0256		−0·1	−0·2	
	0·0257		0·0	−0·1	
0·0500	0·0495	0·0495	−0·5	0·0	0·41
	0·0499		−0·1	+0·4	
	0·0488		−1·2	−0·7	
	0·0498		−0·2	+0·3	
	0·0499		−0·1	+0·4	
	0·0491		−0·9	−0·4	
	0·0500		0·0	+0·5	
	0·0490		−1·0	−0·5	
	0·0496		−0·4	+0·1	
	0·0498		−0·2	+0·3	
	0·0498		−0·2	+0·3	
0·0515	0·0518		+0·3		0·1
	0·0519		+0·4		
0·1000	0·1009		+0·9		
0·1025	0·1025		0·0		

methods for the determination of cobalt. Digestion times, temperatures and pH's are not critical.

A modification is under investigation: To the basic solution potassium persulphate was added, thus acidifying the solution and destroying excess reagent. This appears to reduce the washing time appreciably.

Zusammenfassung—Eine Methode zur Bestimmung von Kobalt durch Fallung als Kobalti-1-nitroso-2-naphthol aus homogener Lösung wird beschrieben. Das Reagens wird in der Lösung synthetisiert durch Behandlung von 2-Naphthol mit salpetriger Säure in Gegenwart von Kobalt(II)-ion. Salpetrige Säure erfüllt zwei Funktionen, einmal oxydiert sie das Kobalt(II) zu Kobalt(III) und zweitens dient sie zur Synthese des Reagenses. Überschüssiges Reagens fällt nach Beendigung des Absetzens des Kobaltniederschlages aus. Eine spezielle Waschvorschrift wird mitgeteilt, welche erlaubt das überschüssige Reagens zu entfernen, ohne Kobaltnaphtholat anzugreifen. Nach waschen und trocknen (115°C) wird der Niederschlag bei als $Co(C_{10}H_6O_2N)_3 \cdot H_2O$ gewogen. Anwesenheit von Fluoridion verhindert Störungen durch Eisen, Wolfram und andere Elemente, die stabile Fluorokomplexe bilden. Genauigkeit und Reproduzierbarkeit ist innerhalb von 0·1 mg bei 10 mg Kobalt und 0·2 mg bei 50 mg Kobalt.

Résumé—Les auteurs ont mis au point une méthode de dosage du cobalt par précipitation du 1-nitroso-2-naphtol cobaltique en solution homogène. Le réactif est synthétisé au sein du mélange réactionnel en traitant du 2-naphtol par le l'acide nitreux en présence d'ions cobalteux. Cet acide nitreux joue le rôle d'oxydant pour les ions cobalteux, ainsi que de corps réagissant dans la synthèse du réactif. L'excès de réactif précipité après que le nitrosonaphtolate de cobalt se soit déposé. Une méthode de lavage a été mise au point pour éliminer l'excès de réactif sans agir sur le nitrosonaphtolate de cobalt. Après lavage pour enlever l'excès de réactif, et filtration, le précipité est séché à 115° et pesé à l'état de $Co(C_{10}H_6O_2N_3) \cdot H_2O$. La présence de fluorure empêche l'interférence du fer, du tungstène et d'autres élèments qui forment des complexes fluorure très stables. La précision est au moins 0,1 mg de Co pour une teneur de 10 mg et au moins 0,2 mg de Co pour 50 mg.

REFERENCES

[1] N. W. Fischer., *Pogg. Ann.*, 1848, **71**, 545.
[2] H. H. Willard and D. Hall, *J. Amer. Chem. Soc.*, 1922, **44**, 2226.
[3] W. J. Williams, *Talanta*, 1958, **1**, 88.
[4] M. Ilinski, and G. v. Knorre, *Ber.*, 1885, **18**, 699.
[5] H. H. Willard, *Analyt. Chem.*, 1950, **22**, 1372.
[6] L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation From Homogeneous Solution.* Wiley & Sons, N.Y., 1959.
[7] R. Duval and C. Duval, *Analyt. Chim. Acta*, 1951, **5**, 84.
[8] C. Mayer and F. Feigl, *Z. analyt. Chem.*, 1932, **90**, 15.
[9] I. M. Kolthoff and E. Jacobsen, *J. Amer. Chem. Soc.*, 1957, **79**, 3677.
[10] F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions.* Academic Press, New York, 1949, p. 254.

Talanta, 1961, Vol. 7, pp. 288 to 290. Pergamon Press Ltd. Printed in Northern Ireland

PRECIPITATION OF PALLADIUM DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

LINDA J. KANNER*, E. D. SALESIN and LOUIS GORDON®
Department of Chemistry and Chemical Engineering, Case Institute of Technology
Cleveland 6, Ohio, U.S.A.

(*Received* 16 *September* 1960)

Summary—Palladium can be quantitatively precipitated from homogeneous solution with dimethylglyoxime generated by the reaction between biacetyl and hydroxylamine. The chelate is precipitated as long yellow needles which are easy to filter and wash. The separation of palladium from platinum and nickel was investigated.

SALESIN and Gordon[1] have precipitated nickel with dimethylglyoxime generated *in situ* from biacetyl and hydroxylamine. This reaction for producing dimethylglyoxime can also be utilised for the precipitation of palladium. A general procedure is described herein which has been applied to the separation of palladium from platinum and from nickel. It should be adaptable, with suitable modifications where required, to systems containing other diverse ions.

EXPERIMENTAL

Reagents

Palladium: $PdCl_2 \cdot 2H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey) was dissolved in distilled water containing a small amount of hydrochloric acid and was standardised by precipitation with dimethylglyoxime.[2]

Platinum: Reagent-grade $H_2PtCl_6 \cdot 6H_2O$ (Mallinckrodt Chemical Works, New York, New York).

Nickel: Reagent-grade $NiSO_4 \cdot 6H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Biacetyl: This reagent was prepared and used according to the directions of Salesin and Gordon.[1]

Hydroxylamine hydrochloride: Reagent-grade (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

All other chemicals were reagent-grade.

Procedure

Dilute the approximately neutral solution containing 1–25 mg of palladium as chloride or sulphate to about 250 ml, and add 9 ml of concentrated hydrochloric acid. Add, with stirring, 25 ml of a solution containing 120 mg of biacetyl, and then 25 ml of a freshly prepared solution containing 400 mg of hydroxylamine hydrochloride. Let the reaction mixture stand at room temperature for at least 16 hr. Before filtering, mechanically stir the solution for 1 hr. Filter through a weighing crucible of medium porosity, washing the precipitate first with dilute (1:99) hydrochloric acid and finally with water. Dry at 110° for 1–2 hr. The chelate, $Pd(C_4H_7N_2O_2)_2$, contains 31·67% of palladium.

RESULTS AND DISCUSSION

Preliminary studies of the precipitation of palladium from homogeneous solution indicated that crystals of palladium dimethylglyoximate with favourable characteristics could be produced in the same acidic medium, *i.e.* 3% by volume in hydrochloric acid, as is often recommended[2,3] for the conventional method using dimethylglyoxime. Nearly identical results could be obtained at pH 1 if 4 to 6 g of ammonium chloride, in a 300-ml volume, were present. Less well developed crystals were obtained in a sulphuric acid medium.

---

* Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

The procedure given was developed for a maximum of 25 mg of palladium simply as a matter of convenience. In terms of this quantity of palladium, the amounts of biacetyl and hydroxylamine hydrochloride are, respectively, three and six times the stoichiometric values needed. With these amounts, in the absence of palladium, dimethylglyoxime will not precipitate by itself.

The precipitate of palladium dimethylglyoximate consists of long yellow needles, virtually identical to, though somewhat shorter in length than those shown in the photomicrographs of nickel dimethylglyoximate.[1] The precipitate filters well.

Because of a slight tendency toward supersaturation, it is necessary to terminate the precipitation process with stirring. As indicated in the procedure, a 1-hr stirring period is sufficient. However, the amount of palladium dimethylglyoximate which remains supersaturated is small and can also be separated if desired by the addition of a small quantity of an alcoholic solution of dimethylglyoxime at the end of the 16-hr reaction period.

Heating the reaction mixture at 50° was tried, both in order to reduce precipitation time and to improve further the physical characteristics of the precipitate. Although the reaction time can be shortened, there is no appreciable change in the precipitate, and in view of the greater possibility of reducing platinum at the higher temperature[4,5] room temperature conditions are prescribed.

In several instances (*cf.* Table I) the quantities of palladium in the filtrates and

TABLE I.—SEPARATION OF PALLADIUM DIMETHYLGLYOXIMATE BY PFHS
(Solutions were not mechanically stirred except where noted)

Palladium taken, *mg*	1.01	1.01	1.01	1.01	10.1	10.1	10.1	25.3	25.3	25.3	24.3[a]
Difference found, *mg*	−0.06	−0.09	±0.00	+0.04	±0.0	±0.0	−0.1	±0.0	±0.0	−0.1	±0.0
Palladium found in filtrate, *mg*		0.05	0.05	0.02	0.02	0.04	0.07	0.09		>0.1	0.08

[a] The reaction mixture was stirred mechanically for 6 hr after the reagents were added, then the solution was filtered.

TABLE II.—SEPARATION OF PALLADIUM DIMETHYLGLYOXIMATE FROM DIVERSE IONS BY PFHS AND CONVENTIONAL PRECIPITATION
(Solutions were mechanically stirred as described in the procedure except where noted)

Number	1	2	3	4	5	6	7	8	9
Method of precipitation	PFHS	Conv.	Conv.	Conv.	Conv.	PFHS	PFHS	PFHS	Conv.
Palladium taken, *mg*	10.1	9.7	9.7	9.7	24.3	24.3	24.3	24.3	24.3
Difference found, *mg*	−0.2	±0.0	+0.1	+0.1	+0.2	−0.3	−0.5	+0.2	+0.2
Diverse element taken, *mg*	Pt, 10	Pt, 10	Pt, 10	Pt, 25	Pt, 25	Pt, 50	Pt, 75	Pt, 75	Pt, 75
Modifications in procedure	a					a	a		

Number	10	11	12	13	14	15	16	17	18	19
Method of precipitation	PFHS	PFHS	Conv.	PFHS	PFHS	Conv.	PFHS	PFHS	Conv.	Conv.
Palladium taken, *mg*	24.3	24.3	24.3	97.3	97.3	97.3	24.3	24.3	24.3	24.3
Difference found, *mg*	+0.4	+0.1	+0.2	+0.6	+2.1	+0.7	+0.3	+0.3	+0.3	+0.1
Diverse element taken, *mg*	Pt, 100	Pt, 100	Pt, 100	Pt, 200	Pt, 200	Pt, 200	Ni, 1000	Ni, 1000	Ni, 1000	Ni, 1000
Modifications in procedure		b		c	c					

[a] No mechanical stirring at the end of the 16-hr reaction period.
[b] One ml of a 1% solution of dimethylglyoxime in ethanol was added before filtration.
[c] About 0.48 g of biacetyl and 1.6 g of hydroxylamine hydrochloride were used.

washings were determined by the addition of nitric and sulphuric acids, evaporation to fumes of the latter, and subsequent determination of the palladium with α-furildioxime.[6] The amount of unprecipitated palladium is negligible.

The results of Table II show that the method of precipitation of palladium dimethyglyoximate from homogeneous solution leads to separation results which are no better than those obtained by conventional precipitation. The only advantage offered by PFHS (precipitation from homogeneous solution) in the present case is an easily filtered and washed precipitate which does not clog a filter medium as is generally the case with the conventionally produced precipitate.

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation reported herein under Contract AT(11-1)-582 and of the Case Research Fund.

Zusammenfassung—Palladium kann aus homogener Lösung quantitativ gefällt werden, wenn Dimethylglyoxim durch Reaktion zwischen Diacetyl und Hydroxylamin gebildet wird. Das Chelate wird in Form langer, gelber Nadeln erhalten, die leicht zu filtrieren und waschen sind. Die Trennung des Palladiums von Platin und Nickel wurde untersucht.

Résumé—Le palladium peut être précipité quantitativement en solution homogène par de la diméthylglyoxime formé par réaction entre du biacétyle et de l'hydoxylamine. Le chélate est précipité sous forme de longues aiguilles jaunes qui sont faciles à filtrer et à laver. La séparation du palladium d'une part, du platine et du nickel d'autre part, a été étudiée.

REFERENCES

[1] E. D. Salesin and L. Gordon, *Talanta*, 1960, **5**, 81.
[2] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis.* John Wiley and Sons, Inc., New York, 2nd Ed., 1953, p. 379.
[3] G. H. Ayres and E. W. Berg, *Analyt. Chem.*, 1953, **25**, 980.
[4] H. Diehl, *The Applications of the Dioximes to Analytical Chemistry.* The G. Frederick Smith Chemical Co., Columbus, Ohio, 1940, p. 40.
[5] C. W. Davis, *J. Franklin Inst.*, 1922, **194**, 113.
[6] O. Menis and T. C. Rains, *ibid.*, 1955, **27**, 1932.

Talanta, 1961, Vol. 7, pp. 291 to 295. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF RADIOACTIVE COBALT IN MIXTURES OF RADIONUCLIDES

RICHARD B. HAHN and DAVID L. SMITH*
Chemistry Department, Wayne State University
Detroit 2, Michigan, U.S.A.

(*Received* 14 *September* 1960)

Summary—A detailed procedure for the separation of radiocobalt from other active material is described. Precipitation as the mercurithiocyanate and as the anthranilate have been compared, and the latter has been shown to be somewhat preferable.

INTRODUCTION

Various radioactive isotopes of cobalt are known: ^{54}Co, ^{55}Co, ^{57}Co, ^{58}Co, ^{58}mCo, ^{60}Co, ^{60}mCo, ^{61}Co, and ^{62}Co.[4] Of these, ^{60}Co is the most important. This isotope is used widely in tracer studies and as a gamma radiation source. It is found frequently in coolant waters from nuclear reactors. Cobalt-60 has a half life of 5·3 years and emits a β-particle of 0·31 MeV energy and two γ-rays of 1·17 and 1·33 MeV.[4]

The following study was made to develop a procedure for the determination of radioactive cobalt in the presence of other radionuclides. No attempt was made to distinguish between the various radioactive isotopes of cobalt. Cobalt-60 was used as tracer in all experiments.

Several methods have been devised for the radiochemical determination of ^{60}Co. Duncan and coworkers[2] extracted the cobalt thiocyanate complex from acid solution using amyl alcohol. Cobalt was stripped from the organic solvent with ammonium hydroxide, then precipitated as cobalt ferrocyanide for β-counting. The ferrocyanide is a bulky precipitate of indefinite composition and not entirely satisfactory for weighing and counting. Meinke[6] gives several procedures for the determination of radioactive cobalt in various targets after bombardment. The cobalt was weighed and counted in various forms: as cobalt^{II} sulphide, as potassium cobaltinitrite, or as the 1-nitroso-2-naphthol compound. None of these compounds is of constant composition, hence they are not suitable for accurate analyses.

The best general radiochemical method is that devised by Burgus.[1] Cobalt is separated from other activities by a series of precipitations and solvent extractions. It is finally electroplated as the metal for weighing and counting. The electroplating, however, is tedious and time-consuming and a simple precipitation method would be more desirable. Various precipitants for cobalt, therefore, were investigated.

Duval[3] studied about thirty different precipitates and two of these, cobalt mercury^{II} thiocyanate, $CoHg(SCN)_2$, and cobalt anthranilate, $Co(C_7H_6O_2N)_2$, appeared most promising for radiochemical use. These were carefully investigated.

EXPERIMENTAL

Reagents

Cobalt carrier: Dissolve 49·4 g of C.P. $Co(NO_3)_2{\cdot}6H_2O$ in distilled water and dilute to 1 litre. Standardise by the following procedure:

---

* Present Address: Department of Chemistry, University of Michigan, U.S.A.

Take 5 ml of the solution and dilute to 50 ml with water, then add 25 ml of 0·1 *M* ammonium mercurithiocyanate reagent. Stir the solution and scratch the walls of the beaker to promote crystallisation. Digest the resulting precipitate for 1 hr at room temperature, then filter through a tared, sintered-glass crucible, using a rubber policeman to ensure complete transfer. Wash with 5 ml of a 0·01 *M* solution of the reagent, followed by 1-2 ml of 95% ethyl alcohol, then dry at 120° for 30 min and weigh.

Nickel carrier, 10 mg/ml: Dissolve 5 g of C.P. $Ni(NO_3)_2 \cdot 6H_2O$ in 100 ml of distilled water.

Palladium carrier, 10 mg/ml: Dissolve 2 g of C.P. $PdCl_2 \cdot 2H_2O$ in 100 ml of distilled water.

Copper carrier, 10 mg/ml: Dissolve 2·7 g of C.P. $CuCl_2 \cdot 2H_2O$ in 100 ml of distilled water.

Ammonium mercurithiocyanate, 0·1*M* with a 10% excess of ammonium thiocyanate: Dissolve 27 g of C.P. $HgCl_2$ and 34 g of C.P. NH_4CNS in distilled water and dilute to 1 litre.

Anthranilic acid, 2%: Dissolve 20 g of $C_6H_4 \cdot NH_2 \cdot COOH$ in 160 ml of 1*N* sodium hydroxide and dilute with 800 ml of distilled water. Filter this solution, and bring the pH to 6 by adding 5% acetic acid.

Thioacetamide, 1M: Dissolve 7·6 g of $CH_3 \cdot CS \cdot NH_2$ in 100 ml of distilled water.

Potassium hydroxide, 10*M*: Dissolve 560 g of potassium hydroxide in 1 litre of distilled water. Store in a polyethylene bottle.

Amyl alcohol-ether mixtures, 35% amyl alcohol, 65% diethyl ether by volume.

Ethyl alcohol, 95%.

Ammonium thiocyanate, solid.

Potassium nitrite, solid.

Acetic acid, 6*M*.

Hydrochloric acid, concentrated, 37·6% by weight.

Nitric acid, concentrated, 70% by weight.

Ammonium hydroxide, concentrated, 28% by weight.

Precipitation as cobalt anthranilate

Anthranilic acid (o-aminobenzoic acid) was investigated as a precipitant for cobalt by Wenger and coworkers.[7] A 2% solution of the reagent is used and cobalt is precipitated as the corresponding salt from neutral or weakly acid solution. Cobalt anthranilate is a pink-coloured, light, flaky precipitate which is easily filtered and washed. This precipitant was investigated for radiochemical use by adding a known amount of ^{60}Co tracer to a solution of cobalt nitrate as carrier, then precipitating the mixture with a 2% solution of anthranilic acid. The resulting cobalt anthranilate precipitate was filtered, weighed, then γ-counted in a well-type scintillation counter. The results are given in Table I and show an average recovery of 99·2% of the radioactive cobalt.

TABLE I. RECOVERY OF ^{60}Co AS COBALT ANTHRANILATE

Sample*	Gravimetric yield, %	Observed counts, *cpm*	Counts corrected for yield, *cpm*	Recovery, %
1	96·2	4361	4533	98·0
2	97·1	4424	4556	98·5
3	93·6	4433	4736	102·4
4	94·8	4293	4528	97·9

* 10·41 mg of cobalt carrier and 4625 cpm of ^{60}Co were added to each sample.

Precipitation as cobalt mercurithiocyanate

Lamure[5] reported the compound, cobalt^{II} tetrathiocyanatomercurate (commonly called cobalt mercurithiocyanate), to be a quantitative precipitate for cobalt. It has the formula $CoHg(SCN)_4$, and contains 11·98% of cobalt. It is a blue-coloured, dense, crystalline precipitate which is easily filtered and washed.

A preliminary study was made to determine whether cobalt activity would be carried completely on this precipitate. A known amount of ^{60}Co tracer was added to a solution of cobalt nitrate carrier and the mixture precipitated by the addition of ammonium mercurithiocyanate reagent. The resulting precipitate of cobalt mercurithiocyanate was filtered, weighed, and γ-counted. The results are given in Table II and show an average recovery of 100·1 % of the cobalt activity.

TABLE II. RECOVERY OF ^{60}Co AS COBALT MERCURITHIOCYANATE

Sample*	Gravimetric yield, %	Observed counts, *cpm*	Counts corrected for yield, *cpm*	Recovery, %
1	96·9	4392	4533	98·0
2	96·4	4503	4671	101·0
3	95·9	4433	4623	100·0
4	95·8	4497	4694	101·5

* 10·21 mg of cobalt carrier and 4625 cpm of ^{60}Co were added to each sample.

Comparison of the mercurithiocyanate and anthranilate methods

On the basis of the previous experiments, both the mercurithiocyanate and anthranilate methods are satisfactory for the determination of radioactive cobalt. In order to gain additional information in regard to the relative merits of these two precipitates, it seemed advisable to study their selectivity for radioactive cobalt. A series of determinations was performed to study the effectiveness of the separation of cobalt activity from foreign activities. Samples, containing known amounts of foreign activities, were analysed by both methods, using the procedures described previously except that no cobalt activity was added to the samples. Both β- and γ-counting were employed. The results, summarised in Table III, are the average of four determinations for each activity tested.

TABLE III. EFFICIENCY OF SEPARATION FROM FOREIGN ACTIVITIES—THE TWO PRECIPITATES COMPARED

Activity added	Radiation measured	Percentage activity carried down	
		Mercurithiocyanate method	Anthranilate method
^{134}Cs	γ	1·1	0·2
^{90}Sr —^{90}Y	β	0·1	58·0
^{95}Zr —^{95}Nb	γ	0·0	8·3
^{106}Ru —^{106}Rh	γ	13·0	44·0
^{32}P	β	0·5	0·2
^{144}Ce —^{144}Pr	β	1·1	82·0
^{131}I	γ	17·0	13·0

The major contaminants in the mercurithiocyanate method were ^{106}Ru —^{106}Rh and ^{131}I, 13 % of the former and 17 % of the latter being recovered on the cobalt mercurithiocyanate precipitate. ^{90}Sr —^{90}Y, ^{106}Ru —^{106}Rh, ^{144}Ce, and ^{131}I activities were carried down quite appreciably on the cobalt anthranilate precipitate. The results of these experiments show the mercurithiocyanate method to be more selective for cobalt. On the basis of these experiments, and also because the mercurithiocyanate precipitate is denser and therefore easier to manipulate, it seemed advisable to employ the cobalt mercurithiocyanate precipitate in the following procedures.

Determination of radioactive cobalt in mixtures of activities

The decontamination procedure for the determination of radioactive cobalt was adapted from a procedure given by Burgus.[1] In this procedure cobalt is separated from fission products and from nickel by precipitation as potassium cobaltinitrite from acetic acid solution, followed by appropriate scavenging steps and extraction of the blue cobalt thiocyanate complex into an amyl alcohol-ether mixture. The cobalt is then precipitated as the sulphide, which is dissolved, and the cobalt finally electroplated from an ammoniacal solution. Certain modifications of Burgus' procedure were made, the most significant being the final form in which the cobalt is counted. Thioacetamide is used in this modified procedure to replace hydrogen sulphide as a precipitant in the scavenging steps. The excess thioacetamide can be destroyed very easily by heating with nitric acid. If hydrogen sulphide gas is employed in place of thioacetamide, the sample must be evaporated to dryness to ensure complete removal of the excess reagent. Nickel "holdback" carrier is added initially to reduce the co-precipitation of radioactive nickel with the cobalt. The entire analysis takes about 3 hr. The procedure finally adopted is as follows:

Step 1. Place a known volume of the radioactive solution to be analysed in a 40-ml centrifuge tube. Add sufficient water to make the volume about 20 ml. Add 2·0 ml of standard cobalt nitrate carrier (10 mg of cobalt per ml) and 1 ml of nickel nitrate carrier. Add 10*M* potassium hydroxide until the solution is basic. Stir thoroughly. Centrifuge, decant and discard the supernate. Wash the precipitate with 20 ml of water. Discard the supernate and washings.

Step 2. Dissolve the precipitate in 3 ml of 6*M* acetic acid. Dilute to 15 ml with water.

Step 3. Precipitate potassium cobaltinitrite by adding 10 ml of a solution of 3*M* acetic acid saturated with potassium nitrite* to the above solution. Stir thoroughly and let stand for 5 min. Centrifuge, discard the supernate, and wash the precipitate with 10 ml of water. Discard the washings.

Step 4. Dissolve the precipitate of potassium cobaltinitrite in 4-5 ml of concentrated hydrochloric acid and evaporate the solution almost to dryness. Add 2 drops of palladium chloride and 4 drops of copper^{II} chloride carriers. Dilute to 20 ml and make about 0·1*M* in hydrochloric acid. Add 2 ml of 1*M* thioacetamide and immerse the centrifuge tube in a beaker of boiling water. When the sulphide precipitate begins to settle in the tube, remove the tube from the boiling water and filter through a Whatman No. 40 filter paper. Catch the filtrate in a 50-ml beaker. Discard the precipitate.

Step 5. Add 2-3 ml of concentrated nitric acid to the filtrate in the beaker, and heat to boiling to decompose the excess thioacetamide.

Step 6. Cool the mixture and add 4 drops of iron^{III} chloride carrier. Add concentrated ammonium hydroxide until basic, then add 1 ml in excess. Pour the mixture into a 40-ml centrifuge tube and centrifuge. Decant the supernate into a 50-ml beaker and discard the precipitate.

Step 7. Acidify the supernate from step 6 with concentrated hydrochloric acid, adding 1 ml in excess. Add 15 g of solid ammonium thiocyanate and stir until dissolved. Pour the solution into a 125-ml separatory funnel and extract the cobalt thiocyanate complex into 50 ml of amyl alcohol-ether mixture. Discard the aqueous layer.

Step 8. Back-extract the cobalt into 20 ml of water to which 4-6 ml of concentrated ammonium hydroxide has been added. The organic layer should now be almost colourless. If it is not, add more ammonium hydroxide. Discard the organic layer into a 50-ml beaker.

Step 9. Heat the solution from step 8 to boiling and add slowly, with constant stirring, about 10 ml of 10*M* potassium hydroxide to precipitate cobalt hydroxide. Continue boiling the mixture for about 10 min, stirring frequently. Transfer the mixture to a 40-ml centrifuge tube and centrifuge. Wash the precipitate with 20 ml of water. Centrifuge and discard the washings.

Step 10. Dissolve the cobalt hydroxide precipitate in 5-6 drops of concentrated hydrochloric acid.

Step 11. Transfer the solution to a 50-ml beaker using 10 ml of water. Add 10 ml of 0·1*M* ammonium mercurithiocyanate reagent. Stir and scratch the walls of the beaker to promote crystallisation. Allow the precipitate to digest at room temperature for about 30 min.

Step 12. Filter the cobalt mercurithiocyanate precipitate through a previously weighed filter paper disc in a Hirsch funnel. Wash with 10 ml of 0·01*M* ammonium mercurithiocyanate solution followed by 5 ml of 95% ethyl alcohol. Dry the precipitate and filter paper disc in a drying oven for about 30 min at 110°. Cool in a desiccator, weigh, then count in a well-type scintillation counter.

Testing the procedure for separation of foreign activities.

The above procedure was tested to determine its efficiency in separating radioactive cobalt from other activities. Two samples were analysed which did not contain any radioactive cobalt, but which

---

* This solution should be prepared immediately before use by adding solid potassium nitrite to 10 ml of 3*M* acetic acid until some solid remains undissolved.

did contain the following counts per min (γ) of other activities: 1·5 × 10^4 cpm ^{134}Cs, 8·0 × 10^4 cpm ^{95}Zr —^{95}Nb, 1·1 × 10^4 cpm ^{131}I, 15·0 × 10^4 cpm ^{144}Ce —^{144}Pr, and 15·7 × 10^4 cpm ^{106}Ru —^{106}Rh. With both samples less than 40 cpm were recovered after correction for carrier yield. The procedure, therefore, gives successful decontamination from these activities.

Testing the procedure for recovery of cobalt activity.

Several samples containing a known amount of ^{60}Co were analysed in order to obtain statistics concerning the accuracy and precision of the method. Table IV summarises the results of these determinations.

TABLE IV. DETERMINATION OF RADIOACTIVE COBALT

Sample*	Gravimetric yield, %	Observed counts, *cpm*	Counts corrected for yield, *cpm*	Recovery, %
1	76·79	3561	4626	100·0
2	79·48	2651	4593	99·3
3	80·41	3710	4614	99·8
4	76·79	3426	4462	96·5
5†	62·05	2848	4590	99·2
6†	52·74	2491	4724	102·1

* 20·42 mg of cobalt carrier and 4625 cpm of ^{60}Co were added to each sample.

† Two scavenging steps with palladium chloride and copper$^{\text{II}}$ chloride carriers were performed on these samples using H_2S gas. This accounts for the lower gravimetric yields of these samples.

Zusammenfassung—Eine detaillierte Beschreibung der Trennung Von Radiokobalt von anderem aktiven Material wird mitgeteilt. Die Fällung als Quecksilberthiocyanate wird der als Anthranilat vorgezogen. Das Kobalt wird in der Quecksilberverbindung gezahlt.

Résumé—Les auteurs donnent une méthode détaillée de séparation chimique du radio-cobalt des autres radio éléments. La précipitation à l'état de mercurithiocyanate est préférée à la précipitation à l'état d'anthranilate, et le cobalt est finalement dosé par comptage sous forme de mercurithiocyanate

REFERENCES

[1] W. H. Burgus, *Collected Radiochemical Procedure*, edited by J. Kleinberg. Atomic Energy Com. mission Report LA-1721 (Rev.), November 18, 1955, pp. 66–72.

[2] J. F. Duncan, T. R. Johnas, E. D. B. Johnson, H. A. C. McKay, W. R. E. Maton, E. W. A. Pike and G. N. Walton, *J. Soc. Chem. Ind.*, 1950, **69**, 25.

[3] C. Duval, *Inorganic Thermogravimetric Analysis*. Elsevier Publishing Company, New York, 1953, p. 207.

[4] G. Friedlander and J. W. Kennedy, *Nuclear and Radio-chemistry*. John Wiley and Sons, Inc., New York, 1955, p. 419.

[5] J. Lamure, *Bull. Soc. chim.*, 1946, 661.

[6] W. W. Meinke, *Chemical Procedures Used in Bombardment Work at Berkeley*. UCRL-432, 1949, part 27.

[7] P. Wenger, C. Cimerman and A. Carbaz, *Mikrochim. Acta*, 1937, **2**, 314.

Talanta, 1961, Vol. 7, pp. 296 to 300. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM—I*

EXTRACTION AND ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM TETROXIDE

GERALD GOLDSTEIN, D. L. MANNING, OSCAR MENIS†
Analytical Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee, U.S.A.,
and J. A. DEAN
Department of Chemistry, University of Tennessee, Knoxville, Tennessee, U.S.A.

(*Received* 27 *February* 1960)

Summary—An ultraviolet spectrophotometric method is presented for the determination of milligram quantities of osmium in solutions of uranyl sulphate. Osmium is first oxidised to the octovalent state and the osmium tetroxide which is formed, is selectively extracted with chloroform. The ultraviolet absorption spectrum of osmium tetroxide in chloroform has a series of absorption bands with peak absorbancies at 282, 289, 297, 304 and 312 mμ and molar absorbancy indexes of 1870, 1760, 1640, 1400 and 1000, respectively. For each wavelength, the optimum concentration range for the determination of osmium was evaluated. From 0·4 to 3·3 mg of osmium can be determined with a coefficient of variation of 3%. Of the elements tested only chloride and octovalent ruthenium interfere; however, both of these interferences can be eliminated.

METHODS were desired for the determination of milligram and microgram quantities of osmium in solutions of uranyl sulphate which contain copper, nickel, iron, and chromium as minor components. The existing methods[4] are not sufficiently selective for the direct determination of osmium without a prior separation. Moreover, osmium can exist in solution in many different valency states and therefore, a further problem was that of obtaining all of the osmium in a single valency state. Accordingly, an extremely selective separation procedure suggested by Sauerbrunn and Sandell[5] was tested whereby osmium is oxidised to the octovalent state and the osmium tetroxide which is formed, is then extracted with chloroform. In the work presented in this paper the osmium is determined by measuring the ultraviolet absorbancy of the extracted osmium tetroxide. Although the ultraviolet absorption spectrum of osmium tetroxide in organic solvents has been previously reported in studies of the vibrational frequencies of the osmium tetroxide molecule,[1] the absorbancy of osmium tetroxide has not been utilised previously for analytical purposes.

In a second method[7] the osmium is oxidised and extracted as before, then the extract is added to an ethanolic solution of 1:5-diphenylcarbohydrazide and a blue-violet coloured complex is formed. This method is also extremely selective for osmium and is about 15 times more sensitive than the method described here.

A further method[8] involves the formation of the osmium complex with 1:5-diphenylcarbohydrazide in an aqueous medium rather than in the organic extract.

---

* Work carried out under Contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Nuclear Co., division of Union Carbide Corp., for the Atomic Energy Commission.

† Present address: Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania, U.S.A.

The complex is then extracted with chloroform and the absorbancy of the extract is measured. Although this method is not as selective for osmium as the two previously described methods, it provides an extremely sensitive means of determining osmium. The molar absorbancy index is about 150,000.

EXPERIMENTAL

Reagents

Osmium tetroxide, 0·38 mg of osmium per ml, in 0·1*M* sulphuric acid: A vial containing 0·5 g of osmium tetroxide was broken under 500 ml of 0·1*M* sulphuric acid. After the osmium tetroxide had dissolved completely, the solution was filtered into a 1-litre volumetric flask and diluted to volume with 0·1*M* sulphuric acid. This solution was standardised by the gravimetric benzotriazole method.[6] More dilute osmium solutions were prepared by appropriate dilution of the standard solution.

Apparatus

Beckman Model DU spectrophotometer, equipped with ultraviolet accessories.

Procedure

Transfer a sample aliquot which contains between 0·4 and 3·3 mg of osmium to a 60-ml separatory funnel. If the osmium is not in the octovalent state, dilute to 5 ml with 6*N* sulphuric acid and oxidise the osmium by the dropwise addition of a 5% potassium permanganate solution until a permanent pink colour persists. Discharge the pink colour with a few drops of a 2% ferrous ammonium sulphate solution. Immediately add 3 ml of 15*M* nitric acid and 2 ml of water and extract the osmium tetroxide with two 10-ml portions of chloroform. Drain the extracts into a second 60-ml separatory funnel which contains 10 ml of 0·1*M* sulphuric acid, and wash to remove any traces of nitric acid. Drain the chloroform phase into a 25-ml volumetric flask containing about 1 g of anhydrous sodium sulphate and dilute to volume with chloroform. Measure the absorbancy of the solution against a chloroform blank at the appropriate wavelength using 1-cm cells.

Prepare a calibration curve by adjusting suitable aliquots of a standard osmium tetroxide solution to a 10-ml volume containing 30 volume per cent of nitric acid and extracting them by the same procedure. The oxidation step is not necessary.

RESULTS AND DISCUSSION

Oxidation and extraction of osmium tetroxide

These procedures are essentially the same as those proposed by Sauerbrunn and Sandell[5] and they are discussed by Sandell.[4] Since osmium is extracted from a nitric acid solution, many elements besides osmium can also be extracted if the solvent is polar and has an oxygen-containing functional group.[2] Therefore a nonpolar solvent is necessary for the selective extraction of osmium. The distribution ratio of osmium tetroxide into chloroform is slightly greater than into carbon tetrachloride. More than 99% of the osmium is extracted into the chloroform phase.

Ultraviolet absorption spectrum of osmium tetroxide

The absorption spectrum of osmium tetroxide in chloroform (Fig. 1) exhibits the same features as the spectra previously reported in carbon tetrachloride and in hexane.[1] Above 320 mμ the absorbancy of the osmium tetroxide solution is very small. Below 260 mμ the absorbancy increases rapidly. However, the absorbancy of the chloroform blank also becomes appreciable below 260 mμ.

Adherence to Beer's law

Calibration data for the determination of osmium were obtained for the 5 absorption bands which centre at 282, 289, 297, 304 and 312 mμ. The molar absorbancy indexes are presented in Table I.

The absorbancies at all of the wavelengths adhere to Beer's law. In addition, the optimum concentration range for the determination of osmium was evaluated for each wavelength by the method of Ringbom[3] and these are shown in Table I. A range of from 0·4 to 3·3 mg of osmium can be determined by proper choice of the wavelength, with a coefficient of variation of about 3%.

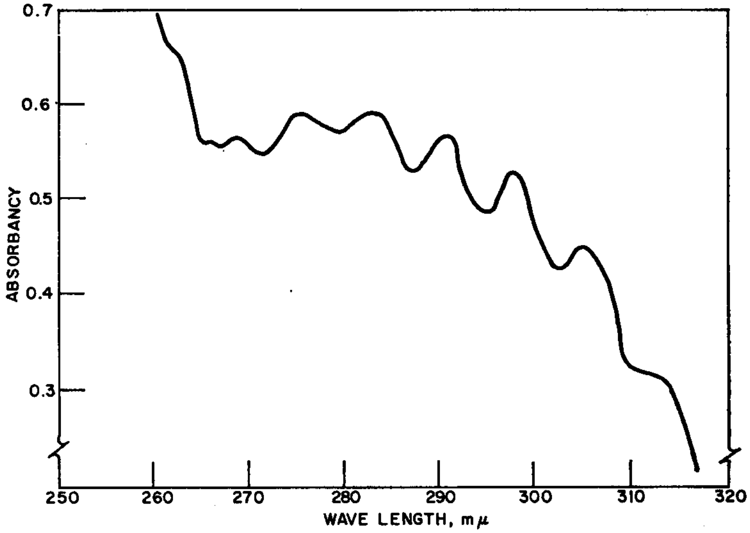


FIG. 1.—Ultraviolet absorption spectrum of osmium tetroxide in chloroform
Osmium, *M*, 3·20 × 10^{-4}
Cells, cm, 1

Effect of foreign substances

The effect of various cations and anions was evaluated by treating solutions containing 1·14 mg of osmium and the foreign substance to be tested by the recommended procedure. The results of these tests are shown in Table II.

Neither the uranyl ion nor the other cations which are normally found as minor components in uranyl sulphate solutions—iron^{III}, copper^{II}, nickel,^{II} chromium^{VI}—interfere appreciably in the determination of osmium. When more than 500 mg of chromium^{VI} was present high results were obtained. The platinum group elements, in their lower valency states, do not interfere. Ruthenium in the octovalent state is

TABLE I—DATA FOR THE ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

Wavelength, mμ	Molar absorbancy index	*Optimum concentration range*[a]	
		M × 10^4	*mg/25 ml*
282	1870	0·8 – 3·7	0·4 – 1·8
289	1760	0·9 – 4·0	0·4 – 1·9
297	1640	0·9 – 4·3	0·5 – 2·0
304	1400	1·1 – 5·0	0·5 – 2·4
312	1000	1·5 – 7·0	0·7 – 3·3

[a] 1-cm cell

TABLE II.—EFFECT OF FOREIGN SUBSTANCES

Conditions:		
	Volume, ml	25
	Wavelength, mμ	289
	Cells, cm	1
	Osmium, mg	1·14

Foreign substance		Osmium, *mg*	
Element	*mg*	Found	Error
U^{VI}	1000	1·19	0·05
Fe^{III}	1000	1·22	0·08
Ni^{II}	1000	1·18	0·04
Cu^{II}	1000	1·19	0·05
Th^{IV}	500	1·17	0·03
Cr^{VI}	500	1·19	0·05
Cr^{III}	500	1·16	0·02
Mo^{VI}	500	1·14	0·00
Pd^{II}	6	1·20	0·06
Au^{III}	5	1·12	−0·02
Rh^{III}	2	1·10	−0·04
Pt^{II}	2	1·17	0·03
Ir^{III}	1	1·16	0·02
Ru^{III}	1	1·19	0·05

an interference since ruthenium tetroxide extracts along with osmium tetroxide[4] and has a similar absorption spectrum.[1] However, osmium can be separated from ruthenium by a modification of the extraction procedure.[4] Of the anions which were tested, perchlorate, sulphate and phosphate did not interfere. When the osmium was initially in a reduced state in the presence of chloride, low results were obtained, since chloride forms complex ions with osmium^{IV} and ^{VI} and inhibits the complete oxidation and subsequent extraction of osmium.[4] For this application, however, the chloride concentration in uranyl sulphate sample solutions is very small and therefore, chloride interference is not significant.

CONCLUSION

The recommended procedure provides a simple and rapid method for the determination of milligram amounts of osmium in solutions of uranyl sulphate. This method is probably applicable to many other types of sample solutions. Of the elements tested only chloride and octovalent ruthenium were found to interfere; however, procedures are available for elimination of both of these interferences.[4]

Acknowledgments—The authors acknowledge the assistance of H. P. House and M. A. Marler in the preparation of this manuscript.

This work was abstracted from a thesis submitted by Gerald Goldstein in partial fulfillment of the requirements for the degree of Master of Science, 1959

Zusammenfassung—Eine uv-spektrophotometrische Methode zur Bestimmung von Milligrammengen Osmium in Uranylsulfatlosungen wird beschrieben. Osmium wird erst in die achtwertige Oxydationstufe gebracht und das Osmiumtetroxyd selektiv mittels Chloroform ausgezogen. Das UV-Spektrum von Osmiumtetroxyd hat mehrere Absorptionsmaxima: 282, 289, 297, 304 und 312 mμ mit den dazugehörigen Absorptionskoeffizienten von 1870, 1760, 1640, 1400 und 1000. Fur jede der genannten

Wellenlängen wurde der optimale Konzentrationsbereich ermittelt. Für Mengen von 0·4–3·3 mg kann die Bestimmung mit einem Variationskoeffizienten von 3% ausgeführt werden. Von den untersuchten Ionen stören nur Ruthenium(III) und Chloride, jedoch sind diese Störungen auszuschaltbar.

Résumé—Les auteurs présentent une méthode spectrophotométrique ultra-violette de dosage de quantités d'osmium de l'ordre du milligramme en solution de sulfate d'uranyle. L'osmium est d'abord oxydé à l'état octavalent, et le tétroxyde d'osmium formé est extrait sélectivement par le chloroforme. Le spectre ultra-violet du tétroxyde d'osmium dans le chloroforme a une série de bandes d'absorption avec des maxima à 282, 289, 297, 304 et 312 mμ, et des coefficients d'extinction molaires de 1870, 1760, 1640, 1400 et 1000 respectivement Pour chaque longueur d'onde, le domaine de concentration le meilleur pour le dosage de l'osmium a été évalué. De 0.4 à 3,3 mg d'osmium peuvent être dosés avec un coefficient de variation de 3 pour cent. Parmi les éléments essayés, seuls le chlorure et le ruthénium octavalent gênent; ces deux interférences peuvent cependant être élimineés.

REFERENCES

[1] A. Langseth and B. Qviller, *Z. phys. Chem.*, 1934, **B 27**, 79.

[2] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*. John Wiley, New York, 1957, p. 140.

[3] A. Ringbom, *Z. analyt. Chem.* 1939, **115**, 322.

[4] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, Inc., New York, 1959, 3rd ed. Chap. XXXI.

[5] R. D. Sauerbrunn and E. B. Sandell, *Analyt. Chim. Acta*, 1953, **9**, 86.

[6] R. F. Wilson and L. J. Baye, *Talanta*, 1958, **1**, 351.

[7] Gerald Goldstein, D. L. Manning, Oscar Menis and J. A. Dean, *Talanta*, 1961, **7**, 301.

[8] *Idem, ibid.*, 1961, **7**, 307.

Talanta, 1961, Vol. 7, pp. 301 to 306. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM—II*

EXTRACTION AND DETERMINATION OF OSMIUM *IN SITU* WITH 1·5-DIPHENYLCARBOHYDRAZIDE

Gerald Goldstein, D. L. Manning, Oscar Menis†
Analytical Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee, U.S.A.,
and J. A. Dean
Department of Chemistry, University of Tennessee, Knoxville, Tennessee, U.S.A.

(*Received* 27 *February* 1960)

Summary—A method has been developed for the spectrophotometric determination of microgram quantities of osmium in uranyl sulphate solutions. The osmium is oxidised to osmium tetroxide, then extracted with chloroform. The extracts are added to an ethanolic solution of 1:5-diphenylcarbohydrazide. A blue-violet coloured reaction product is formed which exhibits maximum absorbancy at 560 mμ. After a period of 2 hr for colour development the molar absorbancy index is about 31,000. Beer's law is adhered to over a range of 30 to 100 μg of osmium with a coefficient of variation of about 4%. A study was made of the effects of foreign substances and only chloride and octovalent ruthenium were found to interfere. Both of these interfering ions can be eliminated.

The previously reported method[2] for the determination of osmium by extraction of osmium tetroxide and measurement of its ultraviolet absorbancy was suitable for milligram quantities of osmium. Since it was also necessary to determine microgram quantities, a survey was made of various chromogenic reagents to determine if any would react with osmium tetroxide in chloroform to form a coloured product and provide a more sensitive method. It was desirable for the chromogenic reagent to react with the osmium tetroxide in the chloroform phase because of the selectivity of the extraction procedure. It was found that 1:5-diphenylcarbohydrazide (DPC) reacted to give a blue-violet coloured product.

EXPERIMENTAL

Reagents

Osmium tetroxide, 12 *μg of osmium per ml:* Prepared as previously described.[2]

1:5-*Diphenylcarbohydrazide* (sym-*diphenylcarbazide; DPC*), 0·2%, *in ethanol:* Dissolve 100 mg of the reagent in 50 ml of ethanol. This reagent is not stable and should be prepared freshly each day.[1]

Apparatus

Beckman Model DU spectrophotometer.

Procedure

Transfer a sample aliquot, containing from 30 to 100 μg of osmium, to a 60-ml separatory funnel. Oxidise, extract, and wash the osmium as previously described.[2] Drain the washed extract into a 25-ml

---

* Work carried out under Contract No. W-7405-3ng-26 at Oak Ridge National Laboratory, operated by Union Carbide Nuclear Co., division of Union Carbide Corp., for the Atomic Energy Commission.

† Present address: Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania, U.S.A.

volumetric flask containing 5 ml of 0.2% DPC and about 1 g of anhydrous sodium sulphate and, if necessary, dilute to volume with additional chloroform. After a 2-hr colour-development period, measure the absorbancy of the solution at 560 mμ *vs.* a reagent blank, using 1-cm cells.

Prepare a calibration curve by carrying aliquots of a standard osmium tetroxide solution through the procedure. The oxidation step is not necessary in this case.

RESULTS AND DISCUSSION

Absorption spectrum of the osmium-DPC complex

The absorption spectrum of the product of the reaction between osmium tetroxide and DPC (Fig. 1) was obtained by treating 48 μg of osmium by the recommended procedure and measuring the absorbancy *vs.* a reagent blank. There is a broad absorption band between 500 and 600 mμ with peak absorbancy at about 560 mμ. Since freshly prepared DPC reagent does not absorb appreciably between 400 and 700 mμ, its spectrum is not shown.

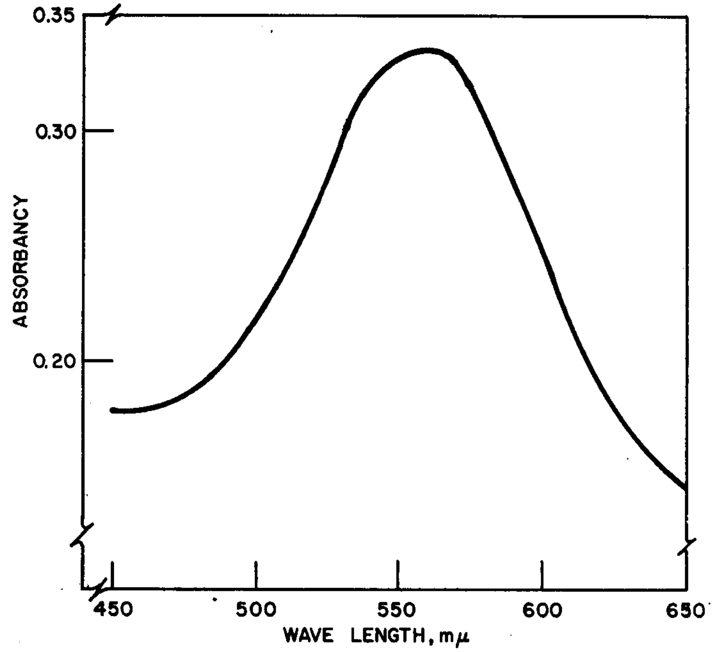


Fig. 1.—Absorption spectrum of the osmium-DPC complex formed in a chloroform medium.

Volume, ml	25
DPC, 0·2%, ml	5
Osmium, μg	48
Colour development	
Time, hr	2
Cells, cm	1

Effect of DPC reagent concentration

Tests were made of the reagent concentration necessary to produce maximum absorbancy by adding extracts containing 96 μg of osmium to various amounts of DPC reagent. From the results, which are shown in Fig. 2, it is indicated that 3 ml of 0·2% DPC in the final 25-ml volume is sufficient for complete colour development. To assure an adequate excess of reagent, however, a 5-ml volume was utilised. This represents approximately an 80:1 molar ratio of reagent to osmium.

Effect of DPC reagent solvent

The DPC reagent can be dissolved in numerous solvents and the effect of several of these on the absorbancy of osmium-DPC solution was tested. A discussion of the solubility and stability of DPC in various solvents is given by Allen.[1] When methanol or acetic acid was utilised as the solvent instead of ethanol, higher absorbancy values were obtained; however, the reproducibility of the measurements was poor. An acetone solution of the reagent gave about the same result as an ethanol solution.

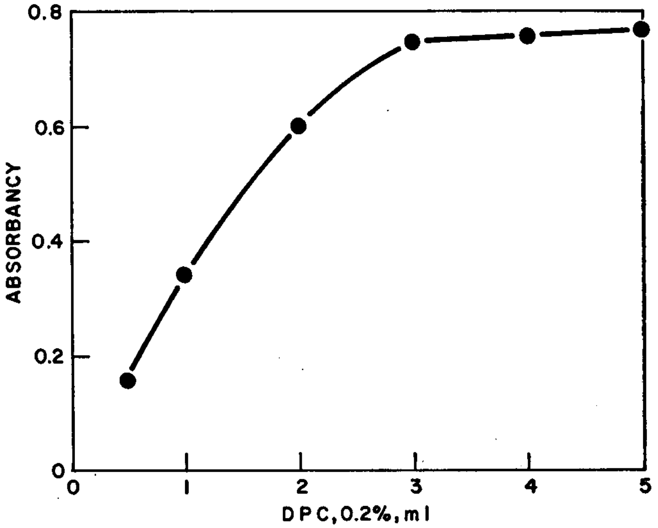


FIG. 2.—Effect of DPC reagent concentration

Volume, ml	25
Osmium, μg	96
Wavelength, mμ	560

The effect of the ethanol concentration was also investigated and it was established that the absorbancies are constant when between 1 and 5 ml of ethanol are present.

Time of colour development

Fig. 3 shows the absorbancy as a function of time, of a typical final solution obtained by treating a solution containing 48 μg of osmium by the recommended procedure. Although the absorbancy increased continually over a period of at least 24 hr, the rate of increase was small after the first hr. For instance, between 30 and 60 min the absorbancies increased by about 5%, between 60 and 120 min by about 3%, and between 120 and 180 min by about 1%. Therefore, within reasonable limits, the time of colour development is not a critical factor for reproducible measurements after the first 2 hr, even though the maximum absorbancy has not yet been attained.

Attempts were made to increase the rate of colour development but these were unsuccessful. When the organic extracts were heated, erratic results were obtained. In some cases the DPC reagent was apparently oxidised, giving the solutions a deep red colour, and in other cases the solutions were completely decolorised.

Order of addition of reagents

The order of addition of the reagents also affected the colour development. If the reagent was added to the extracts, initial absorbancies were very low and the absorbancy increased gradually over a period of about 3 days. Therefore, it is important to add first the reagent solution to the volumetric flasks, then to drain the extracts into the reagent.

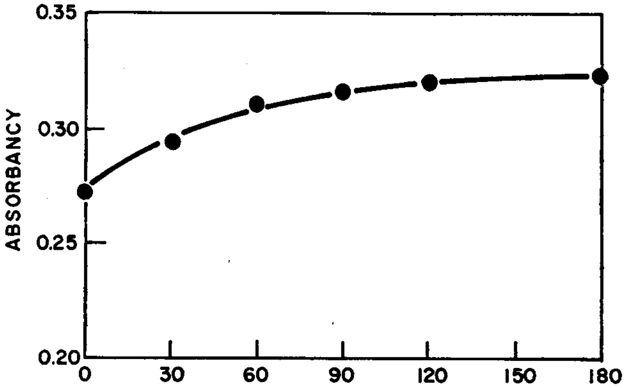


FIG. 3.—Effect of time of colour development

Volume, ml	25
Osmium, µg	48
DPC, 0·2%, ml	5
Wavelength, mµ	560

Adherence to Beer's law

Five calibration curves were prepared on separate days by the recommended procedure (Table I).

TABLE I.— ADHERENCE OF ABSORBANCY OF OSMIUM-DPC SOLUTIONS TO BEER'S LAW

Conditions:	Volume, ml	25
	DPC, 0·2%, ml	5
	Colour-development time, hr	2
	Wavelength, mµ	560
	Cells, cm	1

Osmium, µg	Absorbancy for different series					Average
	I	II	III	IV	V	
12	0·079	0·082	0·080	0·079	0·078	0·080
24	0·162	0·165	0·151	0·164	0·173	0·163
48	0·322	0·314	0·300	0·329	0·342	0·321
72	0·462	0·440	0·450	0·473	0·470	0·459
96	0·615	0·592	0·611	0·650	0·642	0·622
Molar absorbancy index	30,900	30,100	30,400	31,900	32,300	31,300
Coefficient of variation, %	2	6	3	2	5	3

Statistical analysis of the five sets of data showed that there was no significant difference in the molar absorbancy indexes or the coefficients of variation. In no case was the coefficient of variation more than 6%; the average was 3%. The optimum range for the determination of osmium, evaluated by the Ringbom method,[3] is from 30 to 100 μg, in the sample taken for analysis, with a coefficient of variation over this range of about 4%.

Experiments to determine the mole ratio of DPC to osmium in the complex were unsuccessful because of the difficulty in obtaining maximum absorbancy values, and because of the varying rate of colour development when the ratio of DPC to osmium was varied.

Effect of foreign substances

The effect of various elements was evaluated by treating solutions which contained 38 μg of osmium and the appropriate quantity of the foreign substance by the recommended procedure. These results are presented in Table II. The elements commonly found in uranyl sulphate solutions do not interfere in the determination of osmium.

TABLE II.—EFFECT OF FOREIGN SUBSTANCES ON THE DETERMINATION OF OSMIUM

Foreign Substance		Osmium, μg[a]	
Element	*mg*	Found	Error
U^{VI}	500	38·7	0·7
Th^{IV}	500	40·0	2·0
Fe^{III}	1	39·9	1·9
Cr^{VI}	1	38·5	0·5
Cr^{III}	1	39·7	1·7
Ni^{II}	1	40·3	2·3
Cu^{II}	1	39·9	1·9
Co^{II}	1	38·2	0·2
Mo^{VI}	1	37·6	−0·4
Zr^{IV}	1	38·8	0·8
Au^{III}	1	39·0	1·0
Pt^{II}	1	39·3	1·3
Pd^{II}	1	38·7	0·7
Ir^{III}	1	37·1	−0·9
Rh^{III}	1	37·9	−0·1
Ru^{III}	1	38·8	0·8
Ru^{VIII}	0·3	49·3	11·3

[a] 38·0 μg present.

Accurate results were obtained even in the presence of 500-mg quantities of uranium and thorium. Of the platinum group metals, only ruthenium^{VIII} interferes and does so because ruthenium tetroxide is co-extracted with osmium tetroxide[4] and reacts with the DPC reagent to give a violet coloured product. Although it is possible that some of the other elements tested will react with DPC, the extraction procedure selectively separates the osmium. Of the common anions, perchlorate, sulphate and phosphate do not interfere, while chloride hinders the complete extraction of osmium. The interference of both ruthenium^{VIII} and chloride can be eliminated.[4]

CONCLUSION

The procedure presented here is a rapid, selective, and reasonably precise method for the determination of osmium. In addition, the molar absorbancy index of the final solution is about 31,000 so that the sensitivity of this method is 15 times that previously obtained,[2] and about 10 times the sensitivity of the conventional thiourea method.[4]

Since this method also involves the oxidation and extraction of osmium, the discussion of these procedures in the previous paper[2] also applies here.

Acknowledgment—The authors acknowledge the assistance of H. P. House and M. A. Marler in the preparation of this manuscript.

This work was abstracted from a thesis submitted by Gerald Goldstein in partial fulfillment of the requirements for the degree of Master of Science, 1959.

Zusammenfassung—Eine Methode zur Bestimmung von Osmium in Uranylsulfatlösungen wurde entwickelt. Osmium wird erst zur achtwertigen Stufe oxydiert und das Osmiumtetroxyd mit Chloroform ausgezogen. Der Chloroformextrakt wird einer alkoholischen Lösung von 1,5 Diphenylcarbohydrazid zugesetzt. Ein blauviolett gefärbtes Produkt wird gebildet, mit einem Absorptionsmaximum bei 560 mμ. Nach zweistündiger Farbentwicklung beträgt der Absorptionskoeffizient 31000. Für Mengen von 30–100 μg wird Beer's Gesetz befolgt. Die einzigen Störungen werden durch Chlorid und Ruthenium (VIII) verursacht, können jedoch behoben werden.

Résumé—Les auteurs ont développé une méthode de dosage spectrophotométrique de quantités d'osmium de l'ordre du microgramme dans des solutions de sulfate d'uranyle. L'osmium est oxydé en tétroxyde d'osmium et ensuite extrait par le chloroforme. Les extraits sont ensuite ajoutés à une solution éthanolique de 1-5-diphénylcarbohydrazide. Un produit de la réaction bleu violet est formé, il présente un maximum d'absorption à 560 mu. Après une période de 2 heures pour le développement de la couleur, le coefficient d'extinction molaire est environ 31000. La loi de Beer est suivie dans le domaine de 30 μg à 100 μg d'osmium avec un coefficient de variation d'environ 4 pour cent. Une étude des effets des substances étrangères a été faite, et seuls le chlorure et le ruthénium octavalent ont été trouvés gênants. Ces deux interférences peuvent être éliminées.

REFERENCES

[1] T. L. Allen, *Analyt. Chem.*, 1958, **30**, 447.

[2] G. Goldstein, D. L. Manning, O. Menis and J. A. Dean, *Talanta*, 1961, **7**, 296.

[3] A. Ringbom, *Z. analyt. Chem.*, 1939, **115**, 322.

[4] E. B. Sandell, *Colorimetric Determination of Traces of Metals.* Interscience Publishers, Inc., New York, 1959, 3rd ed., Chap. XXXI.

Talanta, 1961, Vol. 7, pp. 307 to 315. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM—III*

REACTION OF OSMIUM TETROXIDE WITH 1:5-DIPHENYLCARBOHYDRAZIDE IN AQUEOUS SOLUTIONS FOLLOWED BY EXTRACTION OF THE COMPLEX

GERALD GOLDSTEIN, D. L. MANNING, OSCAR MENIS†
Analytical Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee, U.S.A.,
and J. A. DEAN
Department of Chemistry, University of Tennessee, Knoxville, Tennessee, U.S.A.

(*Received* 27 *February* 1960)

Summary—A spectrophotometric method has been developed which is applicable to the determination of extremely small quantities of osmium. Osmium is oxidised to the octovalent state, then added to an acidic aqueous solution containing 1:5-diphenylcarbohydrazide (DPC). After heating the aqueous solution to 65°, the osmium-DPC complex is extracted with chloroform. A molar absorbancy index of about 150,000 is obtained. From 7 to 25 μg of osmium can be determined with a coefficient of variation of 6%. It was established that Fe^{III}, Cu^{II}, Ru^{III} and Au^{III} seriously interfere in the determination of osmium by this method, while Cr^{VI}, Ni^{II}, Mo^{VI}, Ir^{III} and chloride interfere only when present in relatively high concentrations.

IN previous work on the determination of osmium with 1:5-diphenylcarbohydrazide (DPC), osmium tetroxide was extracted with chloroform and added to the DPC reagent.[2] Under these conditions a molar absorbancy index of about 31,000 was obtained. From preliminary experiments it was observed that when the DPC was added to aqueous solutions containing octovalent osmium, a blue-violet compound was formed which could be extracted with chloroform. The intensity of the colour of the extract was much greater than the colour intensity of the aqueous solution. It appeared that much greater sensitivity could be obtained by adding the DPC reagent to the aqueous osmium tetroxide solutions, then extracting the complex, rather than adding the DPC to the osmium which had been extracted into chloroform.

EXPERIMENTAL

Reagents

Osmium tetroxide, 5 μg of osmium per ml: Prepared as described previously.[1]

1:5-Diphenylcarbohydrazide (sym-diphenylcarbazide, DPC), 0·2%: Prepared as described previously.[2]

Apparatus

Beckman Model DU spectrophotometer.

Procedure

Transfer a sample aliquot which contains between 7 and 25 μg of osmium, as osmium tetroxide, to a 50-ml beaker containing 2·5 ml of perchloric acid, 2 ml of glacial acetic acid, and 3 ml of 0·2%

---

* Work carried out under Contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Nuclear Co., division of Union Carbide Corp., for the Atomic Energy Commission.

† Present address: Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania, U.S.A.

DPC. Dilute to exactly 25 ml. Heat the solution to 65° over a period of about 5 min, then allow it to cool to room temperature. Transfer the solution to a 60-ml separatory funnel and extract with two 10-ml portions of chloroform. Drain the extracts into a 25-ml volumetric flask which contains about 1 g of anhydrous sodium sulphate, and dilute to volume with chloroform. Measure the absorbancy at 560 mμ *vs.* a reagent blank, using 1-cm cells.

Prepare a calibration curve by treating suitable aliquots of a standard osmium tetroxide solution by the same procedure.

RESULTS AND DISCUSSION

Absorption spectrum of the osmium-DPC extract

The absorption spectrum of the osmium-DPC complex formed in an aqueous medium and then extracted is shown in Fig. 1. Compared with the spectrum of the complex formed in a chloroform medium,[2] the two spectra show the same general features. There is a broad absorption band between 500 and 600 mμ, with maximum absorbancy at 560 mμ. However, the absorption at 560 mμ is much higher when the complex is extracted with chloroform rather than formed in the chloroform solution, and the absorbancies at wavelengths below 500 mμ and above 600 mμ are lower. All further measurements were made at 560 mμ.

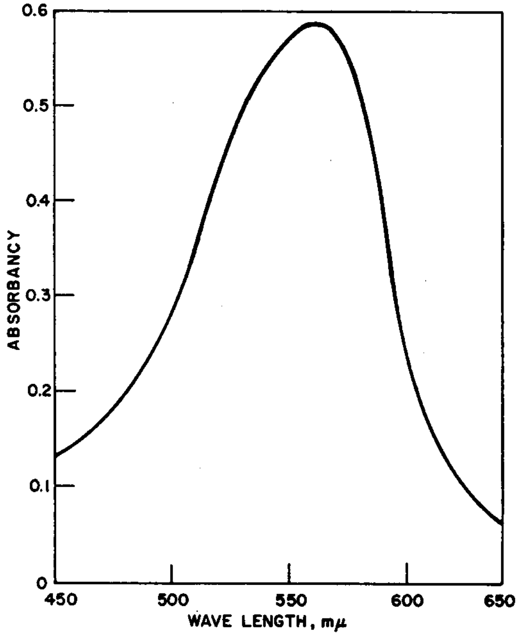


FIG. 1.—Absorption spectrum of the osmium-DPC complex extracted with chloroform from an aqueous medium.

Volume, ml	25
DPC, 0·2%, ml	3
Osmium, μg	19
Cells, cm	1

Organic extractant

Several solvents besides chloroform were tested for the extraction of the osmium-DPC complex. The absorbancy of the extracts at 560 mμ was essentially the same when either chloroform, carbon tetrachloride, or xylene was utilised as the extractant. Lower absorbancies were obtained with bromobenzene, *iso*amyl alcohol, and *iso*amyl acetate, and only a very small absorbancy was observed with methyl *iso*butyl ketone.

Since the extractions were performed with two successive portions of the solvent, the efficiency with which each solvent extracted the osmium-DPC complex could be compared by noting the intensity of the colour in the second extract. In this respect, chloroform was clearly a more efficient extractant than either carbon tetrachloride or xylene, for the second chloroform extract was almost colourless while the second carbon tetrachloride and xylene extracts were substantially coloured. The absorbancies of the reagent blank extracts were about the same in all cases.

Effect of time and temperature

When the osmium-DPC complex is formed in an aqueous solution, then extracted with chloroform, the final absorbancy depends on the temperature of the aqueous solution and on two time factors: (1) the period of time for colour development in the aqueous phase, and (2) the period of time between the extraction of the complex into chloroform and the subsequent absorbancy measurement. Of the two time factors, the former was the more critical. The absorbancy of the extracts depends on the extent to which the osmium-DPC complex forms before the extraction. When the aqueous solutions were heated to 35°, or 50°, then cooled to room temperature, the

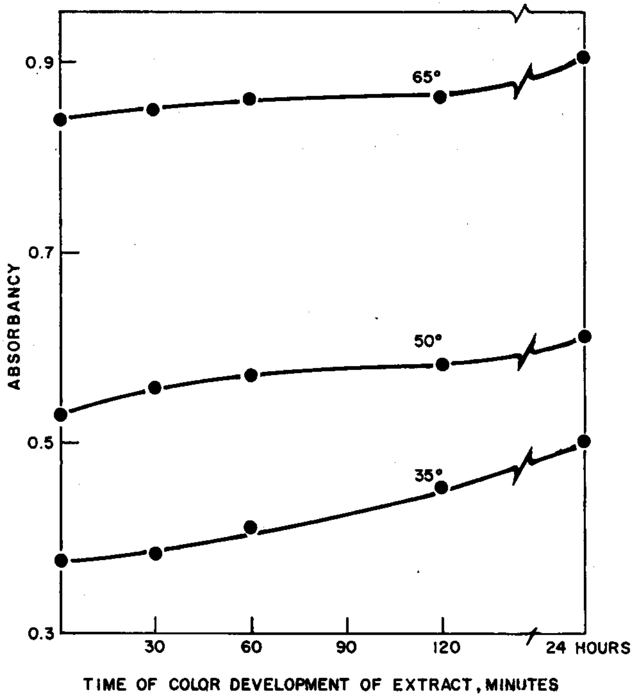


FIG. 2.—Effect of heating the aqueous solutions before extraction

Volume, ml	25
Osmium, μg	28
Wavelength, mμ	560

absorbancy of the extracts was not constant but depended on the time allowed for continuing colour development in the organic phase (Fig. 2). However, when the solutions were heated to 65° over a period of 5 min, and cooled to room temperature before the extraction, much higher absorbancies were obtained and the absorbancy remained reasonably constant. For example, the set heated to 65° exhibited an increase of about 8% over a period of 24 hr.

Although no specific tests were made, it is probable that maximum absorbancy can also be obtained by heating the aqueous solutions at a lower temperature for a longer period of time. At temperatures higher than 65°, there was some tendency for the reagent to oxidise.

Effect of perchloric acid concentration

The absorbancies of the chloroform extracts were found to depend on both the perchloric and the acetic acid concentrations of the aqueous phase as illustrated in Fig. 3. As the perchloric acid concentration was increased up to about 1*M*, the absorbancy also increased and became constant when the perchloric acid concentration was between 1 and 1·5*M*. Further increase in the perchloric acid concentration resulted in a change in the colour of the extracts from blue-violet to red-violet, and an increase in the absorbancy at 560 mμ. Similar results were obtained for all acetic acid concentrations. These absorbancy readings were not as dependent on the perchloric

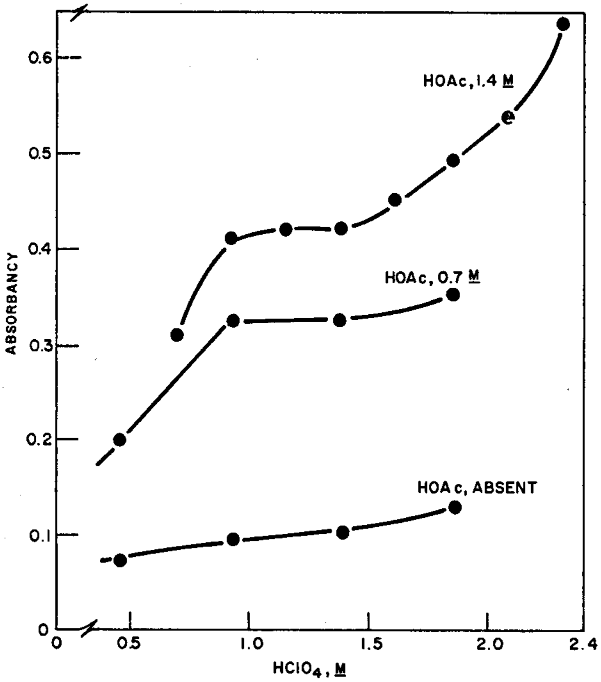


FIG. 3.—Effect of perchloric acid concentration

Volume, ml	25
DPC, 0·2%, ml	4
Osmium, μg	19
Wavelength, mμ	560

acid concentration when acetic acid was absent. The recommended concentration of perchloric acid is 1·2 ± 0·1*M*.

Effect of acetic acid concentration

The absorbancies of the extracts are increased by addition of acetic acid to the aqueous phase. The increase in absorbancy is almost linear with respect to the acetic acid concentration, and occurs at all perchloric acid concentrations (Fig. 4). The sensitivity of the method, therefore, can be increased by increasing the acetic acid concentration. On the other hand, small variations in the acetic acid concentration of the aqueous phase seriously affect the absorbancy of the extracts and, therefore, the acetic acid concentration must be carefully controlled. A concentration of 1·4*M* was chosen for use in further work because this concentration is conveniently prepared and the molar absorbancy index of the extract is sufficiently high so that very small quantities of osmium can be determined.

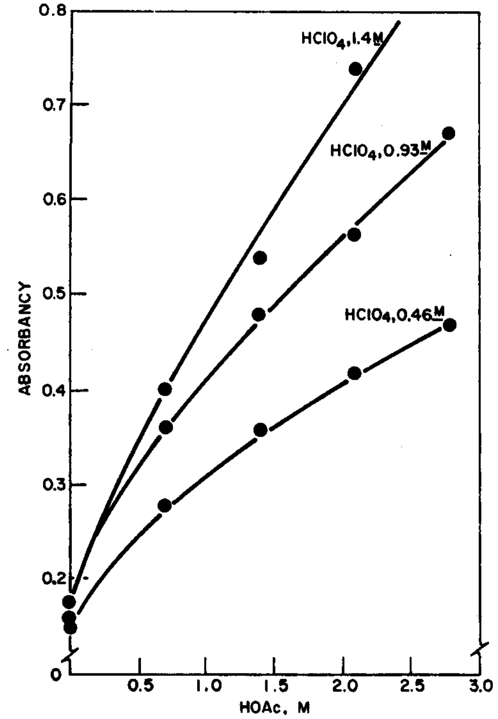


FIG. 4.—Effect of acetic acid concentration

Volume, ml	25
DPC, 0·2%, ml	4
Osmium, μg	19
Wavelength, mμ	560

Effect of reagent and ethanol concentrations

Both the concentration of the chromogenic reagent and ethanol affect the absorbancy. The two effects are interdependent. The effect of varying the DPC concentration at two levels of ethanol concentration is illustrated in Fig. 5. In both cases the absorbancy increases as the amount of DPC added is increased up to 6 mg, after which it decreases somewhat. The absorbancies are higher, however, when 2 ml of ethanol are present than when 5 ml are added, except in the case where 6 mg of DPC were present. This indication that the ethanol concentration affects the absorbancies

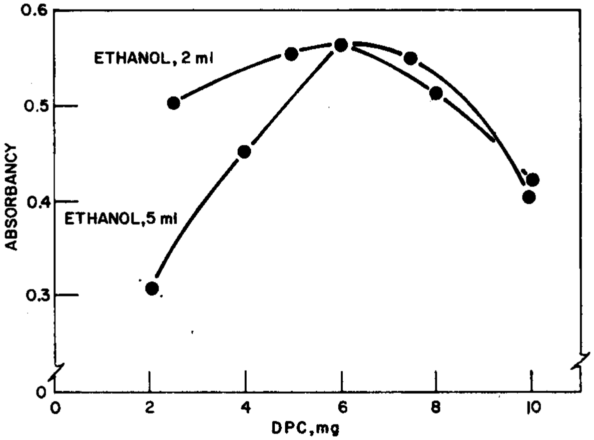


FIG. 5.—Effect of reagent concentration

Volume, ml	25
$HClO_4$, *M*	1·2
HOAc, *M*	1·4
Osmium, μg	19
Wavelength, mμ	560

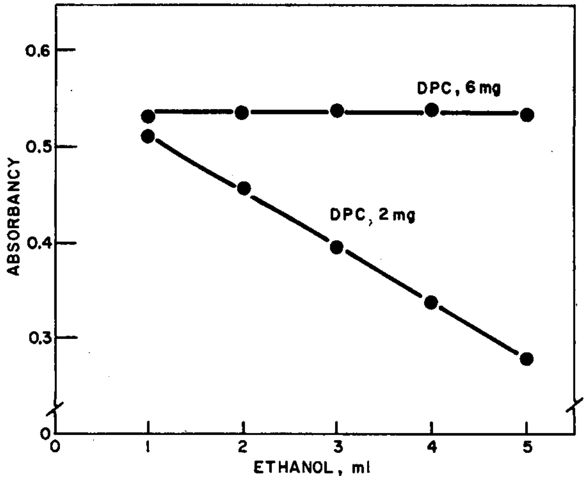


FIG. 6.—Effect of ethanol concentration

Volume, ml	25
$HClO_4$, *M*	1·2
HOAc, *M*	1·4
Osmium, μg	19
Wavelength, mμ	560

at certain concentration levels of DPC was confirmed. The results in Fig. 6 show that when 6 mg of DPC are added the absorbancy does not vary with ethanol concentration. If, however, only 2 mg of DPC are added the absorbancy decreases with an increase in ethanol content.

In general, the optimum quantity of reagent is 6 mg. At this concentration level, the absorbancy of the extracts is at a maximum and does not depend on the ethanol concentration. If higher or lower DPC concentrations are utilised, not only are the absorbancies smaller but they are also dependent on the quantity of ethanol present.

Adherence to Beer's law and effect of order of addition of reagents

The order of addition of the reagents to the aqueous solutions had a substantial effect on the absorbancies of the extracts. Table I shows calibration data obtained by three procedures: in *A* the order of addition of reagents was osmium, acids, DPC; in *B*, acids, osmium, DPC; and in *C*, acid, DPC, osmium. In each case the aqueous solutions were then heated and extracted as described in the recommended procedure. Absorbancies were highest when the osmium was added to acidic aqueous solutions containing the DPC reagent; somewhat lower absorbancies were observed when the osmium was added to the acidic solution before the DPC reagent; the lowest absorbancies were found when the acids and then the DPC were added to aqueous osmium solution. In all three cases the absorbancies adhered to Beer's law with a coefficient of variation of about 6%. No fading of colour was observed over a 24-hr period.

TABLE I.—ADHERENCE TO BEER'S LAW AND EFFECT OF ORDER OF ADDITION OF REAGENTS

Conditions:	Volume, ml	25
	$HClO_4$, *M*	1·2
	HOAc, *M*	1·4
	DPC, 0·2%, ml	3
	Wavelength, mμ	560
	Cells, cm	1

Osmium		Absorbancy		
		Order of reagent addition[a]		
μg	$M \times 10^6$	A	B	C
7·6	1·60	0·137	0·195	0·225
11·4	2·40	0·230	0·293	0·335
15·2	3·20	0·288	0·452	0·483
19·2	4·00	0·387	0·531	0·617
22·8	4·80	0·479	0·632	0·771
Molar absorbancy index		93,600	129,000	148,000
Coefficient of variation, %		6	6	6

[a] See text, p. 312.

To attain maximum sensitivity, therefore, the recommended procedure provides that the sample containing the osmium be added to an aqueous solution of proper acidity which contains the DPC reagent. The optimum concentration range for the determination of osmium by this procedure was evaluated by the method of Ringbom[4] and extends from 7 to 25 μg of osmium in the final 25-ml volume.

Effect of foreign substances

To determine whether other elements also produced coloured extracts, 1-mg quantities of various cations were treated by the recommended procedure. The effects of various anions were determined by preparing osmium tetroxide solutions containing 19 μg of osmium per ml in 0·1M hydrochloric acid, nitric acid, hydrofluoric acid and phosphoric acid, individually. After a period of 24 hr, 1-ml aliquots of these solutions were withdrawn and the osmium determined by the recommended procedure.

TABLE II.—EFFECT OF FOREIGN SUBSTANCES

Conditions:	Volume, ml	25
	$HClO_4$, M	1·2
	HOAc, M	1·4
	DPC, 0·2%, ml	3
	Wavelength, mμ	560
	Cells, cm	1

Foreign substance		Osmium, μg		Amount of substance (μg) equivalent to 1 μg of Os
Element(s)	mg	Present	Found	
$\mathrm{U^{VI}}$, $\mathrm{Th^{IV}}$, $\mathrm{Cr^{III}}$ $\mathrm{Co^{II}}$, $\mathrm{Ti^{IV}}$, $\mathrm{Mn^{II}}$ $\mathrm{Cd^{II}}$, $\mathrm{Zr^{IV}}$, $\mathrm{La^{III}}$ $\mathrm{Pt^{II}}$, $\mathrm{Pd^{II}}$, $\mathrm{Rh^{III}}$	1	0	0	—
$\mathrm{Fe^{III}}$	1	0	54	19
$\mathrm{Cr^{VI}}$	1	0	6·6	150
$\mathrm{Ni^{II}}$	1	0	3	330
$\mathrm{Cu^{II}}$	1	0	14	70
$\mathrm{Mo^{VI}}$	1	0	2·5	400
$\mathrm{Ru^{III}}$	1	0	18	55
$\mathrm{Ir^{III}}$	1	0	4	250
$\mathrm{Au^{III}}$	1	0	25	40
$\mathrm{Cl^-}$	[a]	19·0	12·8	—
$\mathrm{NO_3^-}$	[a]	19·0	20·1	—
$\mathrm{PO_4^{3-}}$	[a]	19·0	19·2	—
$\mathrm{F^-}$	[a]	19·0	19·8	—

[a] 0·1M

The results of these tests are presented in Table II. The cations iron^{III}, chromium^{VI}, nickel^{II}, copper^{II}, molybdenum^{VI}, ruthenium^{III}, iridium^{III} and gold^{III} formed extractable complexes with DPC which would interfere in the determination of osmium. In the case of chromium^{VI} the aqueous solution was intensely red-violet in colour; however, the coloured complex was only partially extractable under these conditions. The other interfering elements produced a brown colour in the aqueous solutions, and red-violet extracts. Palladium^{II} produced yellow-coloured aqueous solutions and extracts which showed no absorbancy at 560 mμ.

Osmium was recovered completely in the presence of perchlorate, sulphate, phosphate, fluoride and nitrate. In the presence of chloride the absorbancies were significantly lower, which was probably due to the formation of osmium chloro-complexes which in turn prevented the complete reaction of osmium with the DPC.

CONCLUSION

The formation of the osmium-DPC complex in the aqueous phase, followed by its extraction with chloroform, provides an extremely sensitive means of determining osmium. With the exception of the catalytic method[3] the proposed procedure is by far the most sensitive means of determining osmium. The molar absorbancy index of 150,000 is 50 times greater than that of the thiourea complex and at least 5 times greater than in most other spectrophotometric methods.

Although it is necessary to sacrifice some of the selectivity for osmium which can be achieved through the extraction of osmium tetroxide, in order to obtain the greater sensitivity, the substances interfering in the determination are no more numerous than in most other methods and they are fewer than those which interfere with the catalytic method. Of the elements tested, iron^{III}, copper^{II}, ruthenium^{III} and gold^{III} interfere seriously while chromium^{VI}, nickel^{II}, molybdenum^{VI} and indium^{III} interfere only when the weight ratio of these elements to osmium is greater than 100:1. High concentrations of chloride (about 0·1*M*) prevent the complete formation of the complex.

Acknowledgments—The authors acknowledge the assistance of H. P. House and M. A. Marler in the preparation of this manuscript.

This work was abstracted from a thesis submitted by Gerald Goldstein in partial fulfillment of the requirements for the degree of Master of Science. 1959.

Zusammenfassung—Eine spektrophotometrische Bestimmung für extrem kleine Osmiummengen wurde entwickelt. Osmium wird zur achtwertigen Stufe oxydiert und die Lösung einer sauren wassrigen Lösung von 1,5-Diphenylcarbohydrazid zugesetzt. Nach Erwärmen auf 65°C wird der Osmium-DPC-Komplex mit Chloroform extrahiert. Ein molarer Extinktions Koefficient von etwa 150,000 resultiert. 7–25 μg Osmium Können mit einer Genauigkeit entsprechend einem Variationskoeffizienten von 3% bestimmt werden. Es wurde gefunden, dass Fe(III), Cu, Ru(III) und Au(III) sehr stark stören. Cr(VI), Ni, Mo(VI), Ir(III) und Chlorid stören nur, wenn in grösseren Konzentrationen anwesend.

Résumé—Les auteurs ont développé une méthode spectrophotométrique applicable au dosage de quantités d'osmium extrêmement faibles. L'osmium est oxydé à l'état octavalent et ensuite ajouté à une solution aqueuse acide contenant de la 1-5-diphénylcarbohydrazide. Après chauffage de la solution aqueuse à 65°, le complexe osmium-DPC est extrait par le chloroforme. Un coefficient d'extinction molaire d'environ 150 000 est obtenu. De 7 à 25 μg d'osmium peuvent être dosés avec un coefficient de variation de 6 pour cent. Les auteurs ont établi que Fe (III), Cu (II), Ru (III) et Au (III) gênent sérieusement dans le dosage de l'osmium par cette méthode, cependant que Cr (VI), Ni (II), Mo (VI), Ir (III) et Cl^- gênent seulement quand ils sont présents à des concentrations relativement grandes.

REFERENCES

[1] G. Goldstein, D. L. Manning, O. Menis and J. A. Dean, *Talanta*, 1961, **7**, 296

[2] *Idem. ibid.*, 1961, **7**, 301

[3] E. B. Sandell, *Colorimetric Determination of Traces of Metals.* Interscience Publishers, Inc., New York, 1959, 3rd ed., p. 751.

[4] A. Ringbom, *Z. analyt. Chem.*, 1939, **115**, 322.

Talanta, 1961, Vol. 7, pp. 316 to 322. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS OF H. H. WILLARD

1. *A New Electrolyte for the Silver Coulometer.* Henry S. Carhart, H. H. Willard and W. D. Henderson, *Trans. Amer. Electrochem. Soc.*, 1906, **9,** 375.
2. *Further Investigation Concerning the Atomic Weights of Silver, Lithium and Chlorine.* Theodore W. Richards and Hobart Hurd Willard, *J. Amer. Chem. Soc.*, 1910, **32,** 4.
3. *Weitere Untersuchungen uber die Atomgewichte von Silber., Lithium und Chlor.* Theodore W. Richards and Hobart Hurd Willard, *Z. anorg. Chem.*, 1910, **66,** 229.
4. *The Preparation of Perchloric Acid.* H. H. Willard, *J. Amer. Chem. Soc.*, 1912, **34,** 1480.
5. *The Colorimetric Determination of Manganese by Oxidation with Periodate.* Hobart H. Willard and Lucien H. Greathouse, *J. Amer. Chem. Soc.*, 1917, **39,** 2366.
6. *Perchloric Acid as aDehydrating Agent in the Determination of Silica.* H. H. Willard and W. E. Cake, *J. Amer. Chem. Soc.*, 1920, **42,** 2208.
7. *The Iodometric Determination of Amino Nitrogen in Organic Substances.* H. H. Willard and W. E. Cake, *J. Amer. Chem. Soc.*, 1920, **42,** 2646.
8. *The Volumetric Determination of Sulfide by Oxidation to Sulfate.* H. H. Willard and W. E. Cake, *J. Amer. Chem. Soc.*, 1921, **43,** 1610.
9. *A Revision of the Atomic Weight of Antimony. The Analysis of Antimony Bromide.* H. H. Willard and R. K. McAlpine, *J. Amer. Chem. Soc.*, 1921, **43,** 797.
10. *The Determination of Bromide in Brines and Mineral Waters.* C. C. Meloche and H. H. Willard, *J. Ind. Eng. Chem.*, 1922, **14,** 422.
11. *The Separation and Determination of Cobalt. I. The Separation of Cobalt by means of Phenyl-thiohydantoic Acid.* H. H. Willard and Dorothy Hall, *J. Amer. Chem. Soc.*, 1922, **44,** 2219.
12. *The Separation and Determination of Cobalt. II. Gravimetric Determination of Cobalt.* H. H. Willard and Dorothy Hall, *J. Amer. Chem. Soc.*, 1922, **44,** 2226.
13. *The Separation and Determination of Cobalt. III. The Volumetric Determination of Cobalt.* H. H. Willard and Dorothy Hall, *J. Amer. Chem. Soc.*, 1 922, **44,** 2237.
14. *The Separation of Copper by Means of Phenyl-thiohydantoic Acid.* H. H. Willard and Dorothy Hall, *J. Amer. Chem. Soc.*, 1922, **44,** 2253.
15. *Bimetallic Electrode Systems in Electrometric Analysis. I. Systems Comprising Two Dissimilar Metals.* H. H. Willard and Florence Fenwick, *J. Amer. Chem. Soc.*, 1922, **44,** 2504.
16. *Bimetallic Electrode Systems in Electrometric Analysis. II. Theory of Bimetallic Systems: Systems Comprising Two Similar Metals.* H. H. Willard and Florence Fenwick, *J. Amer. Chem. Soc.*, 1922, **44,** 2516.
17. *A New Method for the Electrometric Titration of Vanadium in the Presence of Iron and Chromium.* H. H. Willard and Florence Fenwick, *J, Amer. Chem. Soc.*, 1923, **45,** 84.

18. *The Bimetallic Electrode System Applied to Neutralization Reactions.* H. H. Willard and Florence Fenwick, *J. Amer. Chem. Soc.*, 1923, **45**, 715.
19. *The Electrometric Determination of Sulfur in Soluble Sulfides.* H. H. Willard and Florence Fenwick, *J. Amer. Chem. Soc.*, 1923, **45**, 645.
20. *The Electrometric Titration of the Halides in the Presence of One Another.* H. H. Willard and Florence Fenwick, *J. Amer. Chem. Soc.*, 1923, **45**, 623.
21. *The Electrometric Titration of Molybdenum with a Titanous Salt.* H. H. Willard and Florence Fenwick, *J. Amer. Chem. Soc.*, 1923, **45**, 928.
22. *The Electrometric Titration of Selenium in the Presence of Tellurium, Iron and Copper.* H. H. Willard and Florence Fenwick, *J. Amer. Chem. Soc.*, 1923, **45**, 933.
23. *The Preparation and Properties of Magnesium Perchlorate and its Uses as a Drying Agent.* H. H. Willard and G. Frederick Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2255.
24. *The Separation and Determination of Sodium and Lithium by Precipitation from Alcoholic Perchlorate Solution.* H. H. Willard and G. Frederick Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2816.
25. *The Perchlorates of the Alkali and Alkaline Earth Metals and Ammonium. Their Solubility in Water and Other Solvents.* H. H. Willard and G. Frederick Smith, *J. Amer. Chem. Soc.*, 1923, **45**, 286.
26. *Ceric Sulfate as a Volumetric Oxidizing Agent. I. Preparation and Standardization of Solutions. Determination of Calcium.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1322.
27. *Ceric Sulfate as a Volumetric Oxidizing Agent. II. Determination of Iron.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1334.
28. *Ceric Sulfate as a Volumetric Oxidizing Agent. III. The Titration of Iodide.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1368.
29. *Ceric Sulfate as a Volumetric Oxidizing Agent. IV. The Determination of Arsenic.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1372.
30. *Ceric Sulfate as a Volumetric Oxidizing Agent. V. The Determination of Antimony.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1372.
31. *Ceric Sulfate as a Volumetric Oxidizing Agent. VI. The Volumetric Determination of Cerium.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1379.
32. *Ceric Sulfate as a Volumetric Oxidizing Agent. VII. Determination of Vanadium in Presence of Chromium, Tungsten and Iron*, H. H. Willard and Philena Young, *Ind. Eng. Chem.*, 1928, **20**, 972.
33. *Ceric Sulfate as a Volumetric Oxidizing Agent. VIII. The Determination of Chromium in the Presence of Manganese, Iron and Vanadium.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1929, **51**, 139.
34. *Ceric Sulfate as a Volumetric Oxidizing Agent. IX. Preparation and Stability of Solutions.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1929, **51**, 149.
35. *Ceric Sulfate as a Volumetric Oxidizing Agent. X. The Determination of Thallium.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1930, **52**, 36.
36. *Ceric Sulfate as a Volumetric Oxidizing Agent. XI. The Oxidation of Organic Acids.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1930, **52**, 132.

37. *Ceric Sulfate as a Volumetric Oxidizing Agent. XII. The Determination of Tellurous Acid.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1930, **52,** 533.
38. *Ceric Sulfate as a Volumetric Oxidizing Agent. XIII. The Determination of Mercurous Mercury.* H. H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1930, **52,** 557.
39. *Ceric Sulfate as a Volumetric Oxidizing Agent. XIV. Indicator Methods for the Standardization and Use of Ceric Sulfate.* Hobart H. Willard and Philena Young, *J. Amer. Chem. Soc.*, 1933, **55,** 3260.
40. *Vanadium in Chrome-Vanadium-Tungsten Steels.* H. H. Willard and Philena Young, *Ind. Eng. Chem.*, 1928, **20,** 764.
41. *Persulfate Method for Chromium Plus Vanadium in Chrome-Vanadium-Tungsten Steels.* H. H. Willard and Philena Young, *Ind. Eng. Chem.*, 1928, **20,** 769.
42. *Determination of Vanadium in Special Alloy Steels.* Hobart H. Willard and Philena Young, *Ind. Eng. Chem.*, *Analyt.* 1932, **4,** 187.
43. *Indicators for determining Chromium and Vanadium in Alloy Steels.* Hobart H. Willard and Philena Young, *Ind. Eng. Chem.*, *Analyt.* 1933, **5,** 154.
44. *New Procedures for Chromium and Vanadium in Alloy Steels.* Hobart H. Willard and Philena Young, *Ind. Eng. Chem.*, *Analyt.* 1933, **5,** 158.
45. *Direct Determination of Chromium and Vanadium in Steel.* Hobart H. Willard and Philena Young, *Ind. Eng. Chem.*, *Analyt.* 1934, **6,** 48.
46. *Standardization of Potassium Dichromate.* Hobart H. Willard and Philena Young, *Ind. Eng. Chem.*, *Analyt.* 1935, **7,** 57.
47. *The Determination of Trivalent Chromium in Chromic Acid and in Chromium Plating Baths.* Hobart H. Willard and Philena Young, *Trans. Electrochem. Soc.*, 1934, **67,** 347.
48. *The Objectives and Content of the Introductory Course in Quantitative Analysis.* H. H. Willard, *J. Chem. Educ.*, 1928, **5,** 957.
49. *The Determination of Boric Acid in Nickel Plating Baths.* H. H. Willard and G. W. Ashworth, *Monthly Rev. Amer. Electroplaters' Soc.*, 1929, **16,** 7.
50. *The Determination of Sulfate in Chromic Acid and in Chromium Plating Baths.* H. H. Willard and Richard Schneidewind, *Trans. Amer. Electrochem. Soc.*, 1929, **56,** 333.
51. *Modern Trends in Analytical Chemistry.* H. H. Willard, *Ind. Eng. Chem.*, *Analyt.*, 1930, **2,** 201.
52. *A Simple Reference Electrode for Potentiometric Titrations.* H. H. Willard and A. W. Boldyreff, *J. Amer. Chem. Soc.*, 1929, **51,** 471.
53. *Determination of Mercury as Metal by Reduction with Hydrazine or Stannous Chloride.* H. H. Willard and A. W. Boldyreff, *J. Amer. Chem. Soc.*, 1930, **52,** 569.
54. *The Determination of Calcium by Ignition of Calcium Oxalate to Carbonate in Air.* H. H. Willard and A. W. Boldyreff, *J. Amer. Chem. Soc.*, 1930, **52,** 1888.
55. *Preparation and Properties of Lead Perchlorate.* H. H. Willard and J. L. Kassner, *J. Amer. Chem. Soc.*, 1930, **52,** 2391.
56. *Solubility of Lead Sulfate, Chromate and Molybdate in Nitric and in Perchloric Acid.* H. H. Willard and J. L. Kassner, *J. Amer. Chem. Soc.*, 1930, **52,** 2402.

57. *Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid.* Hobart H. Willard and R. C. Gibson, *Ind. Eng. Chem., Analyt.*, 1931, **3,** 88.
58. *Quantitative Separations by the Thermal Decomposition of Anhydrous Mixtures of Metal Sulfates.* H. H. Willard and R. D. Fowler, *J. Amer. Chem. Soc.*, 1932, **54,** 496.
59. *The Electrolytic Oxidation of Iodine and of Iodic Acid.* Hobart H. Willard and Robert R. Ralston, *Trans. Electrochem. Soc.*, 1932, **62,** 239.
60. *Determination of Perchlorate.* H. H. Willard and J. J. Thompson, *Ind. Eng. Chem., Analyt.* 1930, **2,** 272.
61. *The Micro Determination of Halogens and Metals in Organic Compounds,* H. H. Willard and J. J. Thompson, *J. Amer. Chem. Soc.*, 1930, **52,** 1893.
62. *Volumetric and Gravimetric Determination of Mercury as Periodate.* Hobart H. Willard and J. J. Thompson, *Ind. Eng. Chem., Analyt.*, 1931, **3,** 398.
63. *Volumetric Determination of Manganese after Oxidation by Periodate.* Hobart H. Willard and J. J. Thompson, *Ind. Eng. Chem., Analyt.*, 1931, **3,** 399.
64. *Quantitative Determination of Lead as Periodate.* Hobart H. Willard and J. J. Thompson, *Ind. Eng. Chem., Analyt.*, 1934, **6,** 425.
65. *Qualitative Tests for Periodate and Iodate in the Presence of Each Other.* Hobart H. Willard and J. J. Thompson, *J. Amer. Chem. Soc.*, 1934, **56,** 1827.
66. *Periodates of Lead.* Hobart H. Willard and J. J. Thompson, *J. Amer. Chem. Soc.*, 1934, **56,** 1828.
67. *Volumetric Method for Determination of Fluorine.* H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Analyt.*, 1933, **5,** 7.
68. *The Preparation of Potassium Molybdo- and Molybdicyanides.* Hobart H. Willard and R. C. Thielke, *J. Amer. Chem. Soc.*, 1935, **57,** 2609.
69. *A Thermionic Titrimeter without Batteries.* Hobart H. Willard and O. B. Hager, *Ind. Eng. Chem., Analyt.*, 1936, **8,** 144.
70. *Separation of Strontium, Barium and Lead from Calcium and Other Metals by Precipitation as Nitrates.* Hobart H. Willard and Edwin W. Goodspead, *Ind. Eng. Chem., Analyt.*, 1936, **8,** 414.
71. *A Study of the Precipitation of Aluminum Basic Sulfate by Urea.* Hobart H. Willard and Ning Kang Tang, *J. Amer. Chem. Soc.*, 1937, **59,** 1190.
72. *Quantitative Determination of Aluminum by Precipitation with Urea.* Hobart H. Willard and Ning Kang Tang, *Ind. Eng. Chem., Analyt.*, 1937, **9,** 357.
73. *The Separation of Gallium and its Colorimetric Determination by Means of Quinalizarin.* H. H. Willard and H. C. Fogg, *J. Amer. Chem. Soc.*, 1937, **59,** 40.
74. *The Precipitation of Basic Gallium Sulfate by Means of Urea. I. A Study of the Precipitate Produced.* Hobart H. Willard and H. C. Fogg, *J. Amer. Chem. Soc.*, 1937, **59,** 1197.
75. *The Precipitation of Basic Gallium Sulfate by Means of Urea. II. The Separation and Determination of Gallium.* Hobart H. Willard and H. C. Fogg, *J. Amer. Chem. Soc.*, 1937, **59,** 2422.
76. *Determination of Iron in Biological Materials. The Use of o-Phenanthroline.* Frances Cope Hummel and H. H. Willard, *Ind. Eng. Chem., Analyt.*, 1938, **10,** 13.
77. *The Volumetric Oxidation of Iodide and Bromide by Periodic Acid.* Hobart H. Willard and Lucien H. Greathouse, *J. Amer. Chem. Soc.*, 1938, **60,** 2869.

78. *The Periodates of Sodium, Potassium and Barium.* H. H. Willard, *Inorganic Syntheses*, Vol. I, McGraw-Hill Book Company, New York, 1939, p. 168.
79. *Periodic Acids.* H. H. Willard, *Inorganic Syntheses*, Vol. I, McGraw-Hill Book Company, New York, 1939, p. 172.
80. *Bromopentamminocobalti Bromide.* Harvey Diehl, Helen Clark and H. H. Willard, *Inorganic Syntheses*, Vol. I, McGraw-Hill Book Company, New York, 1939, p. 186.
81. *Tetraphenylarsonium Chloride as an Analytical Reagent. Titration by Iodine.* Hobart H. Willard and George M. Smith, *Ind. Eng. Chem., Analyt.*, 1939, **11,** 186.
82. *Tetraphenylarsonium Chloride as an Analytical Reagent. Determination of Mercury, Tin, Cadmium and Zinc.* Hobart H. Willard and George M. Smith, *Ind. Eng. Chem., Analyt.*, 1939, **11,** 269.
83. *Tetraphenylarsonium Chloride as an Analytical Reagent. Determination of Rhenium.* Hobart H. Willard and George M. Smith, *Ind. Eng. Chem., Analyt.*, 1939, **11,** 305.
84. *Arsonium Compounds. II.* F. F. Blicke, Hobart H. Willard and J. T. Taras, *J. Amer. Chem. Soc.*, 1939, **61,** 88.
85. *Thermoelectric Absorptiometer for Analytical Work.* Hobart H. Willard and Gilbert H. Ayres, *Ind. Eng. Chem., Analyt.*, 1940, **12,** 287.
86. *Symposium on Preparation for the Study of Medicine. II. Chemistry.* Hobart H. Willard, *J. Assoc. Amer. Medical Colleges*, 1941, **15,** 73.
87. *Tetravalent Cerium and Its Use in Volumetric Analysis.* G. Frederick Smith and H. H. Willard, *Amer. Soc. Testing Materials Bulletin*, 1941, **108,** 15.
88. *Colorimetric Determination of Phosphorus in Iron Ore.* Hobart H. Willard and E. John Center, *Ind. Eng. Chem., Analyt.*, 1941, **13,** 81.
89. *Colorimetric Determination of Phosphorus in Iron Ore.* John Center and Hobart H. Willard, *Ind. Eng. Chem., Analyt.*, 1942, **14,** 287.
90. *Determination and Separation of Potassium as Periodate.* Hobart H. Willard and Albert J. Boyle, *Ind. Eng. Chem., Analyt.*, 1941, **13,** 137.
91. *Ozone as an Analytical Reagent. Determination of Vanadium, Cerium and Manganese.* Hobart H. Willard and Lynne L. Merritt, Jr., *Ind. Eng. Chem., Analyt.*, 1942, **14,** 486.
92. *Direct Determination of Potassium in Silicate Rock.* Hobart H. Willard, L. M. Liggett and Harvey Diehl, *Ind. Eng. Chem., Analyt.*, 1942, **14,** 234.
93. *The Preparation and Properties of Potassium Oxalatostannate.* Hobart H. Willard and Taft Y. Toribara, *J. Amer. Chem. Soc.*, 1942, **64,** 1759.
94. *A Study of Complex Dioxalatothiometastannates.* Hobart H. Willard and Taft Y. Toribara, *J. Amer. Chem. Soc.*, 1942, **64,** 1762,.
95. *A Volumetric Method for Determining Tin.* Hobart H. Willard and Taft Y. Toribara, *Ind. Eng. Chem., Analyt.*, 1942, **14,** 716.
96. *Volumetric Determination of Bromide in Brines.* Hobart H. Willard and Arno H. A. Heyn, *Ind. Eng. Chem., Analyt.*, 1943, **15,** 321.
97. *The Preparation and Properties of Potassium Thiogermanate and Thiogermanic Acid.* Hobart H. Willard and C. W. Zuehlke, *J. Amer. Chem. Soc.*, 1943, **65,** 1887.
98. *Gravimetric and Volumetric Determination of Germanium.* Hobart H. Willard and C. W. Zuehlke, *Ind. Eng. Chem., Analyt.*, 1944, **16,** 322.

121. *Dimethylglyoxime for the Determination of Nickel in Large Amount.* E. L. Bickerdike and Hobart H. Willard, *Analyt. Chem.*, 1952, **24,** 1026.
122. *Chloric Acid Method for the Determination of Protein Bound Iodine* Bennie Zak, Hobart H. Willard, Gordon B. Meyers and A. J. Boyle, *Analyt. Chem.*, 1952, **24,** 1345.
123. *Precipitation of Basic Stannic Sulfate from Homogeneous Solution.* Hobart H. Willard and Louis Gordon, *Analyt. Chem.*, 1953, **25,** 170.
124. *Tetraphenylphosphonium and Tetraphenylstibonium Chlorides as Analytical Reagents.* Hobart H. Willard and L. R. Perkins, *Analyt. Chem.*, 1953, **25,** 1634
125. *Separation of Cerium from the Rare Earths by Precipitation as Iodate from Homogeneous Solution.* Hobart H. Willard and Silvia T'sai Yu, *Analyt. Chem.*, 1953, **25,** 1754.
126. *Colorimetric Determination of Vanadium (V) and its Separation from Copper; Use of Cupferron.* Hobart H. Willard, Ernest L. Martin and Robert Feltham, *Analyt. Chem.*, 1953, **25,** 1863.
127. *Analytical Chemistry of Fluorine and Fluorine Containing Compounds.* P. J. Elving, Charles A. Horton and Hobart H. Willard. *Fluorine Chemistry*, Academic Press, New York 1954 p. 51–21.
128. *An Experiment in Flame Photometry.* H. H. Willard, K. A. Van Lente and R. E. Van Atta, *J. Chem. Educ.* 1957, **34,** 192–3.
129. *Volumetric Determination of Thorium in Uranium Alloys.* Hobart H. Willard, Arthur W. Mosen and Ross D. Gardner, *Analyt. Chem.*, 1958, 1614–6.
130. *Precise Coulometric Titrations Based on Silver Coulometer Measurements.* K. A. Van Lente, R. E. Van Atta and H. H. Willard, *J. Chem. Educ.*, 1959, **36,** 576–8.

BOOKS

Hobart H. Willard and N. Howell Furman, *Elementary Quantitative Analysis.* D. Van Nostrand, Inc. Princeton, N.J. First to Third Editions. 1933, 1935, 1940.

Hobart H. Willard, N. Howell Furman and Clark E. Bricker, *Elements of Quantitative Analysis.* 4th Edition 1956.

Hobart H. Willard, N. Howell Furman and John F. Flagg, *A Short Course in Quantitative Analysis.* D. Van Nostrand Co. Inc. Princeton, N.J. 1943.

Hobart H. Willard, N. Howell Furman and Egbert K. Bacon, *A Short Course in Quantitative Analysis.* Second Edition, 1957.

Hobart H. Willard and Harvey Diehl, *Advanced Quantitative Analysis.* D. Van Nostrand Co. Inc. Princeton, N.J. 1943.

Hobart H. Willard, Lynne L. Merritt and John A. Dean *Instrumental Methods of Analysis.* D. Van Nostrand Co., Inc. Princeton, N.J. First Edition 1941, Second Edition 1951, Third Edition 1958.

Louis Gordon, Murrell L. Salutsky and Hobart H. Willard, *Precipitation from Homogeneous Solution.* John Wiley and Sons, Inc. 1959.

WILLARD ISSUE 1961 VOLUME 7 NUMBERS 3/4

CONTENTS

PERGAMON PRESS LTD.

4 & 5 FITZROY SQUARE, LONDON W.1 122 EAST 55TH STREET, NEW YORK 22, N.Y.

Printed in Northern Ireland at The Universities Press, Belfast.