An International Journal of Analytical Chemistry

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PERGAMON PRESS
LONDON NEW YORK PARIS LOS ANGELES

VOLUME 6 1960

ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

Proceedings of the Third Conference, Gatlinburg, Tennessee
October 26–29, 1959

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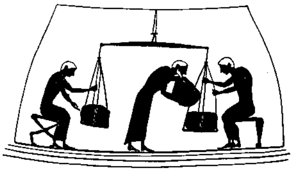

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Published monthly - 3 Volumes per year, each of 4 issues

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An International Journal of Analytical Chemistry

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ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

Analysis of Reactor Fuels, Fission-Product Mixtures and Related Materials: Analytical Chemistry of Plutonium and the Transplutonic Elements

Third Conference
Gatlinburg, Tennessee
October 26–29, 1959

Sponsored by:
Oak Ridge National Laboratory
Oak Ridge, Tennessee
Operated by
Union Carbide Nuclear Company,
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for the
U.S. Atomic Energy Commission

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Talanta, 1960, Vol. 6, pp. i to ii. Pergamon Press Ltd. Printed in Northern Ireland

PREFACE

PROGRESS in nuclear reactor technology is intimately related to and contingent on advancements in other disciplines, of which analytical chemistry is by no means the least in importance. In many widely scattered centers of nuclear energy development, new methods, instruments and facilities are continually being devised while established methods and facilities are likewise being improved and adapted to a wide variety of intriguing problems in the analysis of nuclear reactor components, fuels and fission products. As a contribution toward the coordination of these efforts and the dissemination of this information, a series of conferences on analytical chemistry in nuclear reactor technology was initiated in 1957 by the Oak Ridge National Laboratory.

The Third Conference of this series was held at Gatlinburg, Tennessee, on 26–29 October 1959. At this conference forty-one papers were presented on methods, equipment and facilities for carrying out the analytical work which is, or may be, required following the operation of nuclear reactors. Some indication of the scope of the conference is reflected by the subject-titles of the different sessions: *Analytical Chemistry of Fuels; Analytical Chemistry of Plutonium and the Transplutonic Elements; The Analysis of Fission-product Mixtures*, and also one *General* session on related subjects.

In these Proceedings, a compilation is given of the papers which were presented at this Conference, excepting, in a few cases, those papers which are readily available in publications of the U.S. Atomic Energy Commission or have been submitted for publication elsewhere in the open literature. In lieu of reprinting this latter class of papers, a reference to and abstract of each paper is given at the end of each section.

Drafts of the papers in the Proceedings were revised, when required, in the interest of uniformity of presentation or to convert a paper which had been prepared for oral presentation to a form more suitable for publication; consequently, the Editors must assume all responsibility for errors or omissions which have been occasioned by such review.

The success of an effort of the magnitude of this Conference is, most certainly, dependent on the contributions of many persons. First among those who merit our sincere thanks and appreciation are the writers and speakers, and those who served as presiding chairmen over the different sessions. The Editor is also deeply indebted to the members of the program committee: J. H. Cooper, G. W. Leddicotte, J. A. Norris, R. W. Stelzner and J. P. Young, who laid the groundwork for and directed the conference, and also to Dr. M. G. Mellon of Purdue University for his stimulating and factual after-dinner talk, "Analyses and Analysts."

We are also most grateful to D. D. Cowen and his staff for their efficient services in handling the many details of the conference, and to many others, especially H. P. House and Miss M. A. Marler, for their competent assistance in the preparation of the papers for publication in the Proceedings and for numerous other contributions in the conduct of the Conference.

Whereas the proceedings of the two prior conferences of this series were published by the U.S. Atomic Energy Commission, the Proceedings of this Conference is presented in a special collected issue of *Talanta* through the helpful and understanding cooperation of the staff of Pergamon Press. This departure from prior practice was motivated largely in the knowledge that, because of the extensive experience and contacts of the Pergamon Press in the field of technical and scientific literature, wider dissemination of this useful information could be achieved through the utilization of this service. We are most sincerely grateful to the publishers and staff of *Talanta* for this generous contribution and for their many courtesies in making this compilation possible.

C. D. SUSANO

Talanta, 1960, Vol. 6, pp. iii to xi. Pergamon Press Ltd. Printed in Northern Ireland

THE ROLE OF THE ANALYTICAL CHEMIST IN NUCLEAR REACTOR TECHNOLOGY

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THE developments which have occurred in nuclear physics during the past 20 years have brought about significant and revolutionary changes in the domain of the analytical chemist; in that, whereas prior to the year 1943, he was concerned primarily with the analysis of non-radioactive materials and only rarely with radioactivity, the emphasis has changed to the extent that he has now become a part of a broad over-lapping discipline in which the utilization of nuclear reactions and the concomitant production of radiation and radioactive materials have become matters of the greatest importance and of real concern. In the development of this nuclear technology, many dilemmas have been encountered in that methods and procedures had to be, and are still being, developed for the production in relatively large quantities of materials which previously had been matters of obscure scientific interest. These developments, particularly in the chemical and metallurgical processing of uncommon metals and also in the fields of ceramics, electronics, and chemical engineering, are now being exploited most extensively to secure better materials for the construction, and the hoped for efficient and competitive operation, of nuclear reactors.

If the prediction of the future utilization of nuclear reactors in the production of electricity and of other forms of energy is, in fact, to be attained, two problems of real import face the analytical chemist: (1) the development of new and better methods of analysis, specifically for those materials which are and which will undoubtedly be developed and utilized in the construction and operation of reactors; and (2) the development of methods, techniques, and instruments for the automatic and remote control of processes and of reactors involving the handling of highly radioactive materials as matters of operations control, safety, by-product utilization and waste disposal.

In this new technology, the analytical chemist is perhaps a bit more fortunate than was his lot in the ferrous metals, and in many other industries, in that his role has been a continuing one since the early days of the nuclear weapons program wherein he has been given the opportunity to make his contributions simultaneously with those of the scientists and engineers engaged in the many revolutionary facets of the technology. With this very close association, the analytical chemist has given invaluable assistance to those engineers, chemists and physicists who have been charged with the responsibilities of processing and refining nuclear and other materials, including the fabrication and utilization of these materials into parts and components

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* General Chairman, Conferences on Analytical Chemistry in Nuclear Reactor Technology, held annually at Gatlinburg, Tennessee.

† Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

of reactors. In this connection, it is worth noting that the analytical chemist has already made many real and significant contributions in the development of process methods for the separation of hafnium and zirconium; in the separation, purification and utilization of rare-earth elements; in the winning of uranium from extremely low-grade raw materials and the large-scale separation of this element and the U^{235} isotope from unwanted, deleterious process materials; in the creation of plutonium and the subsequent development of methods for its processing and refinement; and in many other equally important scientific and technological achievements. In citing these few examples, one is particularly impressed because some of these accomplishments, such as the separation and purification of rare-earth elements, represent the solution of problems which had previously been investigated more or less fruitlessly for more than a century by some of the most able chemists of their time. This is not to imply that the analytical chemist was in the main responsible for these accomplishments, but it cannot be denied that his contribution has been indeed most significant.

Even though remarkable advancements have been made in the accumulation of knowledge and of a better understanding of nuclear concepts, much still remains to be done in the utilization of materials in a manner that the full practical significance of these concepts can be understood and utilized for the eventual conversion of nuclear energy to a whole host of beneficial purposes.

In the further growth of an effective nuclear technology, it is important to note that the analytical chemist will be required to develop methods, procedures, and techniques for use in many lines of endeavor, some of which may appear to be completely unrelated to nuclear technology. In this regard, the analytical chemist working in the ferrous and non-ferrous metals industries will be called upon to provide better methods for the continued development of newer metals and alloys which will be useful in the design, construction and operation of reactors and appurtenances. Analytical chemists in other disciplines, such as biology, public health, ecology, food sterilization, agronomy, agriculture, oceanography and many more, will likewise be similarly involved in the development of improved methods of analysis with manifold beneficial effects on all aspects of human endeavor.

The present state of our knowledge of nuclear reactor technology is such that a considerable portion of the total effort in the field of nuclear energy is being directed toward the development of nuclear reactors which ultimately will produce thermal and electric power at economically acceptable prices. With the advent of second and third generation reactors and the launching of the NS Savannah, it is still quite obvious that considerable work needs to be done in the production, fabrication and evaluation of reactor components, and also of a wide variety of appurtenances and of auxiliary units, such as metals of construction, fuels, coolants, moderators, reflectors, shielding materials, control mechanisms, piping materials, pumping devices, pressure vessels, safety devices, instruments, filters, waste-disposal systems and by-product recovery installations. Such properties as corrosion and erosion resistance, neutron absorption characteristics, and the effects of temperature, pressure and radiation on the physical properties of various components will require considerable experimentation and testing in prototypes and in smaller test units extending over a period of perhaps many years. In this work, the analytical chemist will be concerned with the analysis of liquids, solids, and gases which will have been subjected to wide varieties of exposure or produced under a multiplicity of conditions and which will vary considerably in the concentrations of many component substances. For example, in the case of coolant materials, he will be called upon to make analyses of lithium, sodium, potassium, or combinations thereof, for purity, extent of contamination, and to assist in the evaluation of certain corrosion tendencies in heat transfer systems and of the degrees of reactivity of these substances with other materials.

Much of the experimental testing of materials prior to the actual construction of prototypes and test models will be conducted under conditions simulating actual plant operation and, consequently, in these early stages, such experimentation involves the analysis of non-radioactive materials. As one proceeds, however, from the conceptual and experimental stages to the development of critical test reactors, and finally to actual operational reactors of increasingly greater capacity with exceptionally high neutron fluxes and concomitantly greater degrees of radioactivity, one soon reaches the other extreme where all reactor components will most surely be contaminated with hazardous radioactive materials which will require the application of methods of analysis under totally different conditions and with a maximum of consideration for the safety of the analyst and others.

In order to make a presentation such as this, it would be helpful if one could isolate as a first approximation those elements (or isotopes) from the periodic table which would appear to be of prime significance in nuclear reactor technology, but if one attempts to make any such simplifying assumption, he is immediately confronted with the incontrovertible fact that this is not a limited technology of a few elements or of simple mixtures of compounds, but is rather a highly complex technology in which he must be ready to evaluate the inter-relationships of all the elements in the periodic table, including thousands of isotopes. It may be possible at some later date, as knowledge is acquired of the relative merits of certain materials, to eliminate some of these from further consideration, but in the present state of the art any such simplification does not now appear, to put it mildly, to be either possible or warranted.

An awareness of the role of the analytical chemist in nuclear reactor technology is immediately obvious from the veritable flood of papers which have appeared on this subject in the technical literature over the past few years and nonetheless equally obvious is this substantiated further by the number of meetings, conferences and symposia which are being held in ever-increasing numbers. The significance of the application and utilization of remote manipulative techniques in this technology can be readily appreciated from the fact that the eighth in a series of Hot Laboratories and Equipment Conferences[1] is now in the planning stage. Even though not engendered specifically for the benefit of analytical chemists, much of the work that is being done in this field of specialized laboratory and equipment design and operation is of vital importance in the analytical chemistry of highly activated materials.

With regard to the many aspects of the analytical chemistry of radioactive materials alone, it is significant to note that Meinke[2] in a review of recent developments in the analytical chemistry of nucleonics cites no less than 1279 references of papers and reports which appeared in the world-wide scientific and technical literature during the two-year period between late 1955 and late 1957. This review is most extensive and will serve the analyst well in delineating the scope and multiplicity of his interests and responsibilities in the analysis of radioactive materials.

In a recent paper on the role of the analytical chemist in nuclear technology, Kelley[3] spells out the dual functions of the analyst in this field in that one of these is the identification and measurement of radioactive species and the other is the analysis of highly radioactive materials. He also points out the necessity for the development of remote-control instrumentation to effect the safe handling and analysis of substances with ever-increasing degrees of activity which are and will be encountered in the future development and utilization of nuclear reactors.

The historical account, by Rodden,[4] of the role of the analytical chemist in the preparation of high-purity nuclear materials is a magnificent revelation of the importance of trace analysis in the development of suitable materials, particularly uranium, graphite and beryllium, which ultimately led to the production of "workable" atomic weapons during the war. As indicated by Rodden, this work is by no means complete; even though great progress has been made, to attain greater neutron economy, further improvements in methods will be required, specifically greater sensitivity, precision and accuracy at lower concentrations of all elements and, in a large number of cases, of certain isotopes which possess useful nuclear properties. In this respect, the methods for the analysis of uranium; graphite; beryllium, particularly the highly refractory oxide; and others, which have been examined most extensively, must be continued with even greater emphasis on the precise evaluation of minor components in the microgram and extending into the nanogram (10^{-9}) range.

In order to promote greater interchange of information on this subject, the Oak Ridge National Laboratory, in 1957, inaugurated a series of conferences on Analytical Chemistry in Nuclear Reactor Technology in which it was intended that information would be presented which bears directly on some of the scientific, technical and practical aspects of analytical chemistry as they apply specifically to the technology of nuclear reactors. The first conference[5] was devoted to a review of recent developments in the analytical chemistry of certain of the more important reactor materials, specifically uranium, thorium, the rare-earth elements, zirconium, titanium, beryllium, graphite and heavy water, including a brief review of some of the recent applications of the methods of X-ray analysis, emission and mass spectroscopy, solvent extraction, and ion-exchange separations. In addition to providing a summary of recent developments in the analytical chemistry of each of the foregoing subjects, the discussions at that conference pointed out the serious need that now exists for the development and establishment of adequate standard samples and precise methods.[6] This lack of standard authority has been and will continue to be a serious problem until standards of suitable quality become available. The development, design, construction and operation of nuclear reactors will depend in a large measure on the establishment of specification requirements which, most certainly, will be replete with exceedingly strict limitations with regard to the presence of certain substances, particularly those which seriously hamper the operation of reactors from the standpoint of neutron economy or wastage and also with respect to metals possessing high resistivity to corrosion or erosion and with high degrees of structural integrity. This matter of standards development has been investigated for a number of years by the Atomic Energy Commission and its precursor, the Manhattan Engineering District, in cooperation with the Atomic Energy Research Establishment of the United Kingdom, but, even though real progress has been made in the development of some standardization, the job is by no means complete. The recent utilization of newer industrial metals and alloys such as those of zirconium, hafnium, titanium, niobium, yttrium, molybdenum, the alkali metals, rare-earth elements, such as dysprosium and gadolinium, boron, and special ferrous and non-ferrous alloys gives impetus to the urgency of this problem of securing better standard materials and the development of procedures of unquestioned precision and accuracy for evaluating sample purity and composition, coupled with high speed performance and automation.

Not only is the development of standard samples and procedures essential in the usual sense as applied to analytical chemistry, but even more profoundly is this need apparent in the application of the instrumental techniques such as emission and mass spectroscopy, absorption spectrophotometry, throughout the entire useful part of the electromagnetic spectrum, coulometry, flame photometry, radiochemistry, nuclear magnetic resonance, X-ray absorptiometry, fluorimetry, diffraction methods, gas chromatography, nuclear methods of analysis, polarography, and many other electrical methods based on the concept of electron transfer which can be utilized as a measure of the quality of certain materials.

During the fall of 1958, the Second Conference in the series on Analytical Chemistry in Nuclear Reactor Technology[7] was again held at Gatlinburg, Tennessee, at which time analytical chemists from Great Britain, Canada and the United States really got down to the business of discussing some of the more important aspects of this work. Whereas the first meeting dealt specifically in generalities on the more recent developments, the emphasis at the second meeting was directed more toward the applications of analytical chemistry in prototype testing, particularly as it applied to the utilization of certain materials in various types of nuclear reactors. Perhaps one of the outstanding features of this Second Conference was the amount of discussion and interest which was shown in the matter of particle-size evaluation. At first glance, it would appear rather strange that a subject of this nature would be given any consideration in discussions on analytical chemistry. It is quite obvious in reading the papers on this subject, however, that the variety of analytical techniques used in this work does indeed make it a proper subject of analytical chemistry. The matter of particle-size analysis is very important in the operation of the thermal breeder reactor where successful operation depends in a large measure on the thorough knowledge of the flow, settling and nuclear characteristics of slurries and other heterogeneous mixtures which contain fertile and fissionable materials. The analytical techniques involved in these analyses are, in a large number of cases, essentially the same as those that are used in the analysis of solutions but are complicated by the one requirement that the estimation of certain constituents need be made on fractional portions of samples rather than on the basis of the total sample. By and large, these analyses are made by first separating the solids into groups of differing particle size by the application of settling techniques, based primarily on Stoke's law. All the known methods of particle-size evaluation were discussed at this meeting, in addition to which some of the newer techniques, such as flying-spot microscopy, and electronic sizing were also discussed. The intense interest shown in these sessions does indeed reveal that much needs to be done in the development of methods for the analysis of subsieve particulate matter.

In the Second Conference, many of the papers continued the discussions of the first session on the utilization of analytical techniques, particularly on X-ray and emission spectroscopy, nuclear methods of analysis, flame photometry, and instrumentation, but in which the preponderance of interest had to do more with unusual mixtures, such as newly developed alloys, fuel materials, boron and specialized preparations.

The Third Conference,[8] which was held in October 1959, was devoted primarily to the consideration of the analysis of materials and components after having been subjected to different degrees of exposure to neutron activation in operating reactors. The principal point of interest in the analytical chemistry of such materials is the high degree of activity which is encountered and the necessity for carrying out this function in a manner completely foreign to the usual methods of analysis. Much of this work must, of necessity, be carried out in separate installations designed primarily for the remote handling of materials having a high degree of radioactivity. Some of the specially designed laboratories and the details of handling and analyzing extremely "hot" materials in those installations were considered in several of the papers.

In the operation of nuclear reactors, the analytical chemist is called upon to make analyses of mixtures containing a large number of fission products and to continue this assistance through the processing and reprocessing cycles which are intended to separate certain valuable radioisotopes, fertile materials, unburned fuel, plutonium, transplutonic elements and waste products. The successful utilization of by-products and the production of high-purity materials of useful import that will be derived from such reactor operations will constantly rest on the ability of the analytical chemist to develop better methods of control. Typical case histories of some of those more important problems which have been encountered by the analytical chemist were presented in some detail. As was the case at the first meeting, the matter of standardization was again taken up by Dr. Rodden, at which time he also indicated the progress that is being made in this particular field and how different installations are meeting this problem. In order to keep up to date, virtually all of one session was devoted to some of the more recent developments in analytical methodology, even though much of this subject matter did not necessarily follow the main theme of this particular meeting.

At this point, it is interesting to note that, with the advent of nuclear technology, the analytical chemist has again been quick to adapt those instruments and methods of other fields of science, particularly physics, to his repertoire for use in the evaluation of the composition of matter in any form. Even though one ordinarily associates a chemist with the study of chemical reactions, it has always been the attitude of the analytical chemist that if a device or technique can be of any service in establishing the composition of a given sample, the innovation should be used regardless of its source or origin.

In this regard, it is becoming increasingly apparent that mass spectrometry, nuclear magnetic resonance and counting techniques, insofar as they are useful in the evaluation of compositions of matter, to mention only a few of the more recently developed and widely applied methods, are part and parcel of the analytical chemist's "kit of tools" on which he can draw in carrying out his responsibilities. In fact, future workers in this field must of necessity prepare themselves to meet these added responsibilities if they intend to keep pace with the future trends of this profession. There seems to be little, if any, chance that the physicist will ever consider the desirability of developing a new field of endeavor under the heading of, say, analytical physics. If he does, he will find that one of the basic essentials in the performance of this work is a thorough knowledge of the principles and concepts of chemistry and in the end the field of analysis concerned with the composition of matter would undoubtedly be returned to the chemist. In any case, it is doubtful that the analytical chemist need even be remotely or mildly concerned about this possibility.

In considering the role of analytical chemistry in nuclear reactor technology, the analyst's attention is naturally first drawn to the basic raw materials—the fissionable isotopes of U^{233}, U^{235} and Pu^{239} or, more appropriately, the sources of these isotopes, the naturally occurring mixtures of thorium and uranium isotopes. In view of the limited extent of the known world reserves of conventional fuel materials, of the future potential of nuclear power reactors and of the scarcity of known high-grade uranium ore deposits, particularly of domestic origin, considerable activity in exploratory searches has been going on for a number of years in an effort to find high-grade sources of these materials or to utilize low-grade sources economically. This search has not only been concerned with the usual source of valuable minerals but has been extended to an examination of waste materials and by-products of other industries. Regardless of the source of these potential reserves, the methods of establishing the uranium or thorium content are basically those developed by the analytical chemist, be it by the use of wet-chemical procedures or a variety of instrumental techniques. The extremely wide dispersion of these elements, particularly uranium, in virtually insignificant amounts in all varieties of materials in the earth's crust, has dictated the development of procedures suitable for use on materials of considerable variability and of low uranium or thorium concentration. In this regard, the analytical chemist has been of invaluable assistance in the development of methods for the exploration and evaluation of sources of uranium and thorium-containing materials; such as,

1. The monazite sands of India, Brazil and to a lesser extent the low-grade, domestic and Canadian deposits of thorium-containing materials.
2. The high-grade deposits of uranium in Africa and Canada.
3. Lower-grade deposits of uranium in the mineral deposits of the Colorado plateau and the waste stockpiles of low-grade materials from the mining of vanadium and radium.
4. Low-grade sources of shale, lignite, sea water, natural wells and streams, the tailings of the gold mines of South Africa, and the huge piles of waste materials from the phosphate industry.

In all of these and many others, the analytical chemist has been and will continue to be called on to develop methods and procedures, and to make the analyses necessary for the prospecting, mining, milling, processing, and recovery of the mineral values from the so-called ore bodies and control of these operations to provide a product of suitable quality for utilization in the atomic energy industry. Similarly, this activity must be adaptable to the recovery and exploitation of other valuable by-products. As an example, it may be foreseen, but perhaps not too clearly, how the recovery of uranium from lignite may well provide a margin sufficient for the economical utilization of lignite in supplementing the reserves of fossil fuels essential to the petroleum and petrochemical industries.

In all this analytical work, the important function, of course, is the precise and accurate control of the quality of raw materials and intermediates in a highly complex series of processing steps designed to yield fuel materials in a multiplicity of shapes, forms, concentrations, and configurations. Since, as a condition precedent, the feasibility and efficient operability of nuclear reactors is highly dependent on strict limitations of certain impurities in the fuel, it is obvious that methods and procedures for the analysis of fuel components must be inherently sensitive, accurate and precise throughout all the process cycles and recycles of mining, milling, refining, conversion, isotope separation, fuel fabrication and fuel reprocessing. An enumeration of the methods and procedures of analytical control of the fuel cycle is completely outside the scope of this paper; it is sufficient, however, to note that the literature on this subject is voluminous and significantly good but by no means complete. The compilation of Rodden[9] serves as an excellent starting point on the analytical chemistry of uranium, but with the enforced development of methods and procedures occasioned by the search for domestic fuel sources and the increased emphasis on the peaceful utilization of nuclear energy, a large number of methods and procedures have been developed for application to specific types of materials and process cycles. In order to achieve the highest degrees of precision, accuracy, sensitivity and economy of operations, not only in the analytical chemistry of the fuel cycle but in all aspects of nuclear technology, it is interesting to observe that methods of separation, particularly those based on solvent extraction and the use of ion-exchange resins, have received considerable attention with highly fruitful results. An example of the practical importance of solvent extraction and, incidentally, of the utilization of analytical techniques to process application is best exemplified by the adaptation of the solvent extraction of uranyl nitrate with diethyl ether as an efficient war-time method for the purification of uranium. The first successful refining process for preparing zirconium, free of hafnium, was also similarly accomplished by the adaptation of an analytical method based on the use of hexone and ammonium thiocyanate. In the field of ion-exchange adsorption, the work of W. E. Cohn, F. H. Spedding, G. E. Boyd, K. A. Kraus, Robert Kumin and their associates and many others in the separation and purification of the rare-earth elements was particularly brilliant and opened up a wide field which at present is being explored most successfully for other adaptations both in analytical chemistry and process technology. In this regard, the work of Kraus *et al.*[10], Wish *et al.*[11] and others has been most significant in providing break-throughs to what previously had been considered difficult and in some cases insoluble problems. As a further step in the development of separative processes of the highest integrity, the successful use of procedures based on combinations of solvent extraction[12] and ion-exchange separations[13] has given further impetus to the solution of many difficult problems in analytical chemistry, including most particularly the separation and isolation of the components in radioactive mixtures prior to the application of methods of estimation.

In considering further this matter of the analytical chemistry of the fuel cycle, it is to be noted that one of the foremost problems which confront the nuclear technologist is the continued development of in-line instrumentation and automatic devices to measure, evaluate, control and correct the compositional characteristics of process materials as they flow through the many process streams from the mine, through feed preparation, reactor operation, reprocessing, by-product recovery and waste disposal. In carrying out his responsibilities in this regard, the analytical chemist must work in close harmony with the process engineer, the reactor technologist, the safety engineer, the health physicist, the statistician, and the design engineers, interested in the many facets of construction, process development and instrumentation. Even though many operations in the fuel cycle lend themselves to simple methods of control, based on functional and direct measurements of operational variables, much remains to be done in those operational areas wherein the exact parametric relationships have not as yet been established. Until such time as these relationships are evaluated or reasonably understood, the work must be done on an experimental basis with simultaneous consideration being given to the development of these operational methods of control. It goes without saying that much of this work will prove difficult, particularly as it may apply to the control of heterogeneous combinations of materials flowing at high velocities in peculiarly designed and intricate matrices of piping, and heat-transfer units, at high temperatures and at high pressures, exposed to intense neutron fluxes and high degrees of radioactivity behind enormous shields and barricades which rule out the usual, simple methods of control.

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ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

SECTION I. GENERAL

Talanta, 1960, Vol. 6, pp 3 to 19. Pergamon Press Ltd. Printed in Northern Ireland

STANDARDS IN THE NUCLEAR ENERGY PROGRAM

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Summary—The types of standards used in the nuclear energy field will be considered under the heading of chemical, spectrochemical and isotopic standards. The various fuel materials used as standards, such as uranium, plutonium, thorium and their compounds, are discussed. In addition, standards of certain non-fuel materials of special interest in certain operations, such as zirconium and boron, are considered.

ACCORDING to Webster, a standard is defined as "that which is established by authority, custom or general consent, as a model or example, criterion, test in general." To the analyst, a standard is usually considered as a standard sample and is defined as a homogeneous material, which resembles as closely as possible, in chemical and physical nature, the material with which the analyst expects to deal, and which has been analyzed by a sufficient number of methods and analysts to establish its composition with considerable certainty.

Theoretically, the analyst should be provided with as many standard samples as he has different kinds of material to analyze. Such a program would require thousands of samples and is quite out of the question. For many important groups of materials the National Bureau of Standards issues standard analyzed samples.

In addition to standard analyzed samples, the analyst also uses primary standards. To the analyst, the term "primary standard" generally means an element or compound of very high purity which is usually certified as to composition by an organization such as the National Bureau of Standards. From the above, you will note that results on standard analyzed samples are given in terms of composition.

There is a widely prevalent misconception, even among analysts themselves, as to the accuracy of the results obtained in analytical work, and many confuse precision with accuracy. Accuracy is a measure of the degree of correctness. Precision is a measure of reproducibility of results in the hands of a given operator or operators. The precision of a result does not necessarily guarantee its accuracy. It is a comparatively simple matter to establish the precision that can be expected if a certain method of analysis is applied by an analyst or group or analysts to a given material. On the other hand, it may be extremely difficult to judge the probable accuracy of a result, for all results are matters of opinion rather than fact, and so the true value is never known. This is one of the most unsatisfactory aspects of chemical analysis. When an analyst scans a result, he never can be sure whether the determinator provided for all interfering compounds, hoped that they were absent, or was too ignorant to worry. This brings up the question of the definitions of determinators and analysts which was so ably discussed by Dr. G. E. F. Lundell of the National Bureau of Standards in his famous lecture given in 1933 and entitled "The Chemical Analysis of Things as They Are" (*Ind. Eng. Chem. Anal. Ed.* 1933, *5*, 221).

> "So we have two classes of workers in the analytical field, the determinator and the analyst. The determinators, who by far are the more numerous, may in turn be divided into two general classes: first, the common determinators who follow a method explicitly, without knowledge or concern as to the reactions involved; and the second, the educated determinators who can handle perhaps two variables or who, like determinators of pH, are chiefly interested in group effects and make no effort to go beyond this. The first are laborers. They need not be chemists and they require constant supervision. The second are the white-collar workers who exhibit the usual extremes of workers in this classification. The determinator's salvation lies in the development of truly selective methods of analysis, and his final resting place will be a heaven in which he has a shelf containing ninety-two reagents (this number has changed), one for each element, where No. 13 is the infallible specific for aluminum, No. 26 the sure shot for iron, No. 39 the unfailing relief for yttrium, and so on to uranium. As for the analyst, he is a comparatively rare bird and is often referred to as a disappearing species, like the old family practitioner who does the best he can, guided by theory and experience, of which the most comforting is experience. One of the reasons for the scarcity of analysts is perhaps the nature of the special characteristics, some inherent and some acquired, that he must possess. He must have the inquisitive habit of a detective, for oftentimes the composition of the material under test is absolutely unknown. He must be an expert manufacturer of pure chemicals, for on this ability the success of his gravimetric determinations depends. He must be an efficient dispenser of liquids of which he knows the exact effect. And above all, he must serve a long apprenticeship and keep in constant practice.
>
> As for estimating the accuracy of his work, it can be said that the determinator is usually an optimist in thought and expression, while the analyst is a confirmed pessimist. The determinator reports silicon in glass as 71.61, if not 71.611. The analyst, who knows that he is doing nicely to insure results in the first decimal place, reports 71.6 and thus is honest with himself and deceives no one as to his power."

I think we all are in agreement that standard analyzed samples should be analyzed by analysts and the reported results should not imply an accuracy that is greater than can be obtained by the methods used. How many of you have seen results reported out to the second or third decimal, indicating a precision of 1 part in 8000, when you know the analysis was done with a buret where the reading was 26.15 ml which might just as easily have been 26.17 or 26.13 ml? In certain other reported values, you will also see a precision given which only indicates the precision obtained with the instrument used to make the final reading. Many times this is not stated, however, and the recipient of the data believes they are better than they actually are. In such a case, if the results had been referred to a standard of similar composition carried through all stages of the analysis, one would be on much safer ground as to the accuracy achieved.

The advantage of a standard sample is that it behaves like the unknown material which the chemist intends to analyze; consequently, errors arising from factors such as solubility of precipitates, varying concentrations and so forth will affect both sample and standard alike. If the standard and the unknown sample are analyzed at the same time and under practically identical conditions, and if results are obtained for the standard corresponding to those that are certified, the presumption is strong that the values obtained for the unknown material are equally accurate, whereas wide divergence from the certificate results shows that something is radically wrong.

Let us now consider what is desirable in a standard.

It should be a metal, alloy, compound or ore which is homogeneous and is stable under all normal atmospheric conditions. Since we are dealing with materials which do not always follow this criterion, it is desirable that, if any change does occur—such as the absorption of water—the material can be brought to a certain composition by a standard heat treatment (the usual condition is to heat to constant weight at 105° C).

In the case of the very reactive metals with which one deals in the nuclear energy field, one may be forced to use a chemical treatment, such as the pickling of uranium with nitric acid or the electropolishing of plutonium to remove an oxide coating. This is not ideal, but it may be the best that can be done. In certain other instances, materials of a hygroscopic or oxidizable nature are packaged into bottles in a dry box and sealed. Needless to say, this type of sample is not the most reliable. Human fallibility must also be considered in the preparation of standards. There is always the possibility of mislabeling, of mixing samples or using unclean containers in the handling of the materials. All these must be guarded against. The amount of work that goes into the preparation of a reliable standard does not make this a very promising business venture. In addition, the fact that many users want assurance that a financially disinterested, as well as a technically competent, party is concerned has resulted in the greatest reliance being placed on standards certified by the National Bureau of Standards.

In many respects the nuclear energy field is at a disadvantage since there are not enough nationally certified standards available. This has resulted in many companies setting up their own standards. This works very well in running a plant but may cause some problem when inter-company or international transfers occur. It is highly desirable that certified standards acceptable to all parties concerned be available.

URANIUM

Probably the most wanted standards at the present time are those containing varying amounts of U^{235}. Since the accountability of this material is of prime importance, especially with increasing U^{235} content, it is highly desirable that the same standard materials be used by all as reference materials. As far back as 1948, the Atomic Energy Commission constituted the Fissionable Standards Committee and requested it to frame recommendations and to handle the miscellaneous details incidental to providing all standard fissionable materials needed by the Commission laboratories and contractors. This work was taken over in 1956 by the Committee for Uranium Isotopic Standards, whose scope was broadened in 1958 under the Advisory Committee for Standard Reference Materials and Methods of Measurement.

Under these various committees, the Union Carbide Nuclear Company at Oak Ridge prepared two lots of very high U^{235} concentration (99.82 per cent) and one of very high U^{238} concentration (99.9996 per cent). These materials are the Primary Generative Materials and are now at the National Bureau of Standards where they are to be used only for better characterization of their composition, or to prepare Primary Uranium Isotopic Standards at some future date. These Primary Uranium Isotopic Standards will be used only for isotopic certification of relatively large quantities of material which will then be designated as Secondary Generative Materials to be known as Reference Uranium Isotopic Standards. These Reference Uranium Isotopic Standards will be used in the certification of "Uranium Isotopic Standards." A series of such "Uranium Isotopic Standards" is now being distributed by the National Bureau of Standards. They consist of highly purified U_3O_8 of varying U^{235} content.

Table I lists the various isotopic standards now available for distribution.

In the interest of resolving discrepancies, it would be extremely useful if all parties concerned with the determination of U^{235} used these standards of the N.B.S. as reference materials. Any existing bias could be resolved and all concerned would be referring to the same yardstick and not to their own individual standards.

While the determination of uranium may be done with N.B.S. standard potassium dichromate, 136a, in many instances it is highly desirable to standardize procedures with a uranium-containing material. Certain installations have used uranium metal but the greatest use has been made of a purified U_3O_8. Material of this type was originally distributed to the Manhattan Project contractors during the war, and this sample was renewed by the New Brunswick Laboratory under the designation of No. 15. This material has been transferred to the National Bureau of Standards where it is sold as their No. 950. This material, when ignited to 900° C for 1 hr, contains 99.94 per cent U_3O_8. It was made from UO_3 obtained by thermal decomposition of the nitrate. It is well to point out here that the formation of U_3O_8, or of a material corresponding to this analysis, is very temperature-sensitive. If we consider that heating in a furnace is usually practiced, followed by removing and cooling in a desiccator, then 850–900° C appears to be the temperature range necessary. This applies only at sea level. At lower temperatures, there is an excess of oxygen and somewhat above 900° C there is a deficiency of oxygen. The history of the material appears to have some effect; it is quite difficult to obtain complete conversion to U_3O_8 from a nitrate by thermal decomposition. On the other hand, the peroxide or oxalate converts to essentially 100 per cent U_3O_8 quite readily under the above heat treatment.

TABLE I.—URANIUM ISOTOPIC STANDARDS

Standard No.	Isotopic abundances, %			
	U^{234}	U^{235}	U^{236}	U^{238}
U005	0.0023	0.483	0.0046	99.51
U010	0.0054	0.991	0.0067	98.99
U015	0.009	1.51	0.016	98.47
U020	0.012	2.01	0.016	97.96
U030	0.018	3.01	0.020	96.95
U050	0.028	4.95	0.048	94.98
U100	0.068	10.19	0.038	89.70
U150	0.100	15.30	0.066	84.53
U200	0.125	19.80	0.209	79.86
U350	0.249	34.89	0.170	64.69
U750	0.593	75.12	0.252	24.03
U800	0.660	80.07	0.246	19.02
U850	0.64	84.99	0.37	14.00
U900	0.77	90.10	0.33	8.80
U930	1.08	93.27	0.205	5.44

It is well to point out at this time that the atomic weight of uranium must be questioned. The group at Oak Ridge propose that this be changed to 238.037 for normal uranium instead of 238.07. This question will no doubt be considered at the next international meeting of the Committee on Atomic Weights. It may be inadvisable to change at this time since the question of using C^{12} in place of oxygen as the basis for atomic weights is also under consideration.

As shown in Table II, the New Brunswick Laboratory has a group of naturally occurring minerals which were prepared for use in the chemical analysis of uranium-bearing materials. They have been distributed mainly to plants and private analytical laboratories, but some use of these has been made by prospectors. Sample No. 3A was prepared by ball-milling pitchblende ore with dunite. Admittedly, the way that sample 3A was prepared is not the best way to prepare a standard. For use in chemical analysis where a 5-g sample is usually taken, it has proven satisfactory.

TABLE II.—NATURALLY OCCURRING MINERALS FOR USE IN THE ANALYSIS OF URANIUM-BEARING MATERIALS

Sample No	Material	U_3O_8 content, %
1	Phosphate rock	0.029
3A	Pitchblende mixture*	4.3
6	Pitchblende ore	53.5
4	Carnotite	0.18
5	Carnotite	0.11

* Sample No. 3A was prepared by ball-milling pitchblende ore with dunite.

A series of samples, as shown in Table III, was prepared by the New Brunswick Laboratory for use in calibrating counting apparatus to be used in prospecting work. All samples were analyzed after mixing.

TABLE III.—STANDARDS FOR USE IN THE CALIBRATION OF COUNTING APPARATUS USED IN PROSPECTING

NBL No.	Material	U content, %
73	Pitchblende*	1
74	Pitchblende*	0.1
75	Pitchblende*	0.05
76	Pitchblende*	0.01

* Pitchblende diluted with dunite.

For the analysis of impurities in uranium, a sample of uranium metal chips has been prepared by the New Brunswick Laboratory. This is shown in Table IV.

Other materials available from the same source are UF_4 (Tables V and Va) and UO_3 (Table VI).

For the spectrographic analysis of impurities in uranium and its compounds, two series of samples were prepared by the New Brunswick Laboratory. One of these, for impurities in U_3O_8, is given in Table VII.

The U_3O_8 samples 65-1 to 65-5 are synthetic materials prepared from a low-level-impurity U_3O_8 by adding to it solutions of the impurity elements in volumes just sufficient to wet the oxide. Sample No. 65-5 is the matrix material to which the impurities were added. After drying, the material was ball-milled in a plastic container and then ignited at 900° C. The above samples are suitable for the preparation of spectrochemical working curves for the analysis of uranium and its compounds after conversion to U_3O_8 at 900° C. All concentrations listed are the values obtained by chemical analysis, with the exception of cadmium in 65-2 to 65-5, which values are the concentrations added to the U_3O_8.

TABLE IV.—ANALYZED SAMPLE NO. 16. URANIUM METAL

Element	Values, *p.p.m.*
Aluminum	10
Boron	0.23
Carbon	410
Copper	2
Iron	45
Lead	1
Magnesium	2
Manganese	6
Nickel	45
Nitrogen	40
Potassium	<1
Silicon	50
Silver	<0.1
Sodium	2
Thorium	0.3

Note: $<$ = less than.

TABLE V.—ANALYZED SAMPLE NO. 17-A. UF_4. CHEMICAL VALUES ON UF_4 BASIS

Total Uranium	75.8 %
U^{4+}	74.2 %
UO_2 (ammonium oxalate insoluble)	0.31 %
UO_2F_2	2.0 %
UF_4	97.6 %
Fe	20 p.p.m.
Ni	16 p.p.m.
Cr	3 p.p.m.

TABLE Va.—ANALYZED SAMPLE No. 17-A. UF_4. SPECTROGRAPHIC ON URANIUM BASIS (p.p.m.)

Ag	a 0.2	Cu	4	P	<10.0
Al	<8	Fe	26 d	Pb	<1
B	0.2	Mg	25	Si	<20
Ca	<2	Mn	<4	V	<20
Cd	<0.2	Mo	<4	Sn	<1
Co	<2	Na	2	Zn	<20
Cr	<4	Ni	<20		

Note: a = about
d = densitometer.

Since the rare earths are analyzed on a concentrate, a series was prepared for this purpose, to be used with a certain spectrographic procedure. This series is shown in Table VIII.

Several companies use uranium metal as a main standard. From our experience, this is quite satisfactory providing a pure uranium is available. The New Brunswick Laboratory has used "Dingot" metal from the Mallinckrodt Chemical Works for

TABLE VI.—ANALYZED SAMPLE No. 18. UO_3

U	82.10 %
HCl, insoluble	0.6 %
NO_3	0.9 %
H_2O	0.6 %
Fe	12 p.p.m.
Ni	2 p.p.m.
Cu	<1 p.p.m.
Cd	<0.2 p.p.m.
Cr	3 p.p.m.
Mo	<1 p.p.m.
Bulk density	2.6 ± 0.2 g/ml
Tap density	4.0 ± 0.2 g/ml

TABLE VII.—ANALYZED SAMPLE No. 65 (1 TO 5). U_3O_8 SAMPLES FOR SPECTROSCOPIC ANALYSIS

Values in parts per million (based on metal)

Element	65–1	65–2	65–3	65–4	65–5
Boron	2.0	1.0	0.5	0.25	0
Cadmium	1	0.5	0.2	0.1	0
Chromium	45	25	12	8	
Copper	53	23	12	6	about 1
Iron	100	55	28	20	10
Manganese	24	12	6	3	about 0.5
Molybdenum	4	1.5	1.0	0.5	
Nickel	100	48	22	13	6
Phosphorus	200	100	50	20	0
Silicon	125	60	25	17	6
Silver	2.3	1.1	0.6	0.2	
Vanadium	100	50	20	10	1

TABLE VIII.—RARE EARTH MIXTURES FOR THE SPECTROCHEMICAL ANALYSIS OF RARE EARTH CONCENTRATES FROM URANIUM

Analyzed sample No. 28–1 to 28–5

Element	28–1	28–2	28–3	28–4	28–5
Gadolinium	20	10	4	2	0
Dysprosium	20	10	4	2	0
Erbium	20	10	4	2	0
Samarium	20	10	4	2	0
Europium	20	10	4	2	0

Note: Concentrations are in micrograms per milligram of lanthanum.

this purpose. The oxide coating usually present is readily removed with nitric acid, and it does not re-oxidize at an excessive rate. Tables IX and IXa show the values obtained on this material as well as the analysis for the impurities.

While the above samples are available for distribution, many installations use their own working standards. These may be synthetic samples made from reagent grade chemicals, or on the other hand, they may be production materials suitably prepared as to be homogeneous. The value assigned to this material may be from analyses referred to primary standards such as potassium dichromate or to one of the available uranium analyzed samples. Some plants prefer to prepare U_3O_8 which they use as a standard. The question of composition is all important in these instances. In most of these companies, standard local certification is relied upon.

TABLE IX.—ANALYSIS OF DINGOT METAL

Analyst	Uranium, %	Variability
NBL	99.974	$\sigma = 0.0032$
NBS	99.975	$\sigma = 0.0071$
K-25	99.976	±0.009 %

Note: Above corrected for 30 p.p.m. Fe present in sample, and using 238.037 for atomic weight of uranium.

TABLE IXa.—IMPURITIES IN DINGOT METAL

Ag	0.03	Mo	—
Al	10	Na	<5
As	—	Ni	<8
B	<0.1	P	—
Bi	—	Pb	1
Ca	10	Sb	—
Cd	—	Si	70
Co	2	Sn	—
Cr	6	V	—
Cu	1	Zn	—
Fe	30	O	10
Li	<1	C	10
Mg	8	N	8
Mn	5		

Note: —, not detected. Results are in parts per million.

For impurity analyses in uranium, many rely on synthetic spectrographic standards made from analytical reagent grade chemicals in a purified base. The question, of course, of homogeneity of the final mixture, of the chemicals used and of the impurities in the purified base must be resolved in all cases.

Proposed standards

Certain installations have indicated that a uranium compound such as U_3O_8, containing enriched uranium with certified uranium and isotopic content, would be useful.

The use of U^{233} in the analysis of highly radioactive solutions of spent enriched uranium fuel elements indicates that possibly a U^{233} certified as to isotopic content might be useful. This would be used chiefly in mass spectrographic measurements.

In this connection, some interest has also been expressed in standards of known U^{236} content.

PLUTONIUM

Standards for plutonium have been a problem for the past decade or more. Up to the present time, a compound suitable for a standard has not been found. The oxide, PuO_2, as in the case of uranium, is difficult to obtain. One reference[1] states that it is necessary to ignite the metal to 1200° C when preparing PuO_2 from it. When the oxide is made from plutonium salts at 870° C in air, it has a higher molecular weight. The authors suggest that the formula ranges from $PuO_{2.00}$ to $PuO_{2.09}$, depending upon starting material and temperature. From the above, it would seem that a usable oxide could be made by heating to 1200° C. Unfortunately, plutonium dioxide is very difficult to dissolve in acids. It becomes less soluble when heated to a higher temperature. That formed at 1200°C is exceptionally difficult to dissolve. In some instances, even fusing in bisulfate does not effect solution. For the above reasons, PuO_2 has not been used to a great extent.

At the present time, most installations use plutonium metal of known purity as a standard, the atom per cent of plutonium-239, 240, 241 and 242 being determined by the mass spectrometer. There are several drawbacks to the use of plutonium metal. It is readily oxidized in a moist atmosphere, forming an oxide coating which, unlike that of uranium, is not readily dissolved by acids. Also, the question of obtaining pure plutonium metal has not been entirely solved. Iron is a common impurity and is an undesirable contaminant because after reduction it will titrate like plutonium.

In spite of the fact that plutonium metal is not entirely satisfactory, the Advisory Committee for Standard Reference Materials and Methods of Measurement have authorized the preparation of a provisional plutonium metal standard which is expected to be available during the coming year. The samples are to be prepared at the Los Alamos Laboratory and will consist of weighed pieces of plutonium metal of 0.5–1 g, which will be individually sealed in glass tubes in an atmosphere of argon. The isotopic composition will be given since this is necessary for the calculation of the atomic weight of the plutonium. It is hoped that the impurities will be less than 100 p.p.m. and that the Pu^{239} content will be greater than 96 per cent. Distribution will no doubt be handled by the National Bureau of Standards.

As for preparing a plutonium compound of known composition, little has been realized along these lines in spite of a considerable amount of work on various compounds. The New Brunswick Laboratory has prepared $Pu(SO_4)_2 \cdot 4H_2O$. This compound was prepared by dissolving high-purity plutonium metal in 4 *N* sulfuric acid and heating to about 130°C until red crystals formed. The sulfate was washed ten times with 95% methanol and then air-dried for 3 days. The analysis is shown in Table X.

TABLE X.—ANALYSIS OF $Pu(SO_4)_2 \cdot 4H_2O$

	Theoretical, %	Found, %
Pu	47.51	47.61
SO_4	38.17	38.19
H_2O*	14.32	14.20

* By difference.

Because there is a question as to the stability of this compound—especially since it has four molecules of water and since it has been shown that the α-particles from the plutonium will decompose water in an aqueous solution—a series of weights was taken on one sample over a period of about 2 months. Table XI shows the change in weight during this period. A different preparation of 1 g weight shows similar stability.

TABLE XI.—STABILITY OF PLUTONIUM SULFATE TETRAHYDRATE

Date, 1959	Weight of sample, *mg*	Temperature, °*F*	Relative humidity, %
June 18	666.31	—	—
19	666.29	—	—
22	666.33	—	—
24	666.33	—	—
25	666.33	76	78
26	666.42	84	76
29	666.44	85	80
30	666.43	89	68
July 1	666.40	78	79
2	666.40	79	79
6	666.33	81	68
10	666.36	82	76
22	666.37	86	77
August 3	666.29	78	53
4	666.30	79	64
7	666.36	72	77
10	666.35	—	—

At present, while the above work on the sulfate looks promising, it is too early to state that this will be a satisfactory compound to use as a standard.

THORIUM

We now come to a prospective fuel in which the interest is like the appearance of the moon. It waxes and wanes. Several years ago there was considerable interest in thorium, and the New Brunswick Laboratory prepared a sample of thorium metal for impurity analysis as given in Table XII.

TABLE XII.—ANALYZED SAMPLE NO. 19. THORIUM METAL

Element	Values, *p.p.m.*
Aluminum	a 20
Boron	a 1
Beryllium	a 150
Calcium	<10
Copper	<5
Iron	140
Magnesium	<10
Manganese	a 2
Nickel	a 10
Lead	a 4
Silicon	a 20
Uranium	a 2
Nitrogen	60
Carbon	230
HCl, insoluble	1%

Note: a = about

Spectrographic standards of ThO_2 were also prepared, in the same fashion as with the U_3O_8, for use in the carrier–distillation method of analysis. These are shown in Table XIII.

TABLE XIII.—SAMPLE NO. 26–1 TO 26–6. ThO_2 FOR SPECTROSCOPIC ANALYSIS
Values are in parts per million (based on metal)

NBL	26–1	26–2	26–3	26–4	26–5	26–6
Element	A	B	C	D	E	F
Al	500	200	100	50	20	10
Fe	500	200	100	50	20	10
Mo	500	200	100	50	20	10
P	500	200	100	50	20	10
Si	500	200	100	50	20	10
V	500	200	100	50	20	10
Zn	500	200	100	50	20	10
Be	170	70	35	17	7	4
Bi	50	20	10	5	2	1
Co	50	20	10	5	2	1
Cu	50	20	10	5	2	1
Mg	50	20	10	5	2	1
Mn	50	20	10	5	2	1
Ni	50	20	10	5	2	1
Pb	50	20	10	5	2	1
Sn	50	20	10	5	2	1
Ag	5	2	1	0.5	0.2	0.1
B		7*	5*	4*	3*	2*
Cd	5	2	1	0.5	0.2	0.1

Note: Figures given are amounts added except as asterisked. This material is to be used for visual estimation. Cooperative laboratory results indicated that the data given is within ±25 per cent of the stated value.

* Determined values.

The present program, in which a breeder reactor using thorium is to be constructed under the Oak Ridge Operations Office, will no doubt result in increased interest in this element and possibly new standards may be desired.

Many years ago a monazite ore was prepared at the New Brunswick Laboratory for chemical analysis. The composition is as shown in Table XIV.

TABLE XIV.—ANALYZED SAMPLE NO. 7. MONAZITE SAND

	Percentage
ThO_2	9.65
U_3O_8	0.38

This sample is about exhausted and consideration is being given to renewing it. A candidate material is on hand at the New Brunswick Laboratory and may be transferred to the National Bureau of Standards for certification.

A series of thorium standards made from monazite by mixing with dunite was prepared many years ago by the National Bureau of Standards. These standards were exhausted and a new series was prepared by the New Brunswick Laboratory, as shown in Table XV.

TABLE XV.—THORIUM STANDARDS

Sample No.	Thorium, %	Uranium, %
79	1.01	0.04
80	0.101	0.004
81	0.051	0.002
82	0.020	0.0008
83	0.0102	0.0004
84	0.0011	0.00004

These standards have been distributed internationally. All were analyzed chemically after mixing. If—as has happened—a very small sample, in the milligram range, is used, it is doubtful whether these samples are sufficiently homogeneous.

A series of standards of radium in radium-bearing sludge and of radium in pitchblende ore has been prepared under the New Brunswick Laboratory auspices, but since these have been used chiefly in international agreements, and since the amounts prepared are not very great, they are not available for public distribution.

RADIOACTIVITY STANDARDS

For certain work, the National Bureau of Standards has prepared a series of α, β and γ standards, as shown in Table XVI.

TABLE XVI.—ALPHA, BETA AND GAMMA STANDARDS

Radiation	Nuclide	Nominal activity
α	Polonium-210	200 d.p.s.
α	Polonium-210	500 d.p.s.
α	Polonium-210	1000 d.p.s.
α	U_3O_8	15 d.p.s.
β (γ)	Sodium-22	10^4 d.p.s./ml
γ (β)	Sodium-22	10^6 d.p.s.
β	Carbon-14	10^8 d.p.s./ml
β	Carbon-14	10^4 d.p.s./ml
β	Hydrogen-3	10^4 d.p.s./ml
β	Hydrogen-3	10^6 d.p.s./ml
K	Iron-55	10^5 d.p.s./ml
K (γ)	Zinc-65	10^5 d.p.s./ml
γ (β)	Mercury-203	10^6 d.p.s./ml
γ (β)	Krypton-85	10^7 d.p.s./gmol

Note: d.p.s. = disintegrations per second.

The Bureau is preparing less of these materials than in the past, as several commercial sources of reference materials are now available. In most instances, the companies interested in nuclear fuels prepare their own reference materials, such as, for example, plutonium deposited on stainless-steel discs by vacuum distillation as an α-standard or by evaporating aliquots of a cesium-137 solution for use as a γ-standard.

Radium standards for use in radon analysis, as well as radium γ-ray standards, are also available from the National Bureau of Standards. These are shown in Table XVII.

TABLE XVII.—RADIUM STANDARDS

Sample No.	Radium content, *g*	Volume, *ml*
4950	10^{-9}	100
4951	10^{-11}	100
4952	Blank Solution	100
4955	0.1	5
4956	0.2	5
4957	0.5	5
4958	1.0	5
4959	2.0	5
4960	5.0	5
4961	10	5
4962	20	5
4963	50	5
4964	100	5

As you may have noted, nothing has been said of alloy standards. For certain classified work, a program for the preparation of Zircaloy–uranium standards is in progress. The amounts prepared at present, as well as the classification restriction, will not allow these alloys to be made available for general use. It is hoped that in the not-too-distant future, such alloy standards will be available for sale.

The preparation of alloy standards of all types is difficult chiefly because of the lack of homogeneity of such preparations. For certain work—such as the determination of the U^{235} content of fuel elements themselves without destruction of the element—the possibility has been brought up of having a library, so to speak, of fuel elements of known U^{235} composition. The types of fuel elements now in use in the A.E.C. complex are so varied, and so many of them are of an experimental nature, that it would be impractical to attempt an A.E.C.-wide program to provide standardized fuel elements. The Argonne National Laboratory has been asked to collect specific data as to costs, estimated number of fuel elements required, and details of evaluation of elements to be placed in such a library. I am sure many here would be pleased to see such a program put into effect.

Up to the present time, no consideration has been given to the preparation of standards for the various types of ceramic fuel elements which have been proposed. No doubt, before very long, it may be necessary to consider ceramic or cermet fuel elements containing the oxides and/or carbides of uranium, plutonium and thorium; many other fuel elements have been proposed, such as ones in which the above compounds may be used in a metallic or graphitic matrix as well as in a matrix in which carbides of titanium, zirconium, tantalum and niobium may be used.

NON-FUEL MATERIALS

In addition to fuel materials, there are many other materials used which may require standards. Some of these, such as steel and other common materials, will not be considered.

In the analysis of hafnium, niobium, zirconium and uranium base alloys, synthetic standards are made by making known additions to a high-purity matrix material. High purity matrix materials for hafnium, niobium and zirconium are usually difficult to obtain. At present, there are no available primary standards for hafnium, niobium or uranium base alloys. The A.S.T.M. is actively engaged in work on zirconium metal and Zircaloy-2 standards, and have just initiated a program for niobium metal.

Zirconium–Zircaloy

At the present time, only for zirconium and Zircaloy-2 have standards which approach primary standard quality been developed.

Table XVIII shows the zirconium standards values kindly submitted by G. W. Goward of the Bettis Division of Westinghouse.

TABLE XVIII.—ZIRCONIUM STANDARDS

	ZAS-1	ZAS-2	ZAS-3	ZAS-4	ZAS-5	ZAS-6
Al*	42	56	79	125	174	252
B	Not agreed upon					
Cr†	124	110	82	83	108	245
Co*	<0.1	1.6	0.8			<0.1
Cu*	16	479	197	28	97	10
Hf	Not agreed upon					
Fe†	730	820	540	450	630	1120
Mg†	<15	<15	<15	<15	<15	<15
Mn*	26	27	24	20	26	17
Mo*	<0.1	1.2	0.5			0.8
Ni	Not agreed upon					
Pb	Not agreed upon					
Si†	52	58	109	106	82	110
Sn	Not agreed upon					
Ti*	10		4			13
V	Not agreed upon					
W†	312	76	233	290	483	19

* = Accepted values.
† = Provisional values.

Table XIX gives the values for the only Zircaloy-2 standard now available. These zirconium and Zircaloy-2 standards are reserved for contractors working on the Naval Reactor Program.

TABLE XIX.—$5^{Y}303$ ZIRCALOY-2

Sn	1.34%	Hf	70
Fe	0.125%	Pb	90
Cr	0.106%	Mg	12
Ni	0.051%	Mn	26
C	45	Mo	<5
Al	55	Si	46
B	0.3	Ti	<10
Cd	<0.1	V	<5
Co	<2	W	108
Cu	13		

Note: All values in parts per million except where otherwise indicated.

Certain secondary standards for specific elements, such as oxygen, hydrogen, nitrogen, tin, iron, chromium and nickel, are used.

Spectrographic standards for zirconium are made by grinding mixtures of zirconium oxide and the oxides of the elements to be added.

At the present time, the National Bureau of Standards has in preparation two samples of Zircaloy-2 and two samples of reactor-grade zirconium to be used for impurity analysis by spectrographic means. In addition, there is one sample of Zircaloy-2 which has been prepared for chemical analysis. It is expected that this last sample will be available in the not-too-distant future.

Beryllium

In the past, several types of beryllium metal standards were prepared. These materials were of electrolytic flake, pebble and vacuum-cast grade. Since, in the past few years, the interest has been chiefly in vacuum-cast, a series of vacuum-cast beryllium metal standards was prepared under the auspices of the New Brunswick Laboratory. These samples are for use in chemical and spectrographic analysis. The list of these materials with their composition is given in Table XX.

TABLE XX.—TENTATIVE VALUES OF BERYLLIUM METAL STANDARDS
(Based on chemical analyses)

Element	New Brunswick Laboratory standard No. 85	New Brunswick Laboratory standard No. 86	New Brunswick Laboratory standard No. 87	New Brunswick Laboratory standard No. 88
Cu	30	300	210	250
Mo	5	25	32	51
Ni	80	200	210	370
Co	10	30	10	10
Fe	400	1400	1700	2500
Mn	80	120	215	250
Si	580	650	1300	1450
Cr	70	200	250	430
Al	100	1400	1300	1400
Mg	90	60	170	50
B	1.1	>50	1.3	1.0
N	55	70	120	110
C	500	400	500	400
BeO	0.5%	0.5%	0.5%	0.5%
Be	99.0%		99.25%	99.5%

Note: Values in parts per million except where noted otherwise.

In addition, a series of beryllium oxide standards for spectrographic work with the carrier–distillation technique was prepared by the New Brunswick Laboratory. They are shown in Table XXI.

Since the lowest value given on some elements, in the beryllium metal samples, is rather high, and since the beryllium metal of commerce is of better grade, it may be necessary to prepare a sample of lower impurity content.

In addition to the above, interest has also been expressed in the preparation of standards of beryllium alloys.

TABLE XXI.—ANALYZED SAMPLE NO. 72 (1 TO 5). BERYLLIUM OXIDE SAMPLES FOR SPECTROSCOPIC ANALYSIS

Values in parts per million (based on metal)

Element	72–1	72–2	72–3	72–4	72–5
B	5.3	2.3	1.3	0.8	0.3
Fe	2070	1070	570	170	70
Al	a2200	a1150	700	290	180
Mg	500*	200*	100*	50*	a60
Ni	500	200	100	50	<2
Mn	540	200	100	50	<10
Cr	450	180	90	50	4
Cd	6	2*	1.0*	0.5*	<3
Li	5*	2*	1*	0.5*	<0.1
Ca	1000*	500*	200*	100*	a60
Co	20	10	5*	2*	<2
Cu	100	50	20	10	<4
Zn	460	210	115	70	20
Ag	10	5	2	1	<0.1
Pb	50	20	10*	5*	<4
Si	2120	1180	750	480	230
Mo	50	18	8	5	<2

* amount added to blank material 72–5
a, about
<, less than

Boron

Since boron in elemental or carbide form is used in certain fuel elements, it has become increasingly important that isotopic standards for this work be made available. The B^{10} content of naturally occurring boron is still open to question. Values ranging from 18.5 to 20.0 per cent have been reported. In addition, reactor-grade elemental boron of naturally occurring composition appears to give a higher value for B^{10} than is found in naturally occurring sodium tetraborate or boric acid.

It is proposed that three standards be prepared on these materials: (1) a salt or oxide of naturally occurring boron such as the tetraborate or boric acid, (2) a sample of elemental boron of natural origin, (3) a highly enriched elemental boron of about 93 per cent B^{10} content.

OTHER MATERIALS

There appears to be interest in standards of the following materials, listed in Table XXII.

TABLE XXII.—SUGGESTED STANDARDS

1	B_4C
2	B_4C in a Zircaloy matrix
3	Niobium
4	Niobium–uranium
5	Niobium–zirconium–tin
6	Niobium–uranium–tin–zirconium
7	Molybdenum
8	Hafnium

The above discussion on standards is naturally incomplete. Changes in the fuel-elements program and in materials of construction will no doubt result in needs for new types of standards. The Advisory Committee for Standard Reference Materials and Methods of Measurement would be pleased to receive comments on desirable standards for use in the nuclear energy field. We would appreciate the forwarding of your suggestions to: Dr. Samuel C. T. McDowell, Division of Nuclear Materials Management, U.S. Atomic Energy Commission, Washington 25, D.C., U.S.A.

REFERENCE

[1] J. L. Drummond and G. A. Welch, *J. Chem. Soc.*, 1957, 4781.

Talanta, 1960, Vol. 6, pp. 20 to 27. Pergamon Press Ltd. Printed in Northern Ireland

THE HIGH-RADIATION-LEVEL ANALYTICAL FACILITY AT THE OAK RIDGE NATIONAL LABORATORY*†

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Summary—Unusual techniques and remotely controlled manipulations are required in carrying out analytical work on highly radioactive materials. In order to isolate highly radioactive materials for analysis and to centralize remotely controlled operations in one area, a concrete structure, called the High-Radiation-Level Analytical Facility (HRLAF), was built at Oak Ridge National Laboratory (O.R.N.L.) in 1955.

This facility is used for the analysis of samples of radioactivity greater than 1 r/hr at contact; the samples are received from the Power Reactor Fuel Reprocessing Pilot Plant as well as from many other sources. It consists of a sample-storage cell, seven work cells, a "cold" preparation area, a decontamination area, a receiving dock and an office. Barytes concrete, in addition to concrete of normal composition, is used in the cell walls to meet different shielding requirements. Zinc bromide solutions are used for shielding in the work-cell windows, and high-density lead glass is used for shielding in the storage-cell window.

The facility is provided with Master Slave Manipulators, analytical instruments designed for use by remote control, and special equipment for transporting samples, for continuously monitoring air-borne and background radioactivity, for disposing of solid and liquid wastes, and for carrying out decontamination procedures.

THE various studies at the O.R.N.L. which are related to isotope production, reactor experiments and reactor fuel processing require analytical chemistry on highly radioactive samples. Improvised shielding of stacked lead bricks and other barricades, in use, proved to be inadequate in preventing excessive exposure to personnel who worked for extended periods of time on the high-level radioactive solutions. Each individual laboratory unit was confronted with the problem of trying to work on the hazardous materials with limited space, limited shielding and limited equipment for remotely controlled operations. Therefore, in order to isolate the highly radioactive samples for analysis and to centralize remotely controlled analytical operations into one area, a concrete structure, called the High-Radiation-Level Analytical Facility (HRLAF) was designed and constructed[1] at O.R.N.L. It was completed in 1955 at a cost of approximately $500,000. The cost included the purchase of fifteen Master Slave Manipulators.

The purpose of this paper is to familiarize the reader with some of the highlights of the facility, its equipment and some of the operations involved.

The High-Radiation-Level Analytical Facility was built as an annex (Fig. 1) to an existing building already housing a pilot plant and laboratories engaged in chemical processing and analytical work on highly radioactive materials.

RECEIVING SAMPLES

Groups in other buildings must transport their samples in carriers with adequate shielding to protect the personnel handling these containers. Sample carriers are

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* Work performed under contract with the U.S. Atomic Energy Commission.

† This paper was also presented at the Southeastern Regional Meeting of the American Chemical Society, Richmond, Virginia, 5–7 November 1959. The Society has generously released the paper in order that it may be included in these Proceedings.

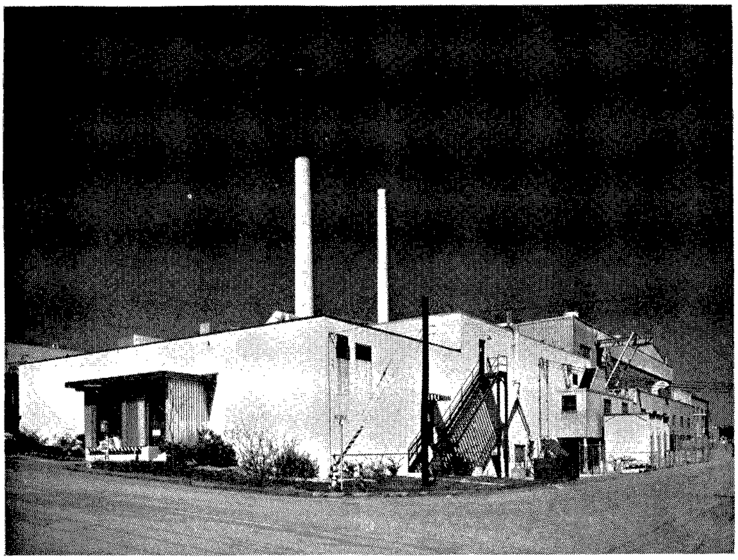

FIG. 1.—Radiochemical Processing Pilot Plant and HRLAF.

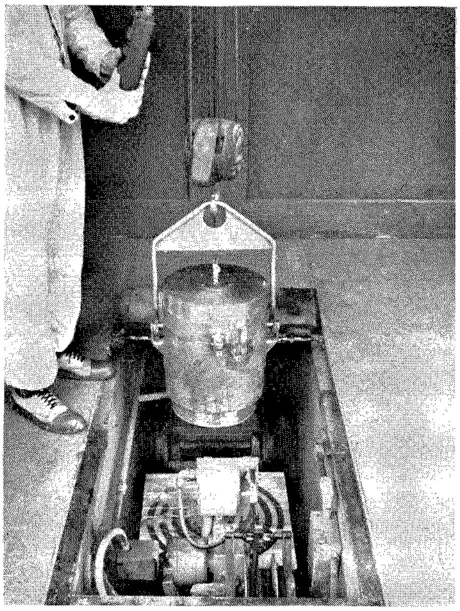

FIG. 2.—Unloading platform and tunnel cart.

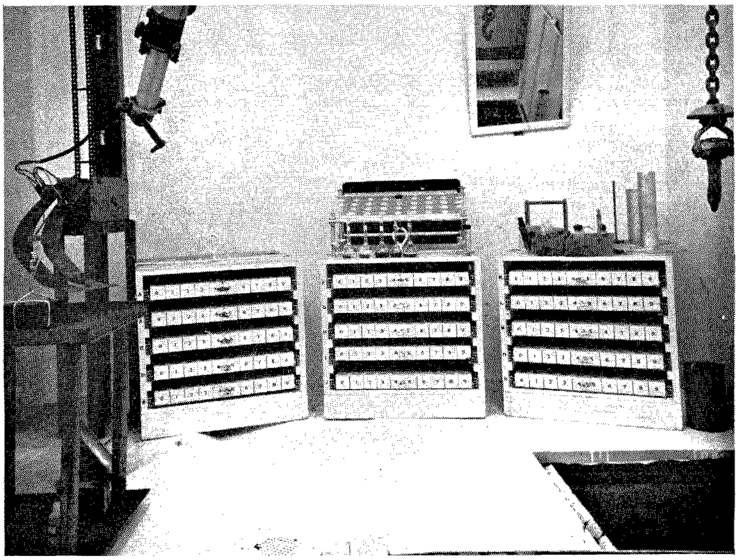

FIG. 3.—Sample storage cell.

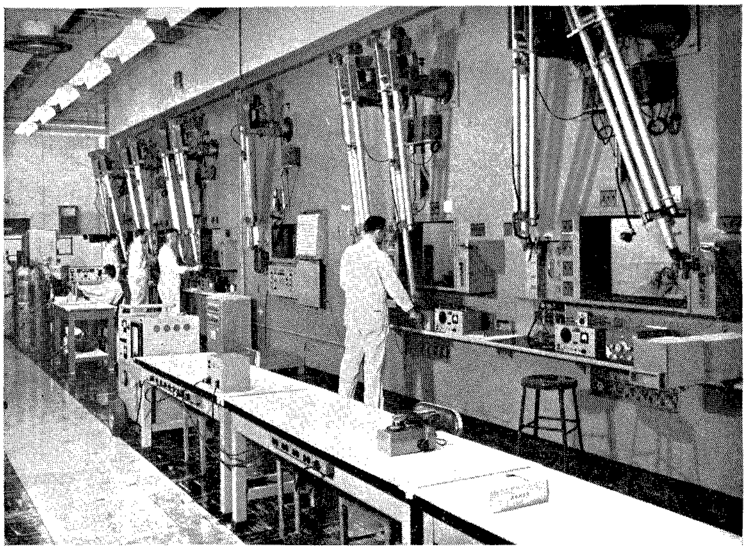

FIG. 6.—Front view of cells.

made in different sizes and shapes to meet varying shielding requirements. The carrier shown in Fig. 2 is a stainless-steel shell filled with lead, and weighs approximately 1000 lb. It is used to transport samples from the Homogeneous Reactor Project. The carrier is designed for a graduated 10 ml centrifuge cone fitted with a screw cap usually containing approximately 5 ml of solution.

In Fig. 2, the carrier is in a position for placement on the target plate of the cart in the tunnel. After loading, the cart is driven electrically 22 ft to the other end of the tunnel. A hydraulic lift then raises the carrier 5½ ft which places it inside the sample storage cell through the opening in the cell floor shown in Fig. 3.

The sample is removed from the carrier in the storage cell and is sent to an adjoining work-cell where the analyses are to be made. It is transferred from one cell to another on a motorized conveyor track. Approximately 10 min are required to send or deliver a sample through the tunnel and to return the carrier to the unloading platform.

Samples received from the Power Reactor Fuel Reprocessing Pilot Plant are loaded onto a chain conveyor in the sampling gallery at the other end of the building. They are carried overhead through lead shielding and down into the sample storage cell where they are unloaded automatically onto a rack. The chain conveyor carries four sets of metal cups (ten cups per set) for holding the sample bottles in transit.

In the storage cell, there are three boxes for the retention of samples after the analytical work is complete. Each box has five drawers wherein 100 standard sample bottles can be stored in each drawer.

BUILDING LAYOUT

On the floor plan of the HRLAF in Fig. 4, the storage cell is centrally located with three work-cells on one side and four on the other. At the present time, there are three analytical chemistry groups using the HRLAF. The spectrochemical laboratory group is using Cell No. 6, the Reactor Analyses Laboratory is using Cells No. 2 and 4, the Pilot Plant Control Laboratory is using Cells No. 1, 3 and 5, and all groups are jointly using Cell No. 7 and the storage cell. The Cold Preparation Zone is the area in front of the cells and is used for the operation of the equipment controlling the work being done inside the cells. It is also used for the preparation of reagents and glassware to be used in the cells. Supporting laboratories which handle low and intermediate level (less than 1 r/hr at contact) radioactive samples are adjacent to the Cold Preparation Zone. The area behind the cells is the Decontamination Zone.

A sectional view of a work-cell is shown in Fig. 5. The walls of the work-cells are 3 ft thick and are made of standard poured concrete. The storage cell walls are made of barytes concrete. Each work-cell has a rear access door made of stacked concrete blocks. The door weighs approximately 9 tons. A steel grill covered with a stainless-steel pan is mounted approximately 3 ft above the actual floor of each work-cell. The pan forms the working surface for the manipulations required in making the analyses. The space beneath the pan is used for the storage of extra equipment. There are four mercury vapor lamps in each work-cell and they are wired so that any two, but only two, can be used at a time. There are also two incandescent work lights in each work-cell.

A view of the front of the cells is shown in Fig. 6. The Master Slave Manipulators

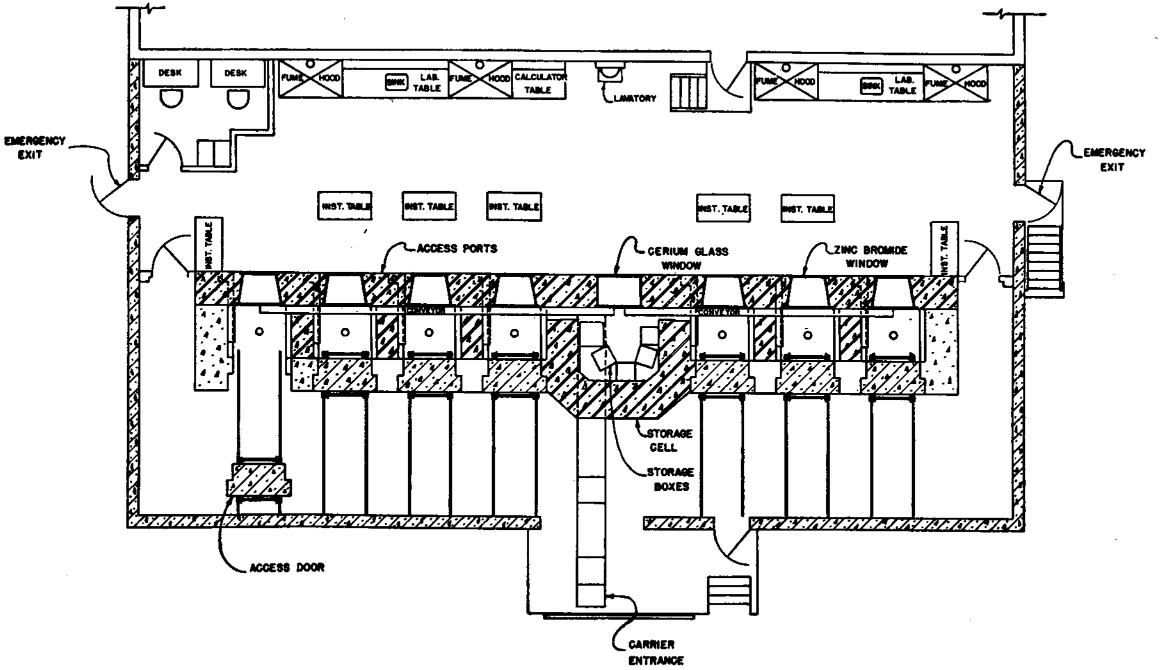

FIG. 4.—HRLAF floor plan.

were manufactured by the American Machine and Foundry Company and were designed from the Argonne National Laboratory Model 8. They cost approximately $7000 a pair. The slaves have been modified with a thumb-activated micro-switch for canting the arm in the cell either forward or backward.

The storage cell window consists of six 6 in. thick sections of lead glass sandwiched together for shielding and cost approximately $10,000. Zinc bromide solution is used for shielding in the work-cell windows at a cost of approximately $3000 per window.

The area opposite the front of the cells is shown in Fig. 7. The work benches and hoods are used for the preparation of reagents and glassware to be used during the analyses in the work-cells. The non-radioactive work relative to an analysis in the cell is done in this area to increase the cell time available for work involving radiation.

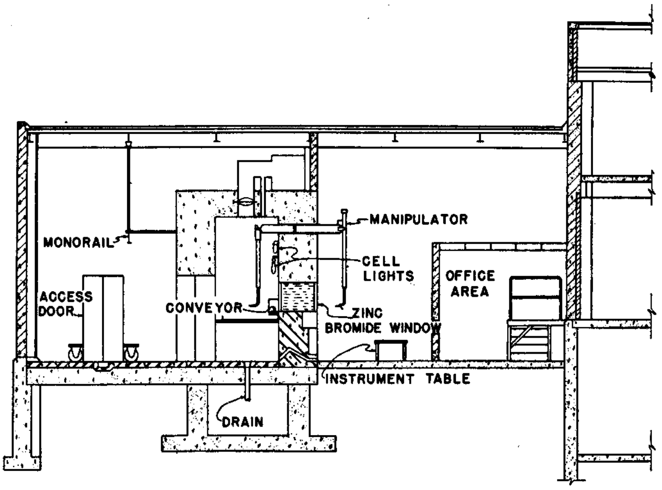

FIG. 5.—Section through work cell.

SAFETY DEVICES

Safety features of the facility include a constant air monitor in the Cold Preparation Zone and one in the Decontamination Zone. It continuously monitors and records any radioactivity which has been airborne in its vicinity.

There is a pressure sensitive device in the off-gas system exhausting the cells. It is activated as an alarm if a change of pressure in the system is outside the limits of safety.

There are two probes in the Cold Preparation Zone, two in the Decontamination Zone, and one in each work-cell wired into the console (Fig. 8) of a Remote Area Monitor. It continuously indicates the background radiation at the location of each probe. An individual setting for each probe can be made so that it will act as an audible alarm at any radiation level up to 100 r/hr. A red light flashes on at the console to indicate the position of the probe where the radiation is greater than the preset limit.

Figure 9 lists some of the analyses made in the HRLAF by the Pilot Plant Control Laboratory. Generally, standard "bench-top" methods are used with modification or adaptation to remotely controlled techniques. In many of the methods, the radioactivity level of the material being determined is reduced during the analysis to less than 1 r/hr at contact and the analysis completed in a supporting laboratory.

Most of the equipment failures encountered in the operation of the HRLAF have been the same as those found in a normal laboratory, e.g., a burned-out exciter bulb on a filter photometer, a faulty salt bridge on a coulometer or a polarograph, a broken buret or electrode on a titration unit, etc.

Frequent breakage of the tongs and inner-finger assemblies (Fig. 10) on the Master Slave Manipulators made it necessary to increase the diameter of the tension cables, and to use tension cables and torsion springs made from stainless steel on the inner-finger assembly. The "tru-arcs" used on the tongs were replaced with stainless-steel washers and the pins braded to hold them in place.

Analysis	Method
U (macro)	Spectrophotometric ammonium thiocyanate
Th	Spectrophotometric thoron
Zr	Spectrophotometric thoron
Al	Spectrophotometric ammonium aurintricarboxylate (aluminon)
P	Spectrophotometric phosphomolybdate
Hg	Spectrophotometric dithizone
NH_4	Spectrophotometric Nessler's reagent
Fe	Spectrophotometric o-phenanthroline
Cr	Spectrophotometric diphenylcarbazide
Ni	Spectrophotometric dimethylglyoxime
gross β	Dilution
gross γ	Dilution
pH	Direct measurement
Cl	Volumetric titration
Free H^+	Volumetric titration
Free H^+	Potentiometric titration
Density	Falling drop
U (micro)	TBP-Amsco extraction—Fluorometric
U^{233}	Hexone extraction
Pu α	Thenoyltrifluoroacetone extraction
Np	Thenoyltrifluoroacetone extraction

Fig. 9.—Some methods used by the Pilot Plant Control Laboratory in the HRLAF. Pretreatments include: dilution, fusion, weighing, resin column separation, precipitation.

A broken tong can be replaced in less than 5 min with the manipulator left in place; however, a broken inner-finger assembly necessitates removal of the manipulator from the cell as shown in Fig. 11. Approximately 1–1½ hr is required for two men to remove a manipulator, repair a broken inner-finger assembly and return the slave to its normal position in the cell. The frame used in removing a manipulator from a cell is movable and can be positioned for the removal of any one of the fifteen manipulators. If the proper precautions are not taken, floor contamination often results from particles of radioactivity falling from the inner arm of the manipulator while it is outside the cell for repair.

CELL EQUIPMENT

Cell No. 1 in Fig. 12 is used for non-routine analytical work requiring a temporary set-up of equipment which is disassembled and removed when the work is finished. The equipment which remains in the cell consists of a densimeter mounted on the pan and a sample disposal unit mounted on the wall. The densimeter is used for the measurement of density by the Falling Drop Method.[2]

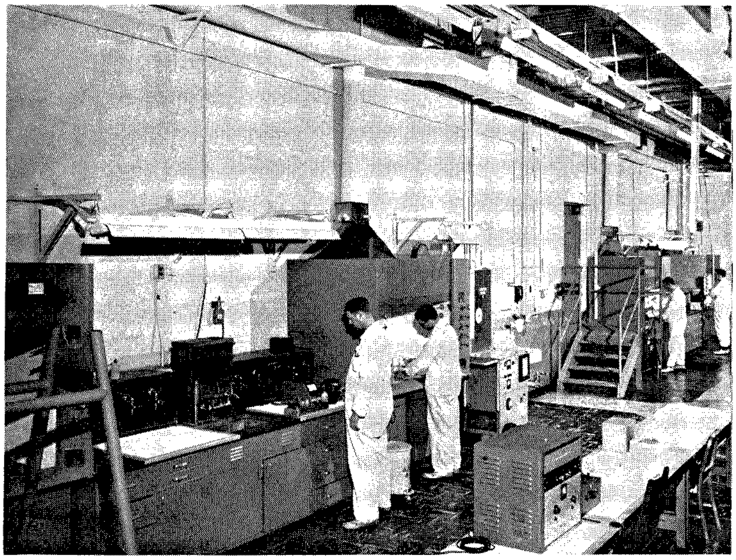

FIG. 7.—Cold Preparation Zone—across from cells.

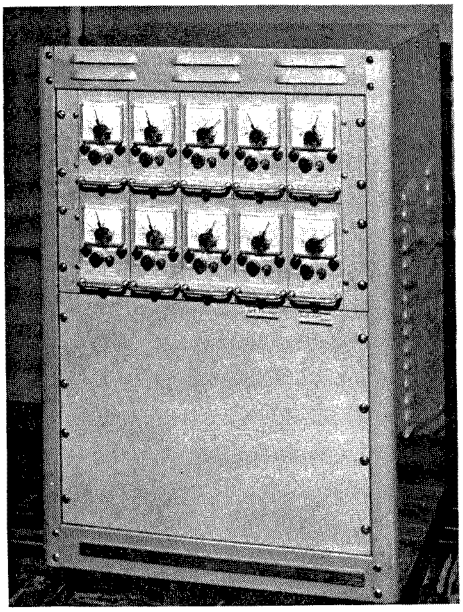

FIG. 8.—Remote area monitoring console.

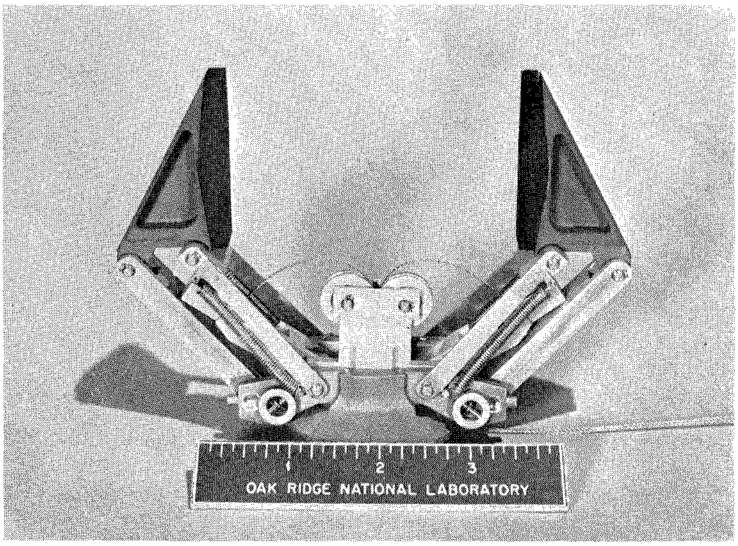

FIG. 10.—Master Slave Manipulator tong and inner-finger assembly.

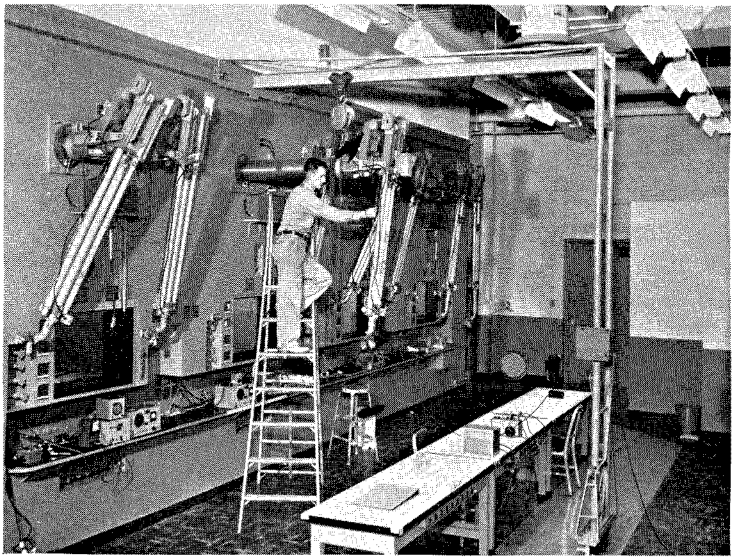

FIG. 11.—Manipulator being removed from work cell.

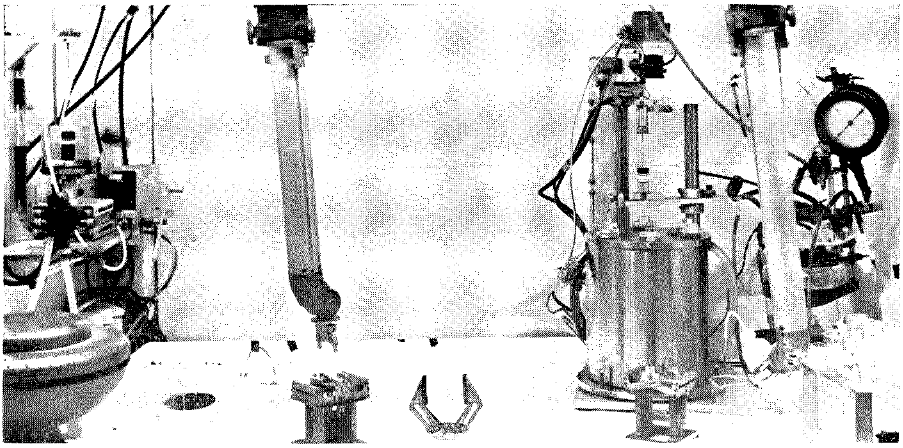

FIG. 12.—Cell No. 1—sample disposal unit and densimeter.

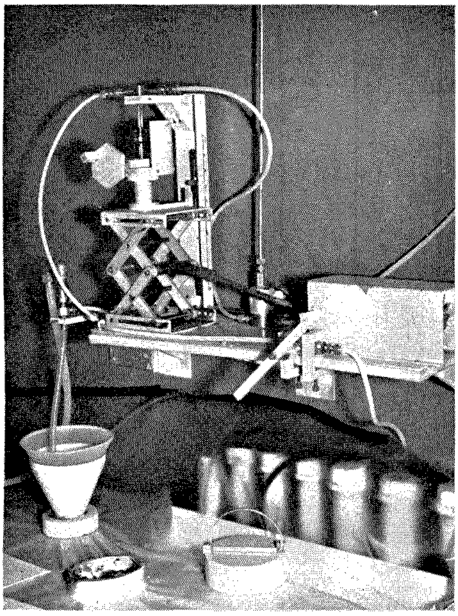

FIG. 13.—Sample disposal unit.

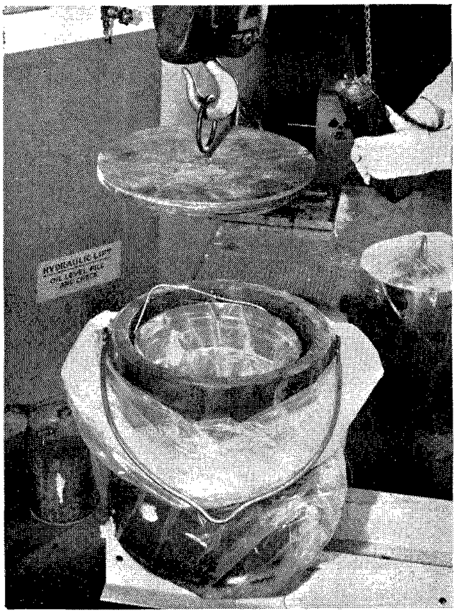

FIG. 14.—Waste materials receptacle.

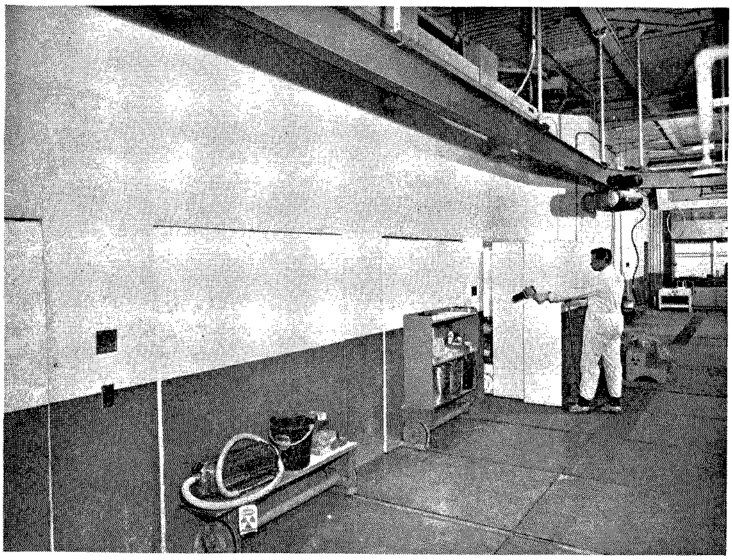

FIG. 15.—Rear of cells—decontamination area.

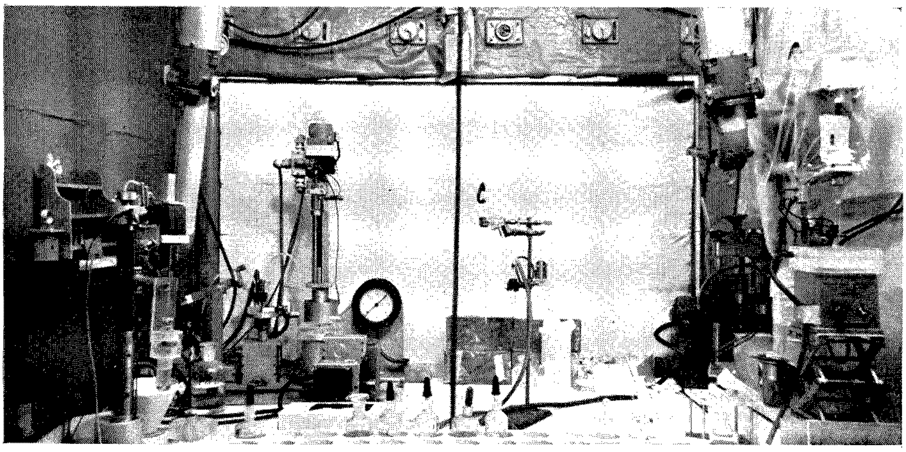

FIG. 16.—Cell No. 2—microelectrodes for pH.

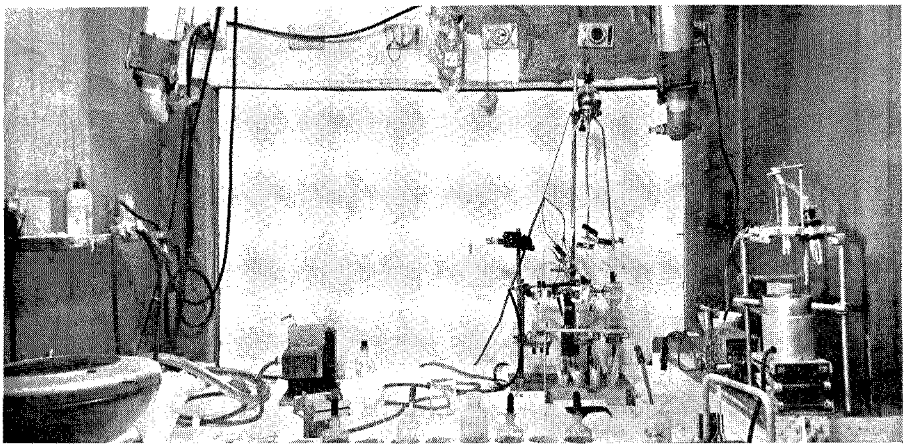

FIG. 17.—Cell No. 4—coulometric titration unit and polarograph cells.

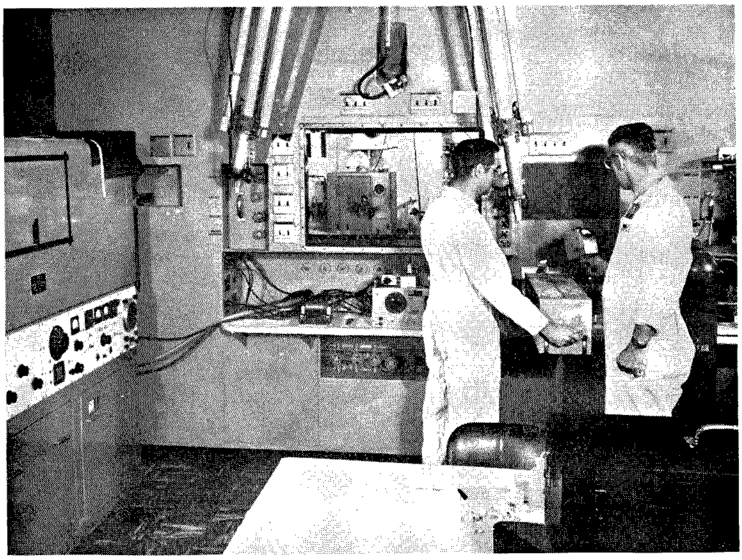

FIG. 18.—Cell No. 6—exterior view showing Jaco-varisource Spectrograph.

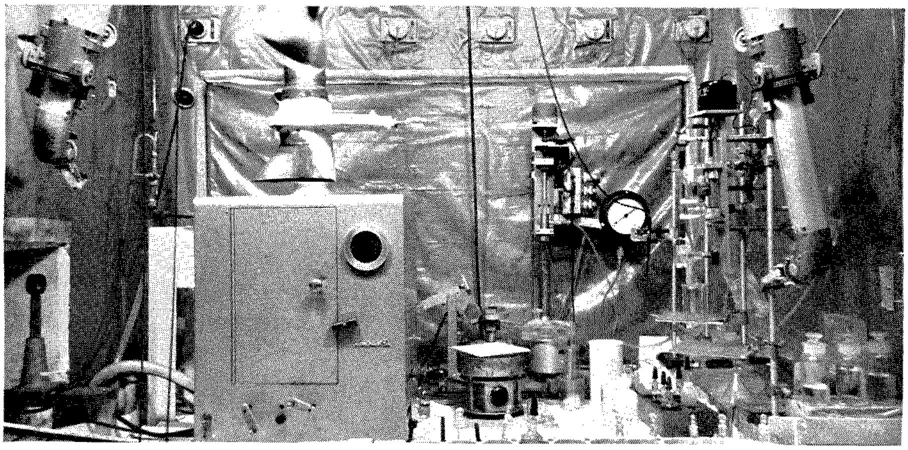

FIG. 19.—Cell No. 6—interior view.

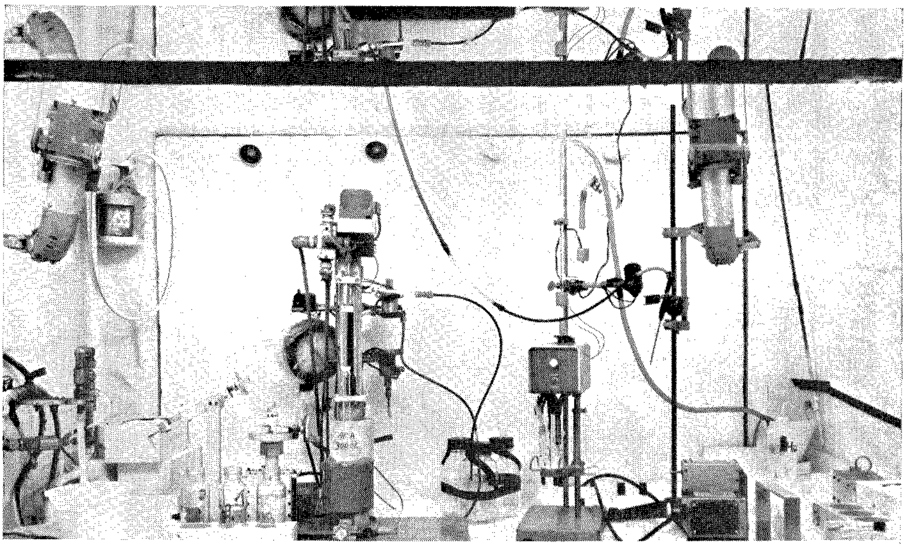

FIG. 20.—Cell No. 3—showing filter photometer and automatic free H^+ titration unit.

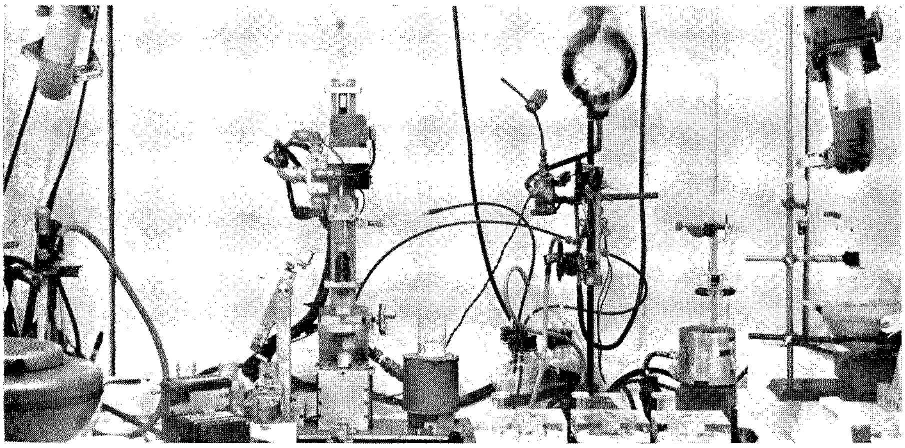

FIG. 21.—Cell No. 5—equipment for liquid–liquid extractions.

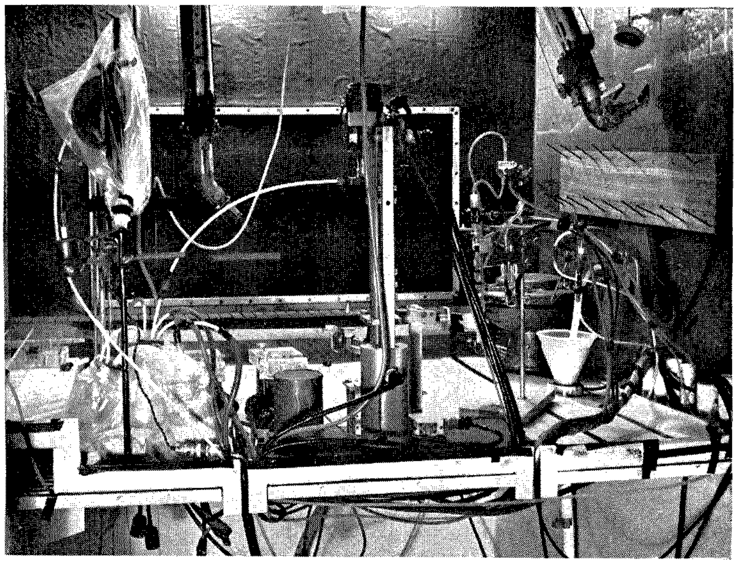

FIG. 22.—Cell No. 5—rear view.

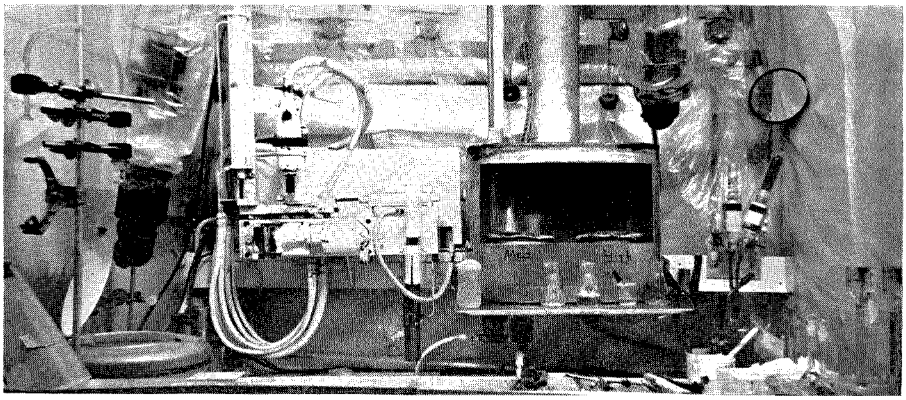

FIG. 23.—Cell No. 7—showing fume hood.

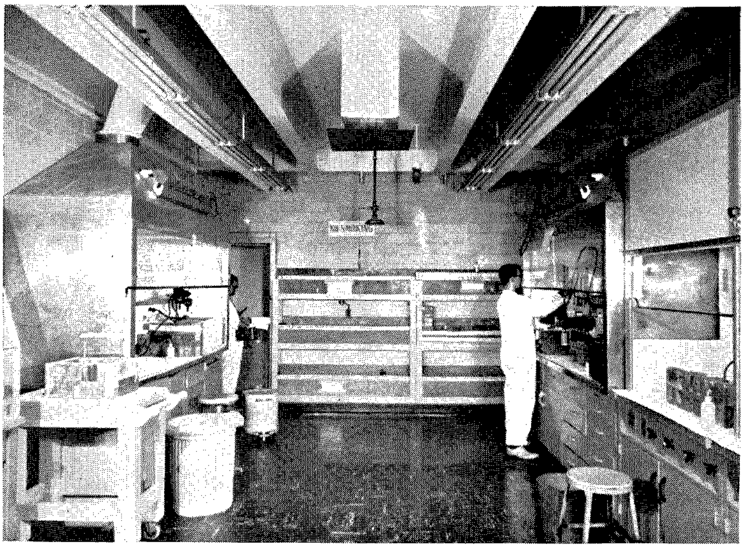

FIG. 24.—Laboratory for receiving, sorting and pretreating samples measuring 1 r/hr at contact.

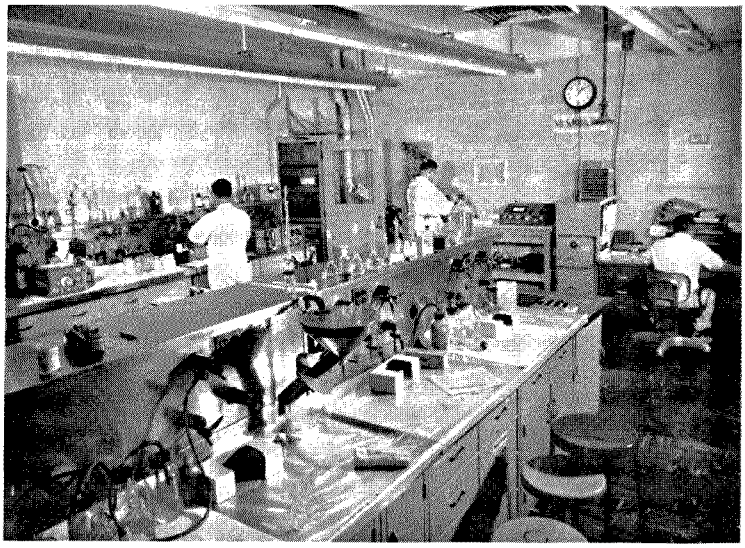

FIG. 25.—Laboratory for analyzing samples containing intermediate and low-level radioactivity.

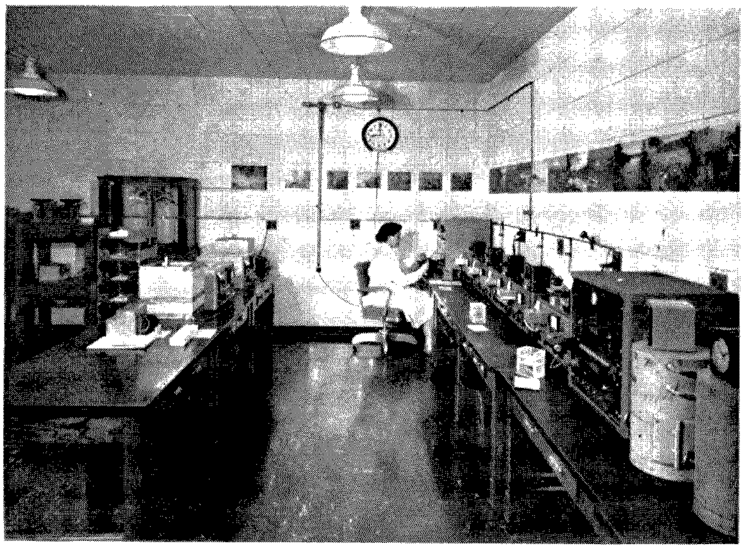

FIG. 26.—Counting room.

The sample disposal unit (Fig. 13) is used for removing the solutions from the sample bottles after the analytical work on them has been completed. The unit is designed for sample bottles which are 2½ in. tall and 1 in. in diameter. Each bottle has a Bakelite top which has been drilled open and sealed with a rubber diaphragm. On disposal, the bottle is clamped onto a motorized lab jack and raised until the two needles have punctured through the rubber diaphragm and extend to within ⅛ in. of the bottom. One of the needles is connected to a stainless steel water aspirator which draws the sample solution out of the bottle and down the drain to a storage tank. The other needle is connected to a solenoid which allows air or water to be drawn through the bottle. After the bottle is rinsed several times, it is removed and dropped through a chute in the cell pan.

A receptacle (Fig. 14) for catching the empty sample bottles is mounted on a bracket attached to the access door of Cell No. 1. It consists of a cheap metal can with a polyethylene bag fitted inside for a liner. The can is in a lead shielded container. As the cell door is opened into the decontamination area (Fig. 15), the receptacle moves out of the cell and into a position under an overhead hoist. The hoist is on a monorail and is used to carry the receptacle to a vehicle for transfer to a burial ground.

The equipment in Cells No. 2 and 4 is used by the Reactor Analyses Laboratory primarily for analyzing materials from the Homogeneous Reactor. Cell No. 2 (Fig. 16) contains a free-acid titration unit; a temporary pipettor (made from a mohr pipet, rubber tube and syringe for pipetting solutions containing halides), a stainless-steel remote pipettor and a microelectrode unit (for measuring the pH of one drop of solution).

Cell No. 4 (Fig. 17) contains a coulometric titration unit, three dropping mercury polarograph cells, a filter photometer and a centrifuge.

Cell No. 6 is used by the Spectrochemical Laboratory, and a Jaço-Varisource Spectrograph is shown on the left in the exterior view shown in Fig. 18. An access drawer is located at the front of each cell for passing glassware and reagents into the cell. The drawer is also used for removing flasks containing dilutions or pretreated radioactive materials but which must measure less than 1 r/hr before they can be safely handled outside of the cell.

Figure 19 shows the interior of Cell No. 6. The equipment is used for chemical separation and preparation of the sample for mounting onto a graphite porous cup. The prepared material is sparked in the housing in the center of the cell. A duct is located directly over the housing which carries the radioactive gases through a filter and empties them into the exhaust system. The duct can be moved by remote control to a position over a drain in the cell and then flushed with water to remove the collected radioactive materials from the filter.

Cells No. 1, 3 and 5 are used by the Pilot-plant Control Laboratory for analyzing samples from the Power Reactor Fuel Reprocessing Pilot Plant, Volatility Pilot Plant and Fission Products Pilot Plant.

Cell No. 3 (Fig. 20) is equipped with a Beckman Model K automatic titrator, a filter photometer and a stainless-steel remote pipettor. The titrator utilizes an electromagnetic buret which has a fill and delivery valve activated by solenoids. The filter photometer is used for colorimetric analyses. The vacuum system is protected by three bottles used as traps for the collection of waste solutions. The bottles are emptied through a line connected to a stainless-steel water aspirator.

The interior of Cell No. 5 is shown in Fig. 21. The cell is used for making liquid–liquid extractions, chloride distillations and colorimetric analyses. By using a magnetic stirrer, an extraction can be made in an enclosed container which prevents the spread of contamination to the cell, cross contamination between extractions, and any change of volume through evaporation during the extraction period. Lucite holders, with holes drilled to support the extraction vessels, are mounted on top of the magnetic stirrers.

A rear view of Cell No. 5 is shown in Fig. 22. The cables attached to the instruments are brought into the cell through conduit embedded in the concrete cell walls and through specially designed plugs in the front wall of the cells.

Polyethylene coverings are used extensively in the cells for protection of the equipment from acids, solvents and radioactive contamination. It is easily and rapidly removed when decontamination of the cells is necessary. It is also inexpensive and can be discarded without the expense of cleaning it.

Cell No. 7 (Fig. 23) is used for analytical work requiring heat. A small fume hood containing two hot plates is used for dissolution and the fuming of samples. The cell is exhausted through the hood. The duct of the hood has a continuous flow of water down the interior walls to dilute or absorb corrosive fumes.

SUPPORTING LABORATORIES

The materials and dilutions removed from the work-cells which measure less than 1 r/hr at contact are sent into a supporting "warm" laboratory such as the one shown in Fig. 24.

Shadow shielding of stacked lead bricks is used for shielding the materials during additional chemical treatment or measurement. The groups submitting radioactive samples also require analytical chemistry on related nonradioactive samples which are analyzed in the supporting laboratories. Open racks are used for storage of the nonradioactive samples after aliquots have been removed for analysis. Samples containing high concentrations of α-emitters, but which are low in Beta activity, and Gamma activity, are analyzed in a glove box.

Another room of the supporting laboratories is shown in Fig. 25. In the Pilot-plant Control Laboratory an average of over 4000 analyses per month have been completed for the past year using the work-cells and supporting laboratories. It is staffed with 19 persons, 12 of whom are on rotating shifts operating 24 hr a day, 7 days a week.

Since many of the analyses require measurement of the α-, β- or γ-activity content, a counting room is necessary and is shown in Fig. 26. The equipment consists of a gamma ionization chamber, scintillation gamma counters, alpha proportional counters and end-window beta counters.

CONCLUSION

Since the initial operation of the High-Radiation-Level Analytical Facility in 1955, analytical chemistry has been applied to thousands of samples containing hundreds of curies each. The personnel operating it have averaged bodily radiation exposures of less than a third of the maximum permissible limits as set by the International Commission of Radiological Protection.

Acknowledgement—The author gratefully acknowledges his indebtedness to S. A. Reynolds and his Radiochemical Methods Development group, and P. F. Thomason and his Ionic Methods Development group for providing methods for many of the analyses, and also to D. J. Fisher and his Analytical Instrumentation group for providing most of the remote-controlled instruments.

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[1] E. J. Frederick, *Nucleonics*, 1954, **12**, 36.

[2] R. B. Quincy, Jr., Method Nos. 1 100 and 9 0060 (2 November, 1956) *O.R.N.L. Master Analytical Manual*, TID-7015, Section 1.

Talanta, 1960, Vol. 6, pp. 28 to 29. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF IRON IN YTTRIUM*

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Cincinnati, Ohio

Summary—An improved method for determining Fe in Y metal or Y_2O_3 was investigated further in order to determine its applicability to a wider range of samples. The method consists essentially of the extraction of Fe^{III} from a 6 *M* HCl solution into a solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane. The Fe is re-extracted into 3 *M* H_2SO_4, an equal volume of HCl is added and the Fe is again extracted with TOPO. An aliquot of the extract is used for development of the 1,10-phenanthroline complex. The method is almost specific for Fe. Only a few elements interfere, even when present in large quantities, and of these elements all but Ga, Te and Si produce a warning turbidity in the colored solution. No interference with the determination of 100 μg of Fe was caused by 10 mg of Al, Sb^{III}, As^{III}, Ba, Be, Bi, B, Cd, Ca, Ce^{III}, Ce^{IV}, Cr^{III}, Cr^{VI}, Cs, Co, Cu, Dy, Er, Eu^{III}, Gd, Ge, Au, Hf, Ho, In, I, Ir, La, Pb, Li, Lu, Mg, Mn^{II}, Mn^{VII}, Hg^{II}, Nd, Ni, Nb, Pd, P, Pt, K, Pr, Re^{VII}, Rh, Rb, Sm, Sc, Se^{IV}, Na, Sr, Ta, Tb, Tl , Th, Tm, Sn, Ti, V, Yb, Zn; 5 mg of Si, Zr; 1 mg of Mo, W, Ga; 0.1 mg of Te, or U, or 100 mg of Br or F.

PROBABLY the most popular method for determining iron colorimetrically is by means of 1,10-phenanthroline. A number of elements interfere, however, with this method of determination, and a preliminary separation is desirable. Dr. White of the Oak Ridge National Laboratory has published data concerning the extraction of the ferric chloride complex with tri-*n*-octylphosphine oxide (TOPO) which can be used to make a preliminary separation. At the 1958 Southeastern Regional Meeting of the American Chemical Society, he and his co-workers reported on a spectrophotometric method for determining iron after separating it in this manner. A number of elements still interfered, however, such as cadmium, cobalt, chromium VI, copper, nickel, etc. Based on the extraction data published by White, we have developed a method for determining iron which is nearly specific.

The sample is dissolved in hydrochloric acid, and the concentration of this acid is adjusted to 6 *M*. The iron is oxidized with bromine water, after which it is extracted with 0.01 *M* TOPO in cyclohexane. The organic extract is shaken with 3 *M* sulfuric acid, wherein the iron reverts to the aqueous phase. When large amounts of indium, hafnium or zirconium are present, the sulfuric acid solution is washed several times with a solution of 0.1 *M* TOPO in chloroform, and these wash solutions are discarded. An equal volume of hydrochloric acid is added to the sulfuric acid solution and the iron is again extracted with TOPO. An aliquot of the organic phase is taken for the development of the 1,10-phenanthroline complex. The absorbance of the complex is measured at 510 mμ. Despite the number of manipulations involved, the procedure is relatively rapid and very precise. The method is accurate to ±3 per cent or 3 p.p.m., whichever is greater, on 1 g samples.

In order to ensure that the method was indeed applicable to the samples to be analyzed, spectrographic analyses of material produced over a 2 year period were

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* Work performed under contract with the U.S. Atomic Energy Commission.

tabulated. The method was expected to be accurate when applied to material containing at least twice the maximum amount of each element found by spectrographic analysis to be present in any sample. Furthermore, the analysis was expected to be accurate in the presence of at least 100 p.p.m. of any element normally determined spectrographically. These requirements were met, as can be seen by the data given in Table I.

TABLE I.—RECOVERY OF IRON IN THE PRESENCE OF OTHER ELEMENTS

Added	Fe added, μg	Fe found, μg	Bias, μg
Y, 1 g	0 100	0 100	— —
Y, 1 g; Zn, Ca, Mg, Sn^{II}, Al, Mn^{II}, V^{V}, Pb, Ba, Cd, B, Si, Li, K, Be, Dy, Ho, Tb, Yb, Co, Ni, Mo^{VI}, Cr^{VI}, W^{VI}, Nb, 100 μg; Cu, 200 μg; Ta, 400 μg; Ti^{IV}, 4 mg; F, 5 mg; Zr, 10 mg.	100 100	97 98	−3 −2

Further investigation of the effects of sixty-eight elements in 10 mg quantities has indicated interference only from silicon, antimony, gallium, molybdenum, tungsten, tellurium and uranium at this level. No interference is caused by 5 mg of silicon, 1 mg of antimony, gallium, molybdenum or tungsten, or 0.1 mg of tellurium or uranium. When interfering amounts of antimony, molybdenum or tungsten are present, the colored solution whose absorbance is to be measured becomes turbid. Only gallium, tellurium and silicon interfere without producing this warning turbidity.

Talanta, 1960, Vol. 6, pp. 30 to 41. Pergamon Press Ltd. Printed in Northern Ireland

SOME APPLICATIONS OF HIGH-FREQUENCY TITRIMETRY

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Summary—A parallel transmission line oscillator operating at 190 Mc/s was demonstrated to be a useful instrument for the performance of high-frequency titrations. The end point is established by graphically recording either the oscillator grid current or the IR drop, which is produced by passing this current through a load resistor, versus the volume of titrant and extrapolating the two segments of the titration graph to a point of intersection. The instrument has been utilized for the titration of Th, free acid and sulfate in solutions of high ionic strength. The method is of particular value in titrating solutions containing substances which mask the color change of indicators or otherwise interfere with visual titrations. Furthermore, it appears to be adaptable for use in the titration of radioactive materials by remote control.

FOR the performance of high-frequency titrations, a vessel containing the solution to be titrated is placed in the field of a high-frequency oscillator. Then, as the reaction between titrate and titrant proceeds, changes occur in plate or grid currents or voltages, or in the frequency of the oscillator which result from variations in the composition of the solution. A plot of any one of these quantities against the volume of titrant results in a curve with a break at the end point, similar to that of a conductometric titration graph.

To locate the end point in a high-frequency titration, electrodes, indicators and physical contact of any nature with the solution are not required. The potentiality of the method, therefore, becomes apparent for titrations in which no suitable color indicators or electrodes for end point detection are available. For high-frequency titrimetry to be applicable, however, a difference must exist between the "loading characteristics" of the reactants and the products. This loading is caused by the time lag of dipoles and ionic atmospheres in reorienting themselves in response to the rapid changes in field strength which are caused by the high-frequency oscillations. When the frequency approximates the relaxation time of the dipole or ionic atmosphere, a maximum amount of energy is removed from the oscillator circuit.

A limitation of the high-frequency titration method at the present time is the inability of the commercially available oscillators, most of which operate in the range of 5–50 Mc/s, to respond to changes in fairly concentrated solutions. Debye and Faulkenhagen[1] in their work on the absorption of radio-frequency energy by electrolytes showed that, for absorption of energy to occur, the frequency of the source must increase in proportion to the concentration of the solution. Thus, whereas a 30 Mc/s instrument may respond to changes in approximately 10^{-3}–$10^{-2}M$ solutions, an oscillator operating at a frequency of hundreds of megacycles per second is required to detect changes in solutions where the electrolyte concentration is of the order of $0.1M$ or greater. The feasibility of applying high-frequency titrimetry, however, to solutions of high ionic strength was first demonstrated by Blaedel and Malmstadt[2] who reported on a 350 Mc/s titrimeter and later by Lane[3] who presented several examples of the use of a 250 Mc/s instrument in carrying out conventional titrimetric procedures.

In this work, a study was made of the application of a parallel transmission line oscillator which operates at 190 Mc/s to chemical analyses. This type of oscillator was investigated by Stelzner and Kelley[4] who made use of an in-line arrangement for the measurement of varying concentrations of alkali in aqueous solutions. As pointed out by Stelzner and Kelley, whenever radio-frequency energy is removed from the circuit, the plate current of the oscillator tube increases and the grid current decreases. Either of the two variables, plate current or grid current, may be measured. In this application, the energy loss which occurs as a consequence of the titration was observed by following the change in grid current. This was accomplished by passing the grid current through a known resistance and recording the voltage drop across the resistance with a 50 mV Brown recorder. The end point is established by extrapolating the two segments of the titration graph to a point of intersection.

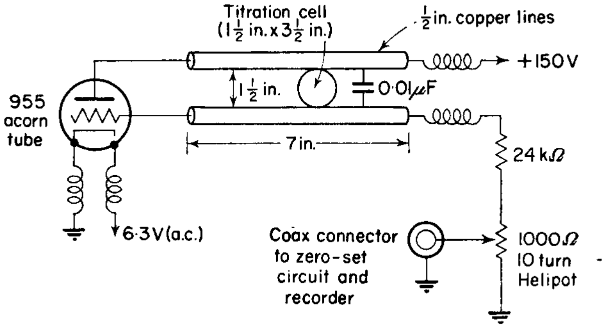

FIG. 1.—Schematic diagram of 190 Mc/s parallel transmission line oscillator.

In this study, the instrument was applied to the detection of the end point in acid-base titrations, and also the titration of free acid in solutions of uranyl sulfate, sulfate with barium, and thorium with oxalic acid and ethylenediaminetetraacetic acid (EDTA).

Description of oscillator

A simple schematic diagram of the 190 Mc/s parallel transmission line oscillator is shown in Fig. 1. The design is based on a parallel transmission line oscillator in which a type 955 acorn vacuum tube is used in a triode circuit. This type of instrument is described in detail by Stelzner and Kelley[4]. The transmission lines are 8 in. sections of copper tubing which are ½ in. in diameter and spaced 1½ in. between centers. Radio-frequency chokes are utilized to isolate the cathode and filament from r–f ground and to keep stray voltages from the power supply. The calculated Q for this circuit is approximately 4000. A holder for the titration vessel is placed between the parallel transmission lines near the shorted ends of the lines.

Description of titrimeter

A photograph of the high-frequency titrimeter, in which a 190 Mc/s oscillator is used, is shown in Fig. 2. The components are, reading from left to right, 190 Mc/s oscillator, motor-driven syringe buret, power supply for the oscillator, zero-set circuit and a 50 mV Brown recorder with a 4 sec response.

The oscillator is housed in a 6 in. by 5 in. by 9 in. metal cabinet. The parallel transmission lines run horizontally and mounted underneath them is a plastic well-type holder for the titration cell. The glass cell, which measures 1½ in. in diameter and 3½ in. in height, is inserted between the copper lines through a circular opening in the top of the housing. The volume of solution in the cell for a typical titration is about 30 ml.

The output of the oscillator is measured in terms of the voltage drop produced when the grid current flows through a known resistance. This resistance is composed of a 1000-ohm, 10-turn helipot which is incorporated into the instrument. The sensitivity of the instrument can be changed by means of the variable resistor. In the majority of cases, if the resistor is set at 500 Ω, the voltage change during a titration will be of the order of 30 mV which is adequate for recording purposes.

The delivery of titrant at a constant rate is accomplished through the use of a 900-S single-speed infusion-withdrawal pump equipped with a 2 r.p.m. synchronous motor. This device delivers 1.304 ± 0.004 ml of titrant per minute. For some of the titrations, however, an alternate motor-driven buret was utilized.

The Fluke power supply, Model 407 d.c., furnishes +150 V for the plate and 6.3 V a.c. for the filament of the 955 tube.

The output of the oscillator is connected to a zero-set circuit which is also housed in a small metal cabinet. This type of zero-set circuit is the same as described by Stelzner and Kelley[4] with the exception that a 6 V "A" battery is used instead of the 1.5 V telephone battery. With this device it is possible to position the pen of the Brown recorder at the start of a titration so that, in recording the titration graph, it will not go off scale, provided the voltage change during the course of the reaction does not exceed the full-scale deflection of the recorder.

Response curves

An idea of the response of the instrument to changes in electrolyte concentrations can be gained from Fig. 3 in which is plotted the response of the oscillator to progressively increasing concentrations of hydrochloric acid and sodium chloride. From a plot of this type, the range of electrolyte concentration over which the instrument is applicable can be ascertained. For the 190 Mc/s oscillator, it can be seen from the steep portion of the curves in Fig. 3 that the optimum response of the instrument to changes in concentration occurs when the electrolyte content of the test solutions falls within the approximate range of 10^{-2}–$1M$. This instrument can, therefore, be used on a wide range of concentrations. Outside of these limits, however, the response decreases markedly.

TITRATIONS PERFORMED

Strong acid–strong base

The response of the instrument to a typical titration of a strong acid with a strong base is illustrated in Fig. 4. The recorded titration curve for this system is very well defined and the end point can be fixed precisely by the break in the curve. When titrating approximately 0.2 mequiv. of a strong acid in a volume of 30 ml with $0.1N$ NaOH, the end point is reproducible with a coefficient of variation of about 0.6 per cent.

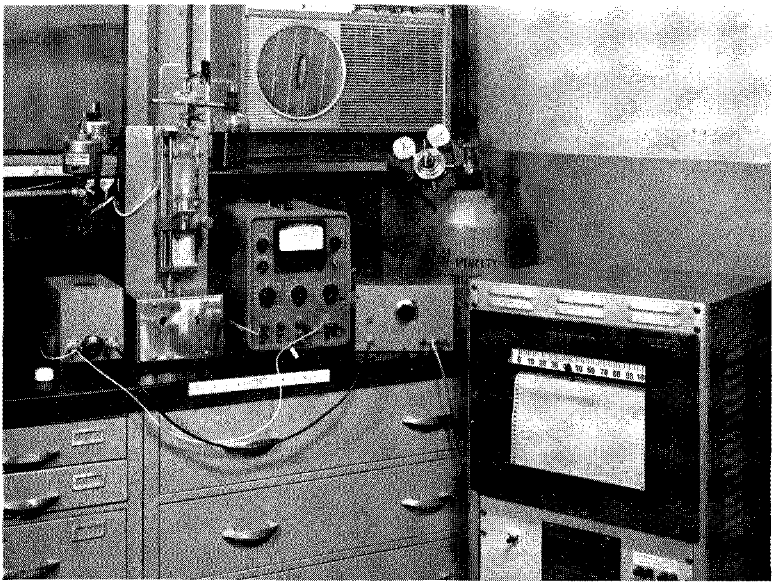

FIG. 2.—Assembled 190 Mc/s high-frequency titrimeter.

The effect of added electrolyte on the response of the oscillator to this system was evaluated by repeating the titrations after making the test solutions 0.1 *M* and 1 *M* in sodium chloride, respectively. Essentially the same shape of titration graph was

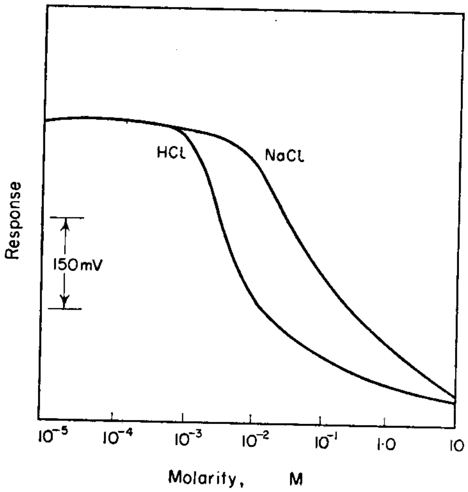

FIG. 3.—Response curves for the 190 Mc/s parallel transmission line oscillator.

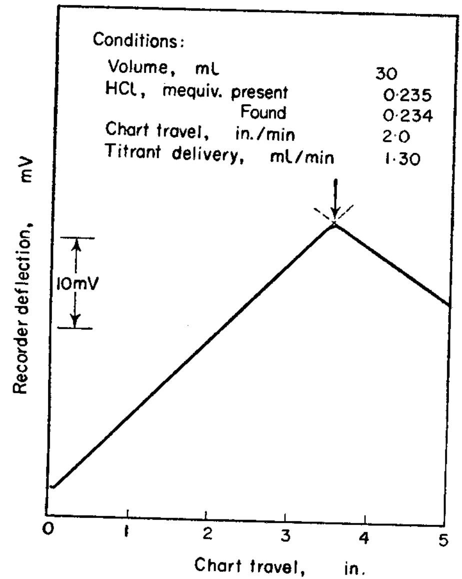

FIG. 4.—High-frequency titration of hydrochloric acid with sodium hydroxide.

btained in the presence of 0.1*M* chloride and no difficulty was experienced in locatg the end point. When the solution was 1*M* in sodium chloride, however, the lopes of the two segments of the titration curve were appreciably decreased and the reak in the graph indicating the end point could not be located with any degree of ertainty. Thus, from a practical point of view, when the 190 Mc/s oscillator is used titrating a strong acid with a strong base, the concentration of electrolyte in the st portion should be less than 1*M*.

Determination of free acid in the presence of uranium

The applicability of the instrument to the determination of free acid in the presence of hydrolyzable substances, in this case uranyl sulfate, is illustrated by the data presented in Table I and also graphically in Fig. 5.

The first end point corresponds to the neutralization of the free acid while the second end point is observed when the hydrolysis of the uranyl ion is complete. The volume of titrant consumed between the two end points is, qualitatively, or roughly quantitatively, a measure of the uranium present. Rodden[5] has also pointed out the feasibility of estimating uranium by a sodium hydroxide titration; but he further emphasized the necessity of utilizing empirical factors inasmuch as the reaction is not a truly stoichiometric one. Since the preliminary results indicated that the titration serves only as an approximation of the uranium present, further tests for the purpose of determining uranium by this technique were suspended. Relatively large amounts of uranium can be present without introducing a significant error in the free acid measurement. The coefficient of variation is of the order of 2 per cent. The uranium does not have to be removed or complexed in any way prior to the acid titration.

TABLE I.—HIGH-FREQUENCY TITRATION OF FREE ACID. EFFECT OF URANIUM

Conditions: NaOH, *N* 0.100
Delivery, ml/min 0.906
Titration volume, ml 35

Uranium, *mg*	Chart to end point, *in.*	Free acid, *mequiv.*		Percent
		Present	Found	
None	2.30	0.210	0.209	99
	2.32		0.210	100
	2.10	0.187	0.190	101
	2.10		0.190	101
14	2.00		0.181	97
	2.05		0.186	100
35	2.00		0.181	97
	2.10		0.190	101
165	2.15		0.195	104
	2.10		0.190	101
	2.15		0.195	104
	2.10		0.190	101
350	2.10		0.190	101
	2.10		0.190	101
			Average	100
			Coefficient of variation	2

Titration of sulfate with barium chloride

The results from the high-frequency titration of sulfate with barium chloride are presented in Table II and in the form of typical titration curves in Fig. 6.

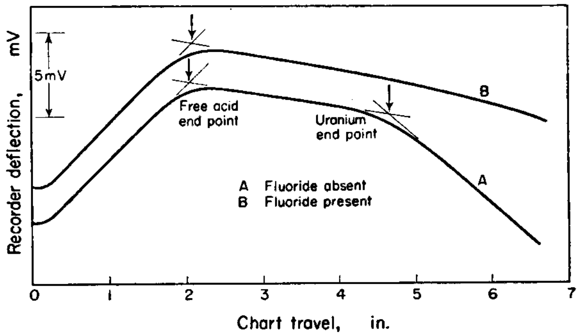

FIG. 5.—High-frequency titration of free acid and uranium with sodium hydroxide.

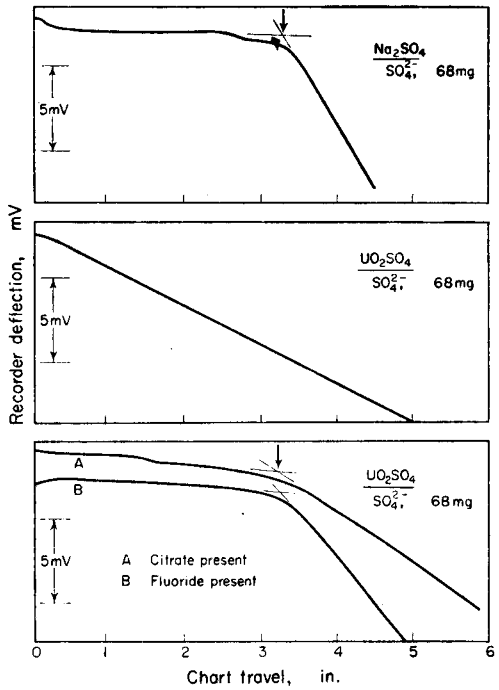

FIG. 6.—High-frequency titration of sulfate with barium chloride.

No difficulty was encountered in titrating aqueous solutions of Na_2SO_4. Well-defined titration curves were recorded as shown by the upper graph in Fig. 6. The coefficient of variation for a limited amount of data is of the order of 1 per cent.

When an aqueous solution of uranyl sulfate was titrated with barium chloride, the resulting high-frequency titration curve (middle graph, Fig. 6) essentially consisted of one continuous straight line instead of the customary two segments of different slopes. The same type of curve was obtained when attempts were made to titrate sulfate as Na_2SO_4 in the presence of uranyl nitrate. In this situation, where the reaction is

$$UO_2SO_4 + BaCl_2 \rightarrow UO_2Cl_2 + BaSO_4$$

the change in the response of the oscillator at the start of the titration is undoubtedly due to the difference between the "loading characteristics" of UO_2SO_4 and UO_2Cl_2. Beyond the end point no change in slope is observed as excess $BaCl_2$ is added. The response of the oscillator consists of one continuous straight line.

TABLE II.—HIGH-FREQUENCY TITRATION OF SULFATE WITH BARIUM CHLORIDE

Conditions: Barium chloride, *M* 0.251
Delivery, ml/min 0.906
Volume, ml 30

Substance	Medium	Chart to end point, *in.*	Sulfate		
			Present, *mg*	Found	
				mg	%
Na_2SO_4	Aqueous	3.8	82.3	81.6	99
		2.5	54	54.7	101
		2.45	54	53.8	100
				Average	100
				Coefficient of variation	1
UO_2SO_4	Aqueous	No end point	68.4	—	—
	Sodium citrate, 0.03*M*	3.2	68.4	68.5	100
		2.10	45.6	46	101
	NaF, 0.03*M*	2.16	45.6	47	103
	NaF, 0.1*M*	2.12	45.6	46.2	102
		3.17	68.4	69.4	101
		2.10	45.6	46.0	101
		2.10	45.6	46.0	101
		2.45	54	53.8	100
		2.45	54	53.8	100
				Average	101
				Coefficient of variation	2

It is possible, however, to titrate the sulfate in a uranyl sulfate solution if a complexing agent such as sodium citrate or fluoride is added. When this is done, the uranyl ion is masked and remains inactivated throughout the titration of the sulfate which is now present as Na_2SO_4. In fact, the titration graphs (curves A and B, Fig. 6) resemble those obtained with solutions of sodium sulfate. Sodium fluoride was found to be preferable to the citrate as a masking agent because, with the fluoride, the titration curves are better defined. Also, the concentration of the fluoride is less critical than citrate. Whereas 50 mg of sulfate as uranyl sulfate can be titrated satisfactorily in sodium fluoride solutions ranging from 0.03 to 0.1*M* (optimum concentration, 0.1*M*), when citrate is used, the citrate concentration must be carefully controlled within the range of 0.03–0.05M, to attain satisfactory results. When masking agents are used, sulfate can be determined in uranyl sulfate solutions by this method with a coefficient of variation of 2 per cent or less.

Titration of thorium with oxalic acid

High-frequency titrations of thorium with oxalic acid were carried out both manually and automatically. A representative titration curve which was recorded manually is presented in Fig. 7. The oscillator response was measured directly as a voltage drop across a 500 Ω resistor in the grid circuit after the addition of each increment of titrant. It is of interest to note when thorium is reacted with oxalic acid, in an unbuffered solution having a pH of approximately 3, two breaks are obtained in the high-frequency titration graph as illustrated in Fig. 7. It appears probable from these observations that the formation of the insoluble thorium oxalate occurs stepwise, according to the reactions:

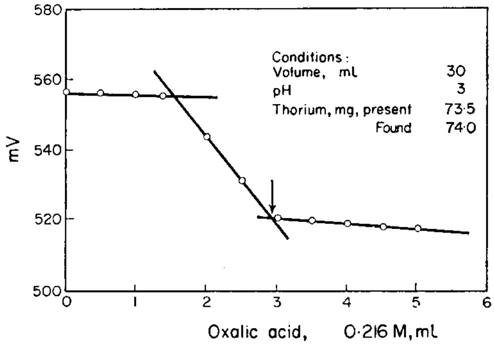

FIG. 7.—Titration of thorium with oxalic acid.

$$Th^{4+} + H_2C_2O_4 \rightarrow Th(C_2O_4)^{2+} + 2H^+ \qquad \text{(first break)}$$

$$Th(C_2O_4)^{2+} + H_2C_2O_4 \rightarrow Th(C_2O_4)_2 + 2H^+. \qquad \text{(first break)}$$

The second break is taken as the end point because the first break is not reproducible enough for quantitative purposes. It was also noted that, in order to obtain two breaks, the pH of the test solution must be at least 3 at the beginning of the titration. When the titrations were performed in more acidic solutions, only one break corresponding to the second break of Fig. 7 was obtained, as illustrated graphically by curve B of the titration graphs in Fig. 8. Other than obscuring the first break in the titration curve, the pH of the solutions to be titrated is not a critical factor. The titrations can be successfully carried out at any pH within the range of 1.5 to 3.5. When determining thorium in amounts of the order of 50–100 mg, the coefficient of variation is approximately 2 per cent.

Titration of thorium with ethylenediaminetetraacetic acid (EDTA)

The applicability of the high-frequency titrimeter to the complexometric titration of thorium with EDTA was studied. In view of recent interest in the determination of thorium in the presence of moderate quantities of uranium, aluminum and corrosion products of stainless steel, the effect of these substances (with the exception of nickel and chromium) on the high-frequency titration of thorium was ascertained. The results of these tests are presented in Table III and graphically in the form of titration curves in Figs. 9, 10 and 11. Finally, in view of the fact that conventional EDTA titrations of thorium with indicators are usually performed in acetate-buffered solutions, it was of interest to evaluate the effect of acetate, i.e. moderately buffered solutions, on the high-frequency titrations. The results of this study are shown graphically in Fig. 12.

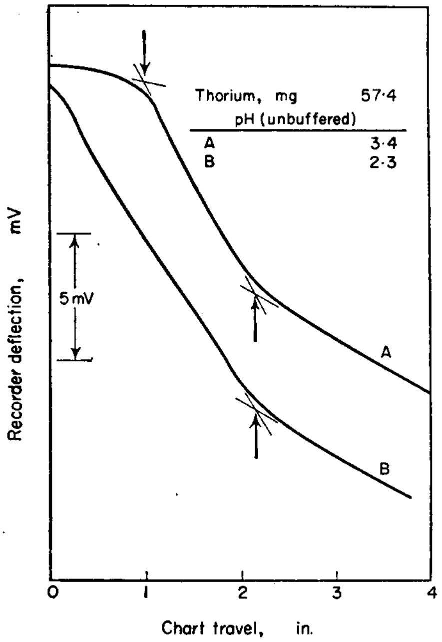

FIG. 8.—High-frequency titration of thorium with oxalic acid. Conditions: oxalic acid, *M*, 0.236; delivery, 0.98 ml/min; chart travel, 2.0 in./min.

TABLE III.—TITRATION OF THORIUM WITH EDTA

Conditions: EDTA, *M* 0.144
Delivery, ml/min 1.30
Chart travel, in./min 2.00
pH (unbuffered) 2.7

Inches of chart to end point	Thorium, *mg*	
	Present	Found
2.66	58	58.2
2.60		57.0
2.62		57.4
2.64		57.8
2.67		58.5
2.61		57.2
2.60		57.0
2.62		57.4
	Average	57.6

It is evident from the results listed in Table III that the 190 Mc/s oscillator provides an accurate means of locating the end point when thorium is titrated with EDTA. A quantitative titration is realized with a coefficient of variation of 1 per cent or less. This compares favorably with visual titrimetric methods for thorium. The governing factor in obtaining reproducible results is the location of the end points from an extrapolation of the two segments of the graph to a point of intersection. In many

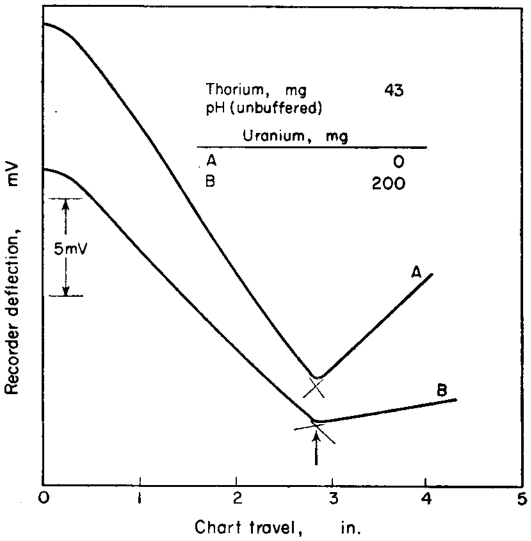

FIG. 9.—Effect of uranium on the high-frequency titration of thorium with EDTA. Conditions: EDTA, *M*, 0.0712; delivery 1.3 ml/min; chart travel, 2.0 in./min.

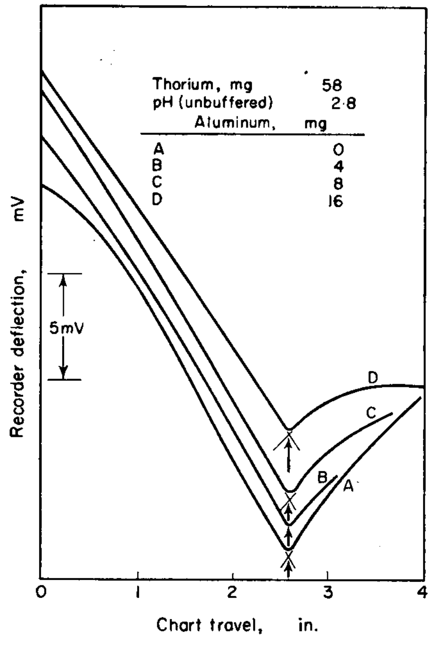

FIG. 10.—Effect of aluminum on the high-frequency titration of thorium with EDTA. Conditions: EDTA, *M*, 0.144; delivery, 1.3 ml./min; chart travel, 2.0 in./min.

instances, however, a very sharp break in the curve is obtained, and an extrapolation is unnecessary.

As is indicated by Figs. 9, 10 and 11, relatively large quantities of uranium and moderate quantities of aluminum and iron^{II} can be tolerated without introducing a significant error in the thorium measurement. Iron^{III} cannot be tolerated as this substance reacts with EDTA along with the thorium. Larger quantities of these interfering substances were not tested since the upper limit already explored far exceeded the amount that would be present in a typical test portion to be analyzed for thorium. Nickel and chromium remain yet to be studied; however, it is expected that moderate quantities of these elements will likewise not interfere.

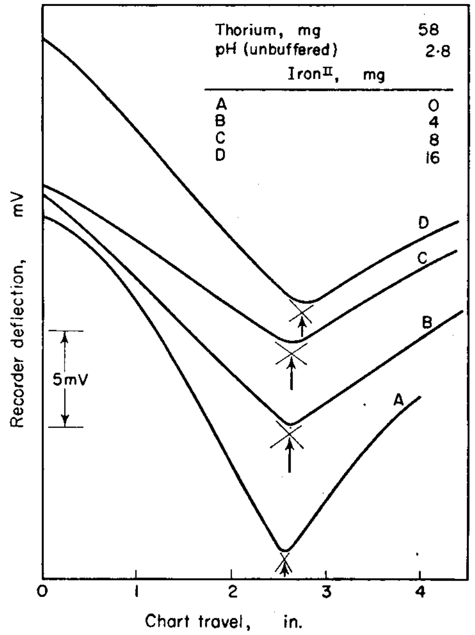

FIG. 11.—Titration of thorium with EDTA. Effect of iron^{II}. Conditions: EDTA, *M*, 0.148; $NH_2OH.HCl$, mg 200; delivery, 1.3 ml/min; chart travel, 2.0 in./min.

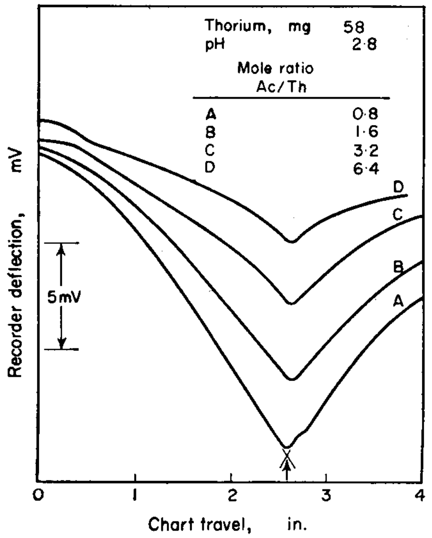

FIG. 12.—Titration of thorium with EDTA. Effect of acetate. Conditions: EDTA, *M*, 0.144; delivery, 1.3 ml/min; chart travel, 2.0 in./min.

The effect of acetate on the high-frequency titration curves is illustrated in Fig. 12. In general, as long as the mole ratio of acetate to thorium does not exceed 3, it makes no difference whether the solution titrated is moderately buffered or not. Nothing is gained, however, by the addition of acetate and, in fact, the titration curves recorded from unbuffered solutions are generally better defined. In the presence of large quantities of acetate, the curve becomes poorly defined although it is still possible to locate the end point.

It is to be concluded from these studies that the high-frequency titrimetric procedure appears to be a relatively precise method for determining thorium under conditions where the only other alternatives would be to use a lengthy gravimetric procedure, a potentiometric titration using the Hg–EDTA electrode, or a less precise colorimetric method. The time required for a high-frequency titration, including aliquoting and pH adjustment, is less than 10 min.

CONCLUSION

It is concluded that the parallel transmission line oscillator is a useful instrument that can be utilized to follow chemical changes in rather complex solutions. The simplicity of the oscillator circuit combined with good stability qualities make it attractive as a high-frequency titration instrument.

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Talanta, 1960, Vol. 6, pp. 42 to 45. Pergamon Press Ltd. Printed in Northern Ireland

X-RAY ABSORPTION EDGE ANALYSIS*

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Summary—Very few industrial laboratories are using the X-ray absorption edge method of analysis at the present time. Without a doubt, it will be used much more in the future, for it has several advantages over other methods. Probably the greatest advantage is the relative freedom from interferences, both direct and matrix. Most elements will have little or no interference, but a few elements will have a direct interference from the absorption edge of one or two elements. Secondly, a wide range of elements can be determined; it should be possible to determine all elements from chromium on, in the table of atomic numbers. In addition, the precision and the accuracy of the method are fairly good. For Zr a relative standard deviation of 1 per cent has been obtained for concentrations down to 1 mg/ml, 3 per cent for 0.2 mg/ml, and 50 per cent for 0.05 mg/ml. Means to improve the precision and accuracy of the method are being planned. The method is also fairly fast. If the sample is in solution, the determination of each element requires from 15 min to 1 hr. Other advantages are that any number of elements can be determined in the same solution, the solution is not consumed or contaminated during the analysis, and only a small amount of solution (0.2–2 ml) is required.

Disadvantages of the X-ray absorption edge method are that elements of low atomic number cannot be determined by this method, and the equipment required is expensive. A satisfactory instrument will cost $15,000 to $20,000.

A NUMBER of chemical determinations are difficult or slow by ordinary methods. It has been shown that some of these determinations can be made quickly and accurately by the use of X-ray fluorescence. When X-ray fluorescence was tried at the Oak Ridge National Laboratory, however, it was found to be unsatisfactory for the accurate quantitative analysis of the variety of samples we receive. By the time we could work out a good set of working curves and correction factors, the people had completed the experiment and had gone to another phase of the project and were submitting a different type of sample. We just could not keep up with the changes that were taking place at the laboratory.

While in another laboratory, the author had done some work on the analysis of uranium by the X-ray absorption edge method. This method was found to be accurate and essentially free from interferences. In fact, it has been used satisfactorily for routine analyses in a service laboratory for some time.

The X-ray absorption edge method uses white X-ray radiation. At a certain wavelength in the white X-ray radiation (the excitation potential of the element to be determined), there is an abrupt change in the absorption coefficient of that element. This abrupt change is referred to as the absorption edge. The position of the absorption edge is different for each element and the magnitude of the break is a function of the amount of the element present. By taking readings on both sides of the absorption edge (Fig. 1), it is possible to make a quantitative analysis for the element. Such analyses are usually performed on solutions.

There are three L absorption edges and also one K absorption edge for each

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* Work performed under contract with the U.S. Atomic Energy Commission.

element. In a few cases the absorption edge of one element will interfere with an edge of another element, but most elements will have no interferences. The direct overlapping of absorption edges is the only type of interference that will give trouble with the X-ray absorption edge method.

This method is applicable to a wide range of elements. It should be possible to determine all elements from chromium up, in the table of atomic numbers. In addition, the precision and the accuracy are fairly good. If the sample is in solution, the determination of each element requires from 15 min to 1 hr. Other advantages are that any number of elements can be determined in the same solution, the solution is not consumed or contaminated during analysis, and only a small amount (0.2–2 ml) is required.

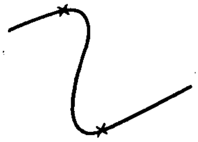

FIG .1.

Disadvantages of the X-ray absorption edge method are that the elements of low atomic number cannot be determined by this method, and the equipment required is expensive. A satisfactory instrument will cost $15,000 to $20,000. Since the equipment is fairly complicated and must be kept in excellent condition, the services of a competent electronic man will be required occasionally.

The equipment required is the X-ray diffractometer with a single crystal replacing the powder sample and the absorption cell mounted between the collimator and the crystal. The X-ray source must be well regulated. Due to the high counting rates (up to 20,000 counts/sec) a low resolving time detection system is needed. In order to correct for resolving time losses, it is necessary to have a constant potential filter. The absorption cell must be mounted in a very reproducible position, perpendicular to the beam.

A consideration of the advantages and disadvantages of the X-ray absorption edge method seemed to indicate that this method would be quite satisfactory for analysis at the Oak Ridge National Laboratory. We had a GE XRD-5 with a constant potential filter and special detection equipment. The equipment seemed adequate, so we decided to try this method.

The basic equation for X-ray absorption is

$$I_\lambda = I_{0\lambda} e^{-\sum_i \mu_{m_i} l C_i}$$

where I_λ is the observed intensity, $I_{0\lambda}$ is the incident intensity, e is the base of natural logarithms, μ_{m_i} is the absorption coefficient of an element at one wavelength, l is the cell length in centimeters, and c is the concentration in grams of element per gram of sample. The total absorption is the summation of all the individual absorptions. To obtain the absorption coefficient for an element, the equation may be written in the form

$$\mu_m = \frac{2.303}{lC} \log_{10} \frac{T_\lambda}{T_{b\lambda}}$$

where T_λ is the time for a specified number of counts at wavelength λ, and T_{b_λ} is the time for the same number of counts at the same wavelength for a blank containing everything except the element for which the absorption coefficient is being obtained. By obtaining the absorption coefficient, μ_m, at two wavelengths, λ_1 and λ_2, the equation may be written in the form

$$C = \frac{2.303}{\Delta\mu_m l} \log_{10} \frac{T_{\lambda_1}}{T_{\lambda_2}} \frac{T_{b\lambda_2}}{T_{b\lambda_1}}$$

where T_{λ_1} is the time for a specified number of counts on the short wavelength side of the absorption edge, and T_{λ_2} is the time for the same number of counts on the long wavelength side of the absorption edge. $T_{b\lambda_1}$ is the time for a specified number of counts for a blank on the short wavelength side of the absorption edge, and $T_{b\lambda_2}$ is the time for the same number of counts for the blank on the long wavelength side of the absorption edge. $\Delta\mu_m$ is the difference in the absorption coefficient at the two wavelengths.

By taking the time for a specified number of counts at λ_1 and λ_2 with a series of Al foils, it has been found that the slope of the white radiation curve changes with the amount of absorbing material in the beam. It has also been found, using other types of foils, that the slope at a given wavelength (i.e. $T_{b\lambda_1}/T_{b\lambda_2}$) is almost independent of the atomic number of the absorbing material. This indicates that the $T_{b\lambda_2}/T_{b\lambda_1}$ or blank ratio (BR) could be read from a curve and a blank would not have to be determined for each sample. The curve was set up by plotting the time for a specified number of counts at λ_1 against the blank ratio. The data for this curve were determined by back calculating to the required blank ratio from a set of standard samples.

It has also been found that there is a change in the slope of the white radiation curve near the absorption edge. This may account for the fact that the concentration of the element has a slight effect on the calculated concentration of that element. This effect may be corrected for by applying a concentration correction,

$$CK \frac{T_{\lambda_1}}{T_{\lambda_2}},$$

where CK is the concentration constant.

The equation now takes the form

$$C = \frac{2.303}{\Delta\mu_m l} \log_{10} \frac{T_{\lambda_1}}{T_{\lambda_2}} BR - CK \frac{T_{\lambda_1}}{T_{\lambda_2}}$$

where BR is the blank ratio and CK is the concentration constant.

The solutions used for standards for the determination of Zr were made from pure Zr metal. The calculated concentrations were obtained using the above equation. The percentage error, both observed and theoretical, was based on a single determination.

Recovery of zirconium was tested for both pure and contaminated Zr solutions. The results are shown in Table I.

It is evident that recovery of zirconium was satisfactory over a wide range of concentration, regardless of the presence of impurities.

It will be noted from the data presented in Table I that the observed error was well below the expected limit of error in a few cases. Of course, this could not be done consistently. The theoretical limit of error is based on statistical considerations only and assumes that all other errors are quite small.

With X-ray absorption edge analysis, it makes no difference whether the impurity is in the solution in the cell or in the beam outside the cell. The components of stainless steel, Y, and U were in the solution in the cell and the Al was outside the cell. The elements selected as impurities were chosen because they have absorption edges near the Zr K absorption edge and were the most likely elements to cause trouble. Since all the data were within the expected limit of error, the impurities evidently cause little or no interference.

TABLE I.—RECOVERY OF Zr IN PURE AND CONTAMINATED Zr SOLUTIONS

Actual Zr concentration, *mg/ml*	Actual impurity concentration, *mg/ml*	Observed Zr concentration, *mg/ml*	Error observed, %	Theoretical limit of error, %
25.04	0.00	25.04	<0.1	0.1
5.007	0.00	5.006	<0.1	0.2
1.001	0.00	1.009	0.8	0.9
0.200	0.00	0.203	1.5	4.6
2.003	4.12 NiMo Alloy*	2.011	0.4	0.8
2.003	1.00 Y	2.008	0.2	0.8
2.003	3.01 U	2.017	0.7	0.8
0.200	~20.00 Al	0.201	0.5	8.0

* Composition: 72 per cent Ni, 5 per cent Cr, 20 per cent Mo, 3 per cent Fe.

The X-ray absorption edge method has been used for several months for the analysis of Zr in a variety of samples. Zr-containing alloys, solutions from solubility studies and precipitates and residues from chemical reactions have been analyzed. Unknown to us, those submitting samples have put known standards in with their samples. We have consistently checked the standards within our limits of error. Also, the material balances obtained using our data have been good.

For the varied type of work done at the Oak Ridge National Laboratory, the X-ray absorption edge method looks very promising.

I would like to express my appreciation to Mr. Cyrus Feldman for his help and encouragement on this project.

Talanta, 1960, Vol. 6, pp. 46 to 51. Pergamon Press Ltd. Printed in Northern Ireland

X-RAY FLUORESCENCE SPECTROGRAPHIC DETERMINATION OF IMPURITIES AND ALLOYING ELEMENTS IN TANTALUM CONTAINER MATERIALS*

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Summary—X-ray fluorescence methods have been used for determining molybdenum, niobium, thorium, tungsten, yttrium and zirconium as impurities or alloying constituents in tantalum and binary tantalum alloys being investigated as container materials for molten plutonium fuels. Various solvents were tested for dissolving tantalum samples, and hydrofluoric acid was found to be the most suitable. Samples are dissolved in hydrofluoric acid and diluted to a known volume; then the solution is analyzed by means of an X-ray tube with a tungsten target. X-ray tube operating conditions and counting times were selected to give good precision in a minimum time. Effects of impurities and variations in X-ray tube voltage and current, scintillation counter voltage, solvent composition, dilution volume and count rate were determined.

Molybdenum, niobium and zirconium as impurities in tantalum within the concentration range of 25–2000 p.p.m. are determined by means of a line-to-background intensity-ratio method with a precision ranging from 17 p.p.m. at the 25–100 p.p.m. level to 43 p.p.m. at the 2000 p.p.m. level. From 0.5 to 10 per cent of tungsten in tantalum–tungsten alloys is determined with an absolute standard deviation of 0.09 per cent by comparing the intensity ratio of the tungsten L_{α_1} to tungsten $L_{\alpha\text{Compton}}$ for the sample with ratios obtained for known standards. Thorium or yttrium in binary alloys is determined in the 0.025 to 10 per cent concentration range, using an internal standard procedure. Thorium is added as an internal standard in the determination of yttrium, and yttrium is added as an internal standard in the determination of thorium. Following sample dissolution, the ThF_4 and YF_3 precipitates are separated from the tantalum, dissolved in H_2SO_4 and diluted to volume, and the intensity ratio of the thorium to yttrium lines is measured. Relative standard deviations of 7 and 2 per cent, respectively, were obtained in the 0.025–0.1 and 0.1–10 per cent concentration ranges for yttrium, and 12 and 3 per cent for thorium in the 0.025–0.1 and 0.1–10 per cent concentration ranges.

INTRODUCTION

HIGH-PURITY tantalum metal and various tantalum alloys are being investigated as container materials for molten plutonium reactor fuels. The concentration of numerous impurities as well as alloying constituents in a sample must be accurately known in order to evaluate its applicability under reactor conditions. Molybdenum, niobium and zirconium are expected to occur in high-purity tantalum metal as impurities in amounts up to 2000 p.p.m. Tungsten in the concentration range of 0.5–10 per cent, and thorium and yttrium in the range of 0.025 to 10 per cent were considered as possible alloying constituents with tantalum. Because X-ray fluorescence spectroscopy offers a rapid method of analysis for most metallic elements, its application to the determination of these elements in tantalum was investigated.

APPARATUS

A North American Philips three-position-head X-ray spectrograph with a Philips FA60 tungsten-target X-ray tube was used in this work. The optical arrangement

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

consisted of a $\frac{1}{8}$ in. source collimator, lithium fluoride crystal with a 2*d* spacing of 4.0276 Å, Philips Type 52189 receiving collimator, and a sodium iodide–thallium iodide scintillation counter. Voltage to the counter was supplied from a Baird Atomic Model 312A Super Stable High Voltage Power Supply. In the determination of tungsten, an Atomic Instrument Company Model 510 single-channel pulse-height analyzer was also used. The inside of the stainless-steel sample cell provided with the instrument was coated with paraffin to prevent dissolution by the concentrated hydrofluoric acid used in the determinations.

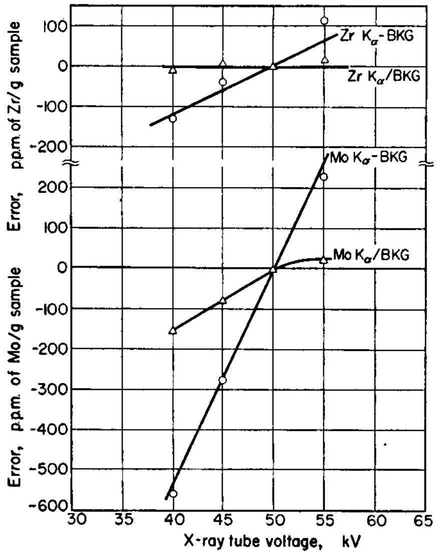

FIG. 1.—Effect of X-ray tube voltage on the X-ray spectrographic determination of molybdenum and zirconium in tantalum.

SAMPLE PREPARATION

Various methods were investigated for obtaining either solid or liquid solutions of the tantalum samples. Fusion with borax, pyrosulfate or sodium hydroxide proved time consuming and unsatisfactory. Tantalum is slowly dissolved by concentrated hydrofluoric acid, and the reaction can be hastened with a drop or two of nitric acid. Because 2 or 3 ml of 35% hydrofluoric acid will hold 1 g of tantalum in solution, this acid was selected as the solvent. Weighed samples are dissolved overnight in 48% hydrofluoric acid, evaporated to 2 or 3 ml on a hot plate, transferred to a quartz 5-ml volumetric flask, and diluted to volume with 35% hydrofluoric acid.

DETERMINATION OF 25–2000 p.p.m. OF MOLYBDENUM, NIOBIUM AND ZIRCONIUM IN TANTALUM

In the determination of 25–2000 p.p.m. of molybdenum, niobium and zirconium in 1-g tantalum samples, scattered background radiation was used as an internal standard to reduce errors caused by daily fluctuations in line voltage, variations in X-ray tube voltage and current settings, fluctuations in noise of the electronic circuitry, and errors in sample preparation. The use of scattered radiation as an internal standard has been discussed by Andermann and Kemp[1]. As an example, Fig. 1 shows that, in the determination of molybdenum and zirconium, the effect of varying the X-ray tube voltage is less on line-to-background intensity ratio than on line intensity corrected for background. Variations of X-ray tube current and scintillation counter voltage also show a lesser effect on the line–background intensity ratio than on line intensity corrected for background. Likewise, errors due to dilution and variations of hydrofluoric acid concentration are minimized by using the ratio method.

A total of 128,000 counts are accumulated at the K_α lines for molybdenum, niobium and zirconium, and at the background 24.00° 2θ. To eliminate bubble formation on the Mylar window of the sample cell during the long counting times involved, the window is coated with a nonwetting agent such as Desicote. The total of 128,000 counts is required in order to obtain a statistical counting error sufficiently small to yield a sensitivity approaching 25 p.p.m.

TABLE I.—STANDARD DEVIATIONS FOR X-RAY SPECTROGRAPHIC DETERMINATION OF Mo, Nb AND Zr IN Ta

Concentration range, p.p.m.	Standard deviation, p.p.m.		
	Mo	Nb	Zr
0–125	16	24	19
300–800	–	22	25
900–1100	31	35	30
1400–1600	—	37	36
1800–2000	54	34	36

The standard deviation of the procedure was determined at various concentration levels for each of the elements studied. Fourteen determinations were made at each point and values obtained are shown in Table 1.

In Table II, niobium concentrations, as determined by the X-ray spectrographic procedure, are compared with values obtained by a spectrophotometric procedure in which the niobium is separated by ion exchange and determined as the thiocyanate complex. Each value shown is the result of one determination. Assuming the chemical values to be correct, only one X-ray value exceeds the 95 per cent confidence limits of two standard deviations.

DETERMINATION OF 0.5–10 PER CENT OF TUNGSTEN IN TANTALUM

The L_{α_1} line for tunsgten was selected for this work because it is the most intense line available and it is not subject to errors from overlap of lines of other elements expected to be present. To correct for errors caused by fluctuations in X-ray tube voltage and current, incoherent or Compton scattered radiation was selected as an internal standard. By comparison of line–Compton intensity ratio and line intensity corrected for background, it was indicated that the internal standard procedure is more precise. Coefficients of variation of 7 and 1 per cent were determined for the ratio method at the 1 and 7 per cent tungsten concentration levels compared to 12 and 3 per cent, respectively, using line intensity corrected for background intensity.

Because niobium in varying concentrations was expected in most samples, the use of a pulse-height analyzer was investigated for eliminating interference of the second order niobium K_α line with the Compton line for tungsten. Although each 0.1 per cent of niobium caused a negative absolute error of 0.06 per cent in tungsten values when no discrimination is used, 3 per cent of niobium causes no error when a pulse-height analyzer is used.

Because the intense L_{α_1} line of tantalum at 44.41° 2θ slightly overlaps the Compton line at 43.75° 2θ, care must be exercised in setting the goniometer. An absolute error of 0.28 per cent in tungsten concentration is caused by a 0.01° 2θ error in goniometer setting. The goniometer setting is approached from the high-energy side each time to avoid backlash in the dial, and standards are analyzed daily to observe any drift in the goniometer calibration.

TABLE II.—COMPARISON OF X-RAY AND SPECTROPHOTOMETRIC METHODS FOR DETERMINATION OF Nb IN Ta

Nb found, *p.p.m.*	
X-ray	Spectrophotometric
120	123
45	78
90	76
55	66
395	420
285	309
1055	1095
95	97
65	60
695	694
50	57
80	67
600	671

For samples containing more than 7 per cent of tungsten, a portion of sample containing 20–70 mg of tungsten is diluted to 1.00 g with high-purity tantalum. This dilution is necessary because it is difficult to maintain more than 70 mg of tungsten in solution during preparation of the sample.

The standard deviation of the procedure, as calculated from twelve to fourteen determinations at each of the concentrations, 1, 5 and 7 per cent of tungsten in 1.00 g samples, was 0.07, 0.10 and 0.09 absolute per cent, respectively. One analyst can perform twenty to thirty determinations per day.

DETERMINATION OF 0.025–10 PER CENT OF YTTRIUM AND THORIUM IN TANTALUM

Samples containing yttrium or thorium are dissolved in hydrofluoric acid as previously described. However, because thorium and yttrium are insoluble in hydrofluoric acid which is the best solvent for tantalum, a separation from tantalum is necessary.

For the determination of yttrium in tantalum, a sample containing 0.25–5 mg of yttrium is dissolved with 48 per cent hydrofluoric acid and a few drops of nitric acid and 3.00 mg of thorium as the nitrate solution are added. The sample is evaporated to a volume of 3–5 ml, transferred to a 15-ml Pyrex centrifuge cone, diluted to 10 ml with water, and centrifuged for 5 min. The precipitate is washed with two 10-ml portions of dilute hydrofluoric acid, four drops of concentrated sulfuric acid are added, and the mixture is evaporated to fumes in a platinum dish. The soluble sulfate residue is transferred to a 5-ml volumetric flask and diluted to volume with water. The time to accumulate 64,000 counts is measured at the K_α line for yttrium and the L_{α_1} line for thorium, and the intensity ratio is compared to ratios obtained for known standards. Standards are prepared by diluting 3.00 mg of thorium as the nitrate solution, four drops of sulfuric acid and various amounts of yttrium to 5 ml with water. If the intensity of the internal standard line for the samples varies by more than 6 per cent from intensities obtained for standards, a poor separation is indicated and the sample is discarded.

TABLE III.—INTERFERENCE OF Al, La, Ta AND H_2SO_4 WITH THE X-RAY SPECTROGRAPHIC DETERMINATION OF THORIUM

Thorium 3.00 mg

Interfering substance	Th/Y ratio		Th L_{α_1} line intensity	
	Th found, *mg*	Error, %	Th found, *mg*	Error, %
Al, 5 mg	2.98	−0.7	3.03	+ 1.0
10 mg	3.01	+0.3	3.00	0
La, 5 mg	2.94	−2.0	2.98	− 0.7
10 mg	2.92	−2.7	2.88	− 4.0
15 mg	2.92	−2.7	2.83	− 5.7
Ta, 1 mg	3.05	+1.7	3.07	+ 2.7
2 mg	2.96	−1.3	2.92	− 2.3
H_2SO_4, 0 drops	3.19	+6.3	3.43	+14.3
4 drops*	3.01	+0.3	3.00	0
6 drops	2.96	−1.3	2.81	− 6.3
10 drops	2.90	−3.3	2.57	−14.3

* Standard procedure.

The procedure for determining thorium is similar to that described for yttrium except the sample size is adjusted to contain 0.25–7 mg of thorium, and 1.00 mg of yttrium is added as an internal standard.

Errors in the determination of thorium attributable to various amounts of aluminum, lanthanum, tantalum and sulfuric acid were studied. Solutions were prepared in the same manner as standards, with no precipitation or centrifugation, and the amount of impurity indicated in Table III was included. These results show that interferences are minimized or eliminated by using the internal standard rather than the line-intensity procedure.

Because no standard alloys of yttrium or thorium with tantalum are available, the reliability of the method is based upon samples prepared by adding known amounts of yttrium or thorium as nitrate solution to weighed amounts of tantalum metal dissolved in 48 per cent hydrofluoric acid. In the concentration range of 0.025–0.075 per cent, 0.25–0.75 mg of yttrium or thorium was added to 1-g samples of high-purity tantalum. In the concentration range of 0.10–10 per cent, samples were taken which contained 1–5 mg of yttrium or 1–7 mg of thorium. Average recoveries and coefficients of variation are shown in Table IV.

TABLE IV.—RECOVERY OF 0.025–10 PER CENT OF Y OR Th FROM Ta

Element determined	Concentration range, % in Ta	Number of samples	Average recovery, %	Coefficient of variation, %
Y	0.025– 0.075	9	103	7
Y	0.10 –10	33	100.1	2
Th	0.026– 0.075	6	98.7	12
Th	0.10 –10	18	100.2	3

TABLE V.—PRECISION FOR DETERMINING Mo, Nb, Zr, W, Y AND Th IN Ta

Element determined	Concentration range	Coefficient of variation
Nb	100 p.p.m.	24
	1000 p.p.m.	3.5–4
	2000 p.p.m.	1.7–2
Mo	100 p.p.m.	16
	1000 p.p.m.	3.1–3
	2000 p.p.m.	2.7–3
Zr	100 p.p.m.	19
	1000 p.p.m.	3
	2000 p.p.m.	1.8–2
W	1%	7
	5%	2
	7%	2
Y	0.025–0.075%	7
	0.10 –10	2
Th	0.205–0.075%	12
	0.10 –10	3

By using the internal-standard technique for determining thorium or yttrium in tantalum, corrections are made for variations in sample composition as well as for small sample losses during sample preparation. The procedure shows no bias in the recovery of yttrium or thorium from tantalum, whereas calculations based on line intensity show a negative bias of 3.2 per cent for the recovery of thorium.

REFERENCES

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Talanta, 1960, Vol. 6, p. 52. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF MODERATOR TURBIDITY PARTICLE SIZE BY AN ANGULAR-DEPENDENT LIGHT-SCATTERING TECHNIQUE*

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Summary—In the characterization of the moderator in heavy-water reactors, information is frequently required concerning the size of the suspended particulate matter. A rapid analytical procedure adaptable to routine control has been developed whereby the particle-size distribution may be derived from angular-dependent light-scattering measurements. A commercial instrument, the Meeco Scattermaster, designed originally for measurements on transparent films, has been adapted for use with liquid samples. Measurements are made of the intensity of the light scattered by the sample over a wide angular range, and converted to a special graphical form in which log $I\theta^2$ is plotted against log θ, where I is the light intensity and θ is the angle of scattering.

This method is based on the assumption that a light-scattering curve for a distribution of size groups is a composite curve in which the individual contributions of the size groups appear as steps in the decline of intensity with angle.

Although not quantitative, the method is, under controlled conditions, capable of providing the following semiquantitative information: uniformity of particle size, presence of particles in a specific range, maximum particle size and most frequent particle size.

This analytical procedure is applicable to particle matter ranging from 0.2–50 μ in diameter.

Particle-size distributions determined by this method on mono- and poly-disperse systems of polystyrene spheres and on representative moderator samples are in satisfactory agreement with the distribution data obtained with the electron microscope.

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* Work performed under contract with the U.S. Atomic Energy Commission.

ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

SECTION II. THE ANALYTICAL CHEMISTRY OF FUELS

Talanta, 1960, Vol. 6, pp. 55 to 62. Pergamon Press Ltd. Printed in Northern Ireland

THE ANALYSIS OF A LIQUID METAL REACTOR FUEL*

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Summary—A procedure has been developed for the analysis of a uranium–molten bismuth fuel containing 1400 p.p.m. of uranium-235, 350 p.p.m. of magnesium and 250 p.p.m. of zirconium. Analyses are performed for the above elements and for the corrosion products, iron, nickel, chromium and manganese. The activity of the bismuth is approximately 0.2 r hr^{-1} g^{-1} at one foot and contains an approximate alpha activity of 10^9 d min^{-1} g^{-1} in the form of polonium-210.

The sample is dissolved in 50% nitric acid, whereupon zirconium and iron can be extracted directly by 0.5*M* 2-thenoyltrifluoroacetone in xylene. The absorbance due to the iron complex is measured directly on the organic phase. The zirconium is stripped into a fluoride solution and determined spectrographically.

For magnesium and the remaining corrosion products, an aliquot of the original solution is diluted tenfold. The polonium along with the bismuth is extracted by a 0.5*M* solution of the acid chloride form of tri-iso-octylamine in methyl isobutyl ketone. Three contacts are sufficient to reduce a solution originally containing alpha activity of 10^7 to less than 10^2 d min^{-1} ml^{-1}.

To decontaminate the aqueous solution from rare earth elements, a praseodymium fluoride precipitation is used. Finally, to decontaminate from the alkali and alkaline earth elements, bismuth hydroxide is used to coprecipitate the magnesium and corrosion products. This precipitate is then dissolved in such a way that the usual matrix for spectrographic analysis is obtained.

Uranium is determined in a separate aliquot by a modified dibenzoyl methane method; 1,2-diaminocyclohexane-tetra-acetic acid is used to chelate the bismuth and other interfering materials. After adjustment of the pH to between 6 and 7, the uranium dibenzoyl methane complex is extracted into amyl acetate. An adequate decontamination is thus obtained.

THE use of liquid reactor fuels is being investigated at a number of laboratories. Extensive studies have been devoted to the use of uranium in bismuth as a liquid metal reactor fuel at Brookhaven National Laboratory. Most of the chemical investigations have centered around metallurgical studies of corrosion, mass transfer and stability of fuel systems.

Elements in the fuel, for which analyses are required, are uranium, zirconium, magnesium, iron, nickel, chromium and manganese. Approximately 250 p.p.m. of zirconium and 350 p.p.m. of magnesium are added to the fuel as stabilizers and corrosion inhibitors. The presence of iron, nickel, chromium and manganese, in the parts-per-million range, is due to the corrosion of the container material.

In the past, most of the samples submitted for analysis have been "cold". In order to cope with the large number of samples, a spectrographic technique has been used. The sample is dissolved in 50% nitric acid with a resulting bismuth concentration of 10 per cent by weight. Analyses for zirconium, magnesium, iron, nickel, chromium and manganese can be obtained simultaneously, utilizing a solution technique with a rotating disc and a high voltage spark as the source.[1] The instrument used is a Baird 3-m spectrograph with a direct reader attachment. The uranium analysis is done colorimetrically by a modified dibenzoyl methane (DBM) method.[2,3,4]

In order to test the effects of radiation on corrosion and fuel stability, it has been decided to circulate a bismuth fuel containing approximately 1400 p.p.m. of uranium-235 in the Brookhaven Reactor. It became necessary to devise a method to analyze

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* Research performed under the auspices of the U.S. Atomic Energy Commission.

samples containing an α-activity of 10^9 d min^{-1} g^{-1} in the form of polonium-210 and a fission-product β,γ-activity of 0.2 r hr^{-1} g^{-1} at one foot. Ideally, this problem could have been solved by putting an arc-spark stand in a shielded α facility, and indeed this approach was used for samples containing one thousandth of this β,γ-activity and one tenth of this α-activity. In order to handle samples of the higher activity, it was thought advisable, because of the limitations of our facilities, to use prior chemical separation of the polonium and a major part of the fission-product activities. The approach pursued was to make use of, as much as possible, our existing spectrographic and chemical techniques.

The procedure is divided into three sections, each of which is described below.

1. THE DETERMINATION OF URANIUM

The main feature of this method is the formation of the DBM complex in an aqueous phase at a pH of 6–7, followed by an extraction into amyl acetate, and a spectrophotometric determination. The use of 1,2-diaminocyclohexane-tetra-acetic acid (DCTA) prevents interference from bismuth and other elements. The amyl acetate extraction serves as a means of obtaining the uranium free of polonium and fission-product activity. The resulting polonium activity in the organic phase is less than 100 d min^{-1} ml^{-1} with negligible fission-product activity. The polonium activity can be reduced still further by washing the organic phase with a blank solution of the appropriate pH. Identical results are obtained in the presence or absence of bismuth. A detailed procedure for the determination of uranium is presented.

Reagents

Combine in order:

2 mg Brom cresol green
600 ml H_2O
50 ml NH_4OH (conc.)
200 g NH_4Cl
100 g 1,2-diaminocyclohexane-tetra-acetic acid (available as Chel 600 from Geigy Industrial Chemical Co., Saw Mill River Road, Ardsley, N.Y.).
Dilute to 1 liter in a graduated cylinder.
Dibenzoyl methane solution (1,3-diphenyl-3-propanedione), 1 g in 125 ml of acetone.

All other chemicals are of standard laboratory grade.

Procedure

Add to centrifuge tube:

10 ml of DCTA buffer solution.

A sample aliquot of appropriate size containing 10 per cent of Bi in 50% HNO_3.

Adjust the pH with 2*M* NH_4OH until a blue color is obtained. (If already blue, omit addition of NH_4OH.)

Immediately return to a faint yellow color by the dropwise addition of 1*M* HCl.

Add 2 ml NH_4OH (2*M*), and 1 ml of dibenzoyl methane solution.

Wait 10 min, and extract with 10.0 ml of amyl acetate.

Determine the absorbancy at 412 or 426 mμ. (For less than 10 μg of U, extract with 5.0 ml of amyl acetate and measure the absorbancy at 404 mμ.)

Process appropriate standards and a blank through the same procedure as the sample.

2. THE DETERMINATION OF IRON AND ZIRCONIUM

Iron and zirconium are extracted directly from an aliquot of the 10% bismuth–50% nitric acid solution into 0.5*M* 2-thenoyltrifluoroacetone (TTA) in xylene. If the amount of sample is limited, the aqueous phase after this extraction can be used for the uranium determination.

TABLE I.—SPECTROGRAPHIC ZIRCONIUM ANALYSIS

Direct, *p.p.m.*	Extract and strip, *p.p.m.*
254	250
248	240
240	231
258	249
251	242
245	236
Average 249 ± 5	241 ± 7

Moore has adequately demonstrated that zirconium is quantitatively extracted from nitric acid solutions[5], and we have found no deleterious effect due to the presence of high concentrations of bismuth. The zirconium is re-extracted from the organic phase (TTA in xylene) into 1*M* fluoride solution containing, as the standard matrix for the subsequent spectrographic analysis, 50% nitric acid and 10% bismuth. An internal standard consisting of 0.05 mg of yttrium per milliliter is added to the solution. The results obtained for the direct spectrographic determination of zirconium are compared in Table I with those obtained after the TTA extraction and fluoride stripping steps. There appears to be a negative bias of approximately 3 per cent; however, if one compares the averages they are found to be statistically the same. If desired, this effect can be adequately compensated for by using a calibration curve obtained by carrying standards through the procedure.

Bolomey and Wish[6] have recommended that the pH of the aqueous phase be within the range of 2–4 for the analytical extraction of iron by TTA. However, in a review article by Moore it was reported that iron can be extracted efficiently from perchloric and nitric acid solutions.[7] Furthermore, iron invariably appears as a contaminant in TTA extractions of metals from acidic media. It appeared that it might be feasible to extract iron quantitatively from nitric acid solutions, and indeed, this approach has been utilized in a recent publication.[8] We have investigated the percentage of iron extracted from 50% nitric acid by 0.5*M* TTA-xylene as a function of shaking, number of contacts and the organic/aqueous volume ratios. The results are presented in Table II. As can be seen, the 10 min shaking time is sufficiently long to yield almost equilibrium extraction. It was calculated that an organic/aqueous ratio of 4 should yield essentially quantitative extraction of the iron from solutions containing 10 per cent bismuth and 50 per cent nitric acid.

Experience has shown that it is difficult to obtain meaningful iron analyses in the low p.p.m. range if the chemical and manipulative steps are not kept to a minimum. It was, therefore, decided to ascertain whether a spectrophotometric determination of the iron could be made directly in the organic phase. The absorbance of the iron–TTA complex versus an appropriate blank is shown in Fig. 1. A plateau is observed between 470 and 510 mμ. A Beer's law plot at 490 mμ is presented in Fig. 2. Blanks were found to be of the order of 0.01 absorbance units. If the lower limit of measurement is considered to be twice that of the blank, 5 p.p.m. of iron can be determined in bismuth on the basis of a 10% bismuth solution and an organic/aqueous volume ratio of 4. In practice, it has been found that this lower limit is adequate for our needs. If a still lower limit is desired, various manipulative techniques can be resorted to.

TABLE II.—PERCENTAGE OF IRON EXTRACTED FROM $8M$ HNO_3 BY $0.5M$ TTA

Shaking time, *min*		10		30		60	
Number of contacts		1	2	1	2	1	2
Organic/Aqueous, (Volume ratio)	1/1	81	96	84	96	86	—
	2/1	90	—	93	—	93	—
Used Fe^{59} Tracer		concentration of Fe = 1 μg/ml					

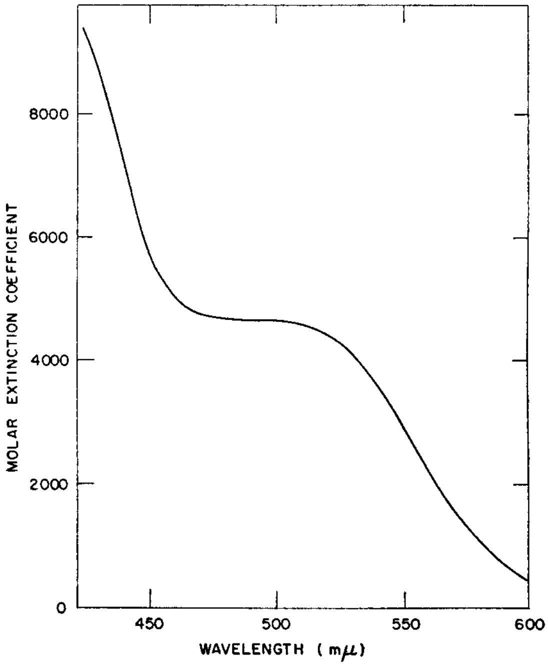

FIG. 1.—The absorbance of iron in $0.5M$ TTA in xylene.

3. THE DETERMINATION OF MAGNESIUM, CHROMIUM, NICKEL AND MANGANESE

Considering the chemical properties of these elements, it seemed most feasible to decontaminate from α-activity by the removal of the polonium. Using bismuth as a model, it would appear that a chloride anion-exchange approach could be used.[9,10] On the basis of ease of handling, speed, versatility and maintaining small solution volumes, it is desirable to separate the polonium by means of solvent extraction. Consequently, the use of tertiary amines as liquid anion exchangers was investigated. Tri-iso-octylamine (TIOA) has been used as an extractant for uranium from sulfate[11] and chloride[12] media.

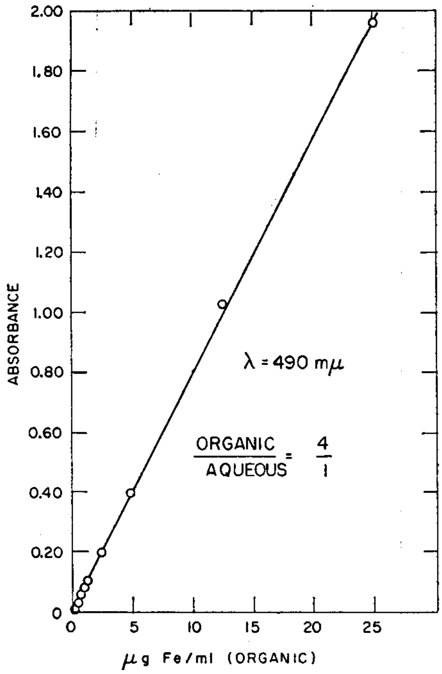

FIG. 2.—Beer's law plot of iron–TTA complex in xylene.

A study was made of the extraction of bismuth by TIOA* as a function of the molarity of hydrochloric acid in the aqueous phase. A 0.5*M* solution of TIOA in methyl isobutyl ketone (MIBK) was pretreated with 2*M* hydrochloric acid to put the amine in the hydrochloride form. This solution was then contacted with an equal volume of aqueous solution containing 100 mg Bi/ml and hydrochloric acid in concentrations varying between 2 and 8*M*. The results for the extraction of bismuth after one and two amine contacts are shown in Fig. 3. The relatively low distribution coefficient after the first contact is due to the fact that the amount of bismuth extracted approaches the capacity of the amine solution. The results obtained for the amine liquids anion exchange are in good qualitative agreement with those obtained by Nelson and Kraus[9] for resin anion exchange.

Fronaeus has shown, for the case of resin anion exchange, that a maximum in the

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* Purchased from Union Carbide Chemical Company, New York 17, N.Y.

distribution coefficient should appear when the concentration of the neutral complex in the aqueous phase is at its maximum.[13] The mathematical details were later explored by Marcus and Coryell.[14] The same mathematical relationships apply to the liquid anion exchange situation and, indeed, the interpretation might be simplified due to a smaller "resin invasion" by the hydrochloric acid.

On the basis of the theory, the distribution coefficient increases until the aqueous concentration of the neutral complex attains its maximum value, in this case $BiCl_3$. When the formation of anionic complexes becomes more important, the distribution coefficient decreases. According to the data of Newman and Hume[10], the maximum in the distribution coefficient should appear at a chloride concentration of approximately 0.1*M*. This low chloride concentration could not be used due to the precipitation of BiOCl. However, we have observed that, if the TIOA in the hydrochloride form is contacted with a nitric acid solution, the amine is distributed according to equation (1):

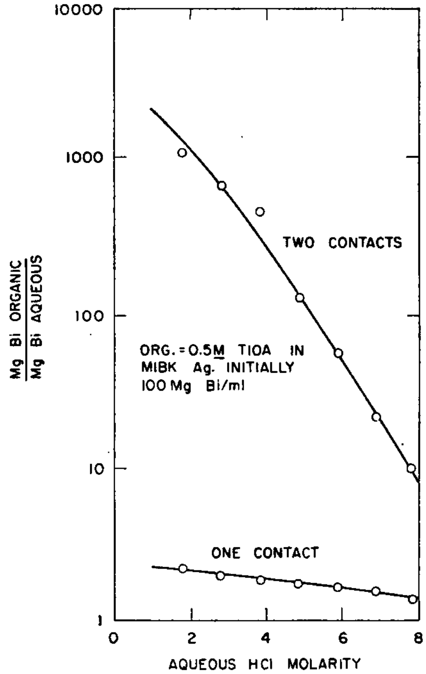

FIG. 3.—Extraction of bismuth by tri-iso-octyl amine hydrochloride.

$$R_3NH^+Cl^- \text{ (org.)} + NO_3^- = R_3NH^+NO_3^- \text{ (org.)} + Cl^-. \qquad (1)$$

Now, if bismuth is present in the aqueous solution, the following two equilibria would predominate:

$$3\,Cl^- + Bi^{3+} = BiCl_3 \qquad (2)$$

$$R_3NH^+Cl^- \text{ (org.)} + BiCl_3 = R_3NH^+BiCl_4^- \text{ (org.)} \qquad (3)$$

Therefore, bismuth can be extracted from a nitric acid solution as a chloride complex by contact with an amine solution in the hydrochloride form. Furthermore, considering that the bismuth samples are made up in nitric acid, it is the most convenient medium for the extraction. If the nitric acid concentration is made too low, then BiOCl can once again precipitate upon contact of the aqueous solution with the amine. In order to avoid precipitation, the maximum permissible dilution of the original 10% bismuth–50% nitric acid solution is approximately ten to fifteen-fold.

It then remained necessary to test whether the decontamination from polonium was sufficient at the optimum conditions found for bismuth extraction. The original 10% bismuth–50% nitric acid solution was diluted ten-fold and "spiked" with some neutron irradiated bismuth to yield a resulting α-activity of 1.4 × 10^6 d min^{-1} ml^{-1}.

TABLE III.—RESIDUAL Po ACTIVITY AFTER EXTRACTION WITH 0.5*M* TIOA IN MIBK

Initial activity = 1.4 × 10^6 d min^{-1} ml^{-1}

Number of extractions	d min^{-1} ml^{-1}
3	203, 97
4	96
3, aqueous transferred to clean vial for third	60
3, aqueous transferred to clean vial for second and third	34

TABLE IV.—ANALYSIS OF THE BISMUTH HYDROXIDE FRACTION

	Mg	Cr	Ni	Mn
	244	148	88	107
	245	150	86	112
	233	128	67	108
	242	153	116	104
	240	149	82	111
	235	146	107	103
	238	118	74	102
	238	129	78	105
Found	233 ± 4	140 ± 13	87 ± 16	107 ± 4
Added	236	145	82	105

A 0.5*M* solution of TIOA in MIBK pretreated with 2*M* hydrochloric acid was used for the extraction which was performed in vials. The results for the polonium decontamination are presented in Table III. The polonium activity is reduced to approximately 100 to 200 d min^{-1} ml^{-1} after three contacts with the amine; however, high results were sometimes encountered. Although spurious high results were not encountered after a fourth contact, the decontamination was not significantly increased. The organic phase was removed from the vial between contacts by applying suction to a transfer pipet. It was reasoned that droplets of the organic phase adhering to the sides and top of the vial could contaminate the pipet used in taking the aliquot for residual polonium determination. The simple expedient of pouring the aqueous phase into a clean vial after contact with the organic liquid was found to yield better and more consistent polonium decontaminations.

Decontamination was next achieved from rare-earth fission products by a fluoride precipitation, using praseodymium as a carrier. Finally, to separate the magnesium, chromium, manganese and nickel from the alkaline and alkaline-earth fission products, a hydroxide precipitation was performed using bismuth as a carrier. The precipitate was redissolved and analyzed by the standard spectrographic technique. The results after this decontamination procedure are presented in Table IV. They are in agreement with the amount added and the precision compares favourably with the spectrographic analyses obtained on a direct aliquot of a cold sample.

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Talanta, 1960, Vol. 6, pp. 63 to 70. Pergamon Press Ltd. Printed in Northern Ireland

A METHOD OF URANIUM ISOTOPE ANALYSIS BY DIRECT READING EMISSION SPECTROSCOPY

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Summary—A special-purpose direct reading spectrometer has been developed for the determination of U^{235}, U^{236} and U^{238}, using the spectral lines at 4244.12, 4244.22, and 4244.37 Å, respectively. The parallel-channel integrating method is used, in which the ratios of U^{235} and U^{236} to U^{238} are determined simultaneously. A 5 A 2400 Å a.c. arc is used, the sample (uranium oxide) being held in a graphite crater. The three spectral lines are separated by optical means; exact optical alignment is maintained automatically. At 3 per cent concentration of U^{235}, a coefficient of variation of 1 per cent of the amount present is achieved. The sensitivity for U^{236} is better than 0.1 per cent. Sample preparation is simple and straightforward. Less than 3 min is required for an analysis.

INTRODUCTION

EMISSION spectroscopy has been recognized as an extremely promising method for the analysis of uranium isotopes.[1,2,3] In measuring the relative intensities of the shifted isotope components of a single spectrum line, emission spectroscopy should approach its theoretical limit of precision. This is due to the fact that all the isotope components are homologous and have identical self-reversal or absorption properties. An additional advantage of emission spectroscopy is that it is free from memory effects.

Emission spectrographic techniques fall into two major categories: photographic methods and direct reading methods, in which spectrum line intensities are converted into electronic signals by photomultiplier tubes. Photographic emission spectroscopy has the disadvantage that errors may be introduced in plate development and densitometry. An additional disadvantage, which is applicable in the case of isotope analysis, is that intense spectrum lines may cause halation within the photographic emulsion and consequent broadening of the spectrum line image on the photographic plate. Such broadening may interfere with the accurate densitometry of adjacent lines. These disadvantages point toward the use of direct reading techniques, of which there are several. In choosing between the alternative direct reading techniques, a scanning technique is attractive in the separation of closely adjacent lines. However, a scanning method requires exceptional source stability, and invites the use of such cumbersome sample excitation devices as cathode lamps. A parallel channel technique offers the advantage of allowing the simultaneous integration of the intensities of all the spectrum lines measured. This somewhat relieves the requirements on source stability and consequently on sample preparation. The problems of a parallel channel technique in isotope analysis are principally problems of optical alignment. They concern the optical manipulation necessary to bring light from closely spaced spectrum lines to separate photomultipliers, and the rather stringent requirements for stability placed on such a system.

This paper describes a method of analyzing the 235, 236 and 238 uranium isotope components in the vicinity of 4244 Å (Figs. 1 and 2). The method employs parallel channel, direct reading spectrographic equipment of standard design. To this equipment has been added a special device to obtain the required optical manipulation.

APPARATUS

The instrument, a standard Baird-Atomic three-meter concave grating eagle-mounting spectrograph is used in the third order with a 25,000 line/in. grating blazed for this application. An interference filter transmitting about 75 per cent at 4244 Å is used in front of the entrance slit, preventing higher orders from reaching the focal curve. The entrance slit is 15 μ, and the dispersion of the instrument under these conditions is about 0.8 A/mm.

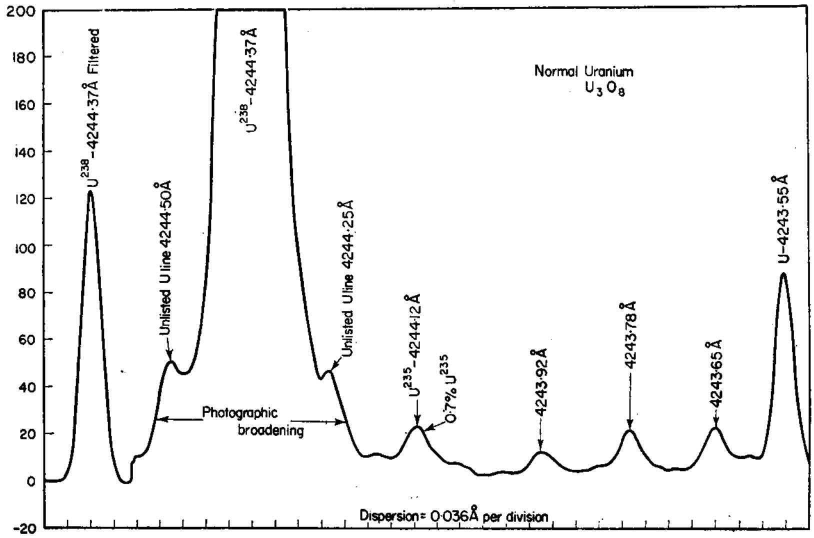

FIG. 1.—Densitometer recording of the spectrum (obtained by photographic spectroscopy) of normal uranium in the 4244 Å region. The 4243.55 Å line at the extreme right is the nearest line listed in Harrison's tables to the short wavelength side of the 4244.37 Å line. Between these two lines are weak unlisted uranium lines at about 4243.65 Å, 4243.78 Å, 423.92 Å and 4244.25 Å, as well as the isotope-shifted components of the 4244.37 Å line. The line at 4244.25 Å is only about 0.03 Å longer wavelength than the position of the 236 uranium istope line. The line at 4244.50 Å on the long wavelength shoulder of the broadened 4244.37 Å line is also an unlisted uranium line. Considerable work was done to establish the validity of the conclusion that the 4244.25 Å and 4244.50 Å lines are indeed uranium lines and not satellites of the 4244.37 Å line, nor Rowland ghosts of some strong uranium line, nor any impurity in the uranium. This conclusion was also reached earlier by personnel of Westinghouse Atomic Power Division. The 4244.25 Å uranium line has frequently been mistaken for the 236 isotope line by other workers.

The densitometer trace of the 4244.37 Å uranium 238 isotope line reduced in intensity by a filter appears at the extreme left. It is evident that in the absence of photographic broadening this line is adequately sharp to permit optical separation from other isotopic lines in direct reading work.

The portion of the apparatus described above can be used for photographic spectrographic analysis of uranium isotopes. Photographic plates with a Spectrum Analysis No. 1 emulsion are used. This emulsion is insensitive to the second and third order wavelengths.

The spectrograph is equipped with devices which enable it to be used for direct reading work. The plateholder is removed and a direct reading head inserted in its place. The direct reading head contains a focal curve, upon which exit slits can be mounted, and means for mounting photomultiplier tubes. The exit slits can be precisely positioned on spectrum lines by manual controls on the front of the spectrograph.

The separation of the three spectrum lines of interest, the 235, 236 and 238 isotope lines at 4244 Å constitutes a special problem. Whereas the 235 and 238 isotope lines are about 300 μ apart on the focal curve, since the focal curve is inclined at about 45° to the direction of the light, the actual physical separation of these two extreme lines is only about 210 μ. The 236 isotope line is about 84 μ from the 235 isotope line. Although a 15 μ entrance slit was used, the lines are believed to be about 30 μ wide. Some of this width is presumably Doppler broadening.

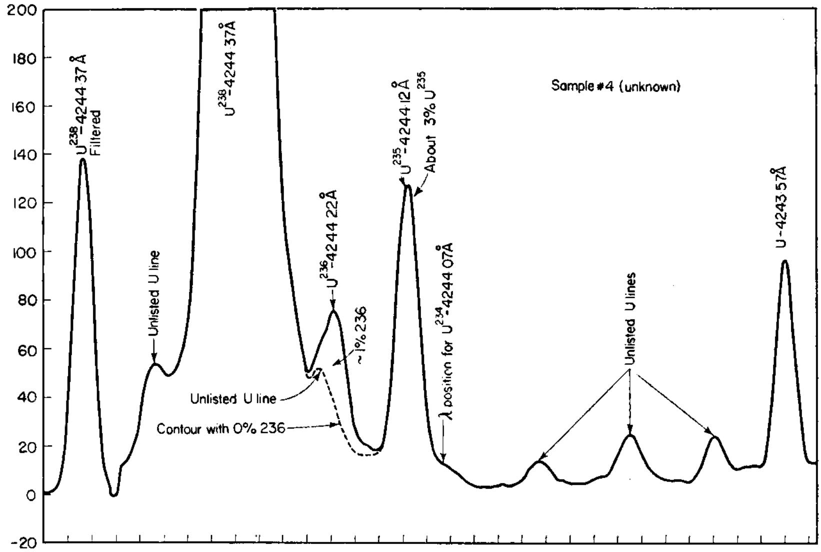

FIG. 2.—Densitometer recording similar to Fig. 1 except that the exposure has been made with an enriched sample. Note that the 236 isotope line is very nearly superimposed on the unlisted uranium line at 4244.25 Å. Since this interfering line is a uranium line, its contribution to the 236 signal is constant and its effect on the 236 calibration curve is exactly the same as background.

The line separation problem is solved by a beam-splitter (Fig. 3). The beam splitter consists of three glass prisms. The coplanar face of the three prisms is placed on the focal curve facing the grating. The prism is adjusted so that the U^{236} isotope line at 4244.22 Å is accepted by the narrow leading edge of the central prism, while the U^{235} and U^{238} components fall on the side prisms and are reflected to the right and left by the aluminized interfaces between prisms. The front surfaces of the side prisms are masked to exclude unwanted portions of the spectrum.

From consideration of the geometry of the apparatus (the long focal distance required for adequate dispersion, and the small and critical dimensions of the beam splitter), it is obvious that some extraordinary means of maintaining optical alignment is required. This is supplied by the automatic servo monitor (Fig. 4) which is a standard component, only slightly modified for this application.

Briefly described, the servo monitor is a servo system which adjusts the apparent position of the entrance slit in response to any change in spectrum position on the focal curve. The sensing device is a tilted slit and two photomultiplier systems. The slit is aligned on a mercury spectrum line produced by a mercury light source which is projected through the entrance slit by a quartz plate. Any lateral misalignment of the mercury line causes an unbalance in the photomultiplier outputs, and this unbalance is corrected by the automatic rotation of a plane parallel quartz deflection plate located between the entrance slit and the grating. The correction is made on mercury light but, because the sample light from the analytical gap follows the same path, all corrections are valid as well for the uranium spectrum. This device holds the spectrum to within 1 μ of the desired position, and is absolutely necessary in overcoming shifts due to temperature and pressure variations as well as mechanical dislocations transferred from external sources to the inside of the spectrograph. Although the lateral stability required of the spectrograph for uranium isotope analysis is one order of magnitude greater than the stability required for most direct reading spectrographic applications, no loss of precision due to spectrum shift has been detected even though

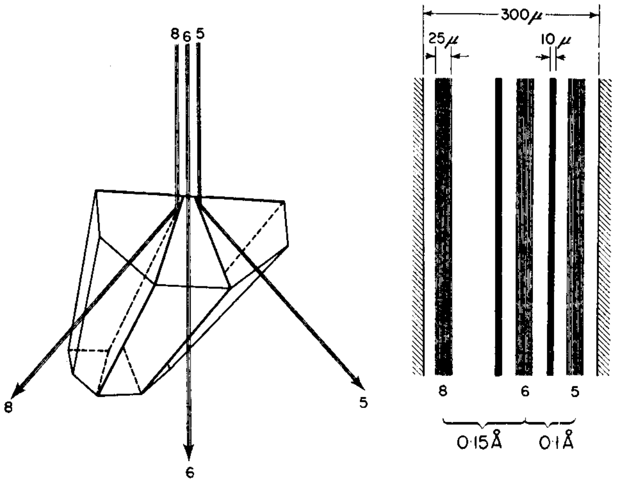

FIG. 3.—Optical device for separating spectrum lines.

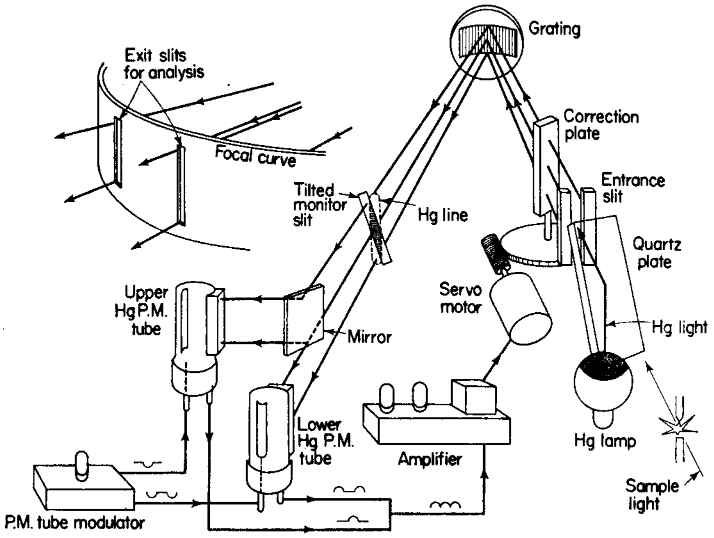

FIG. 4.—Baird-Atomic automatic servo monitor.

repeatability runs have been made under unfavorable conditions of laboratory temperature variation.

The readout system is the same as used with a standard Baird-Atomic direct reading spectrometer and Spectromet. During the exposure period, condensers are charged by photomultiplier tube currents simultaneously for all the unknown channels as well as for the internal standard or reference channel. Photomultiplier tube dark currents are automatically cancelled. During the measuring period, all unknowns are read out simultaneously in terms of ratios of voltages of the unknown channels to the voltage of the internal standard. This is accomplished by discharging the internal standard condenser through a resistance, and recording the time taken for the internal standard condenser voltage to decline so as to equal the unknown condenser voltages being measured. Thus, the following equation applies,

$$t = -RC \log_e \frac{V_u}{V_s}$$

where C is the capacity of the internal standard condenser, R is the resistance through which the condenser discharges, V_u is the voltage on an unknown element condenser, V_s is the voltage on the internal standard condenser and t is the time required for V_s to become equal to V_u. If V_s is greater than V_u, t is positive. Percentage concentrations can thus be plotted against t (time or clock readings) on semilog paper, resulting in approximately linear calibration curves, except at concentrations close to the background level. Readout precision is usually better than 0.5 per cent in terms of voltage ratios, but can be increased to almost any extent by using a larger RC constant.

In normal uranium and uranium enriched with low concentrations of U^{235}, the U^{238} line is the internal standard. In highly enriched samples, the U^{235} line is made the internal standard. Yet the change need not be made at the 50 per cent concentration. It is acceptable to use the 235 component as the internal standard from 35 per cent to 95 per cent.

Since this method is based upon the determination of isotope ratios, that is, 235/238 and 236/238, the concentration of the 236 isotope affects the 235 result. If a calibration curve has been established for the 235 isotope based on the 235 to 238 ratio with standards containing no 236 isotope, then as the concentration of 236 increases the true 235 concentration will be smaller than the value read directly from the calibration curve. If the value read from the calibration curve is, say, 3.00 per cent and the sample contains 1.0 per cent of 236, then the actual 235 concentration would be 3.00 per cent less 0.03 per cent, or 2.97 per cent.

BACKGROUND CORRECTION

In addition to measuring the isotope line intensities, the spectrograph is equipped with an exit slit which is positioned to accept background light from a portion of the spectrum near 4244 Å. The ratio of background intensity to reference line intensity is recorded on a clock in the usual manner. The measurement thus obtained may be used to correct for variations in the background light which falls on the isotope photomultipliers. Although such corrections appear to be helpful in some cases, the results obtained so far are contradictory on this matter, and more data must be obtained to prove or disprove the value of background correction.

SAMPLE PREPARATION AND EXCITATION

A weighed quantity of U_3O_8 is mixed with an equal weight of powdered graphite and mixed in a Wig-L-Bug for 2 min. The lower electrode is a $\frac{1}{8}$ in. diameter graphite rod having a 2 mm diameter crated $2\frac{1}{2}$ mm in depth. The electrode is loaded by pushing the rod several times down into the capsule in which the sample was mixed. About 10 mg of uranium oxide are consumed per run. The upper electrode is a flat tipped $\frac{1}{8}$ in. diameter rod. A 2 mm arc gap is used, imaged on the grating of the spectrograph.

The discharge is an automatically ignited a.c. arc, 5 A at 2400 V. A pre-arc period of 80 sec is used. During the pre-arc period, a bead of uranium-containing material, glossy and refractory in appearance, forms on the lower electrode; as the bead forms, the discharge becomes increasingly stable and quiet. During the pre-arc period, the analytical gap widens to such an extent that, at the beginning of the exposure period, the images of the electrode tips no longer fall on the grating. Exposure periods used are 80 sec for photographic analysis, and 40 sec for direct reading analysis.

TABLE I.—U^{235} CALIBRATION DATA

	0.7%	2.0%	4.0%	6.0%
	Clock	Clock	Clock	Clock
	31.0	22.8	14.7	9.5
	31.0	22.8	14.5	9.8
	31.0	22.7	14.5	9.6
	30.9	22.6	14.5	9.9
Average	30.98	22.73	14.55	9.70

ANALYTICAL PERFORMANCE

A typical calibration series is given in Table I. When these data are plotted on semilog paper, with the percentage of U^{235} as ordinate and U^{235} clock reading as abscissa, a U^{235} calibration curve is obtained as shown in Fig. 5. The point at 0.1 per cent can be obtained by calculation. The curve at diminishing percentage concentration becomes steeper because 0 per cent is at infinity. Hence the curve approaches a vertical line asymptotically, the position of the vertical line representing the intensity of the background. These properties are easily calculated from the logarithmic equation given previously

Figure 6 is a calibration curve for U^{236}. This curve should be considered as only approximate due to some uncertainties in the actual U^{236} content of the standards used.

Figure 7 is a combination of the calibration curves in Figs. 6 and 7 with a calibration curve for U^{238} in the range from 5.5 per cent to 50 per cent.

The precision* is close to 1 per cent of the amount present at approximately 3 per cent U^{235}. Work on other samples, for example, nearly equal concentrations of the 235 and 238 isotopes, has indicated possible reproducibility of 0.2 per cent of the ratio.

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* In this discussion, precision is given the same meaning as coefficient of variation, or standard deviation of a single run expressed in terms of percentage of the amount present. Standard deviation is calculated by the usual formula:

$$\text{standard deviation} = \left(\frac{\Sigma d^2}{n}\right)^{1/2}.$$

Improvement of precision in this case is believed to be due to the fact that the background intensity is an insignificant fraction of the light intensities measured.

At 93 per cent U^{235}, the precision of U^{238} is about 1.2 per cent, and consequently the precision of U^{235} (calculated by difference) is on the order of 0.07 per cent.

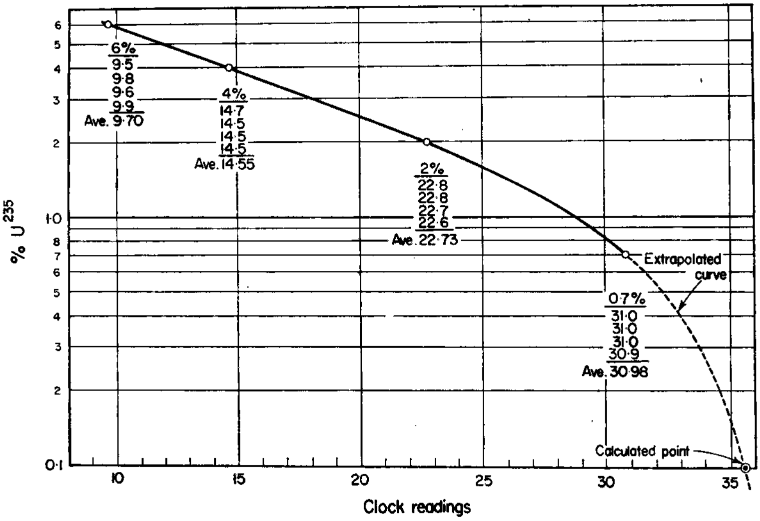

FIG. 5.—U^{235} calibration curve.

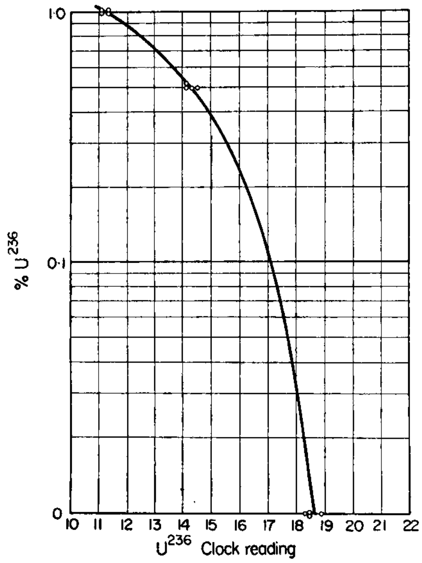

FIG. 6.

The precision for the determination of the 236 isotope is a few per cent of the amount present at 1 per cent concentration. Thus, less than 0.1 per cent should be detectable by suitable calibration. There appears to be a leak of about 5 per cent of the 235 light into the 236 channel. For wide variations in the 235 concentration, a suitable correction could be made to improve the accuracy of the 236 result.

CONCLUSIONS

(1) By the use of equipment which automatically maintains optical alignment of a mercury line on an exit slit with a precision of about 1 μ, it has been proved feasible to separate the three closely spaced spectrum lines of the 235, 236 and 238 isotope lines of uranium near 4244 Å for photoelectric measurements. Separation of the three lines is accomplished by a specially constructed optical device which operates as three closely spaced slits.

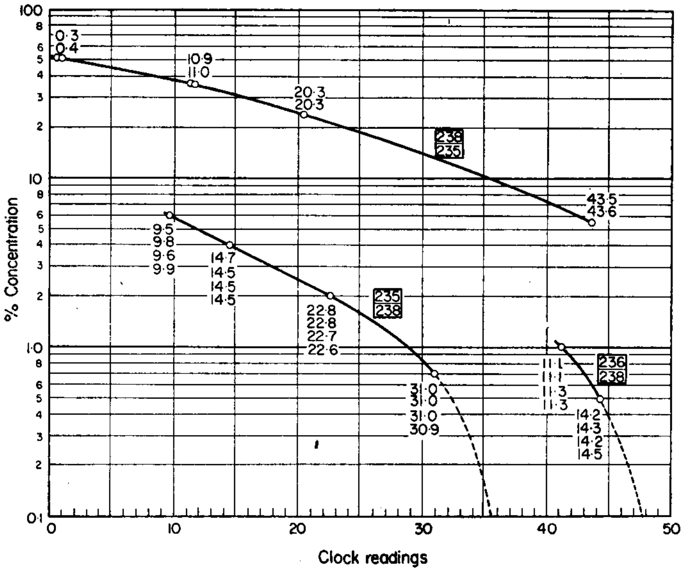

FIG. 7.—For each of the three calibration curves in this Figure, the ordinate is percentage concentration of the isotope listed uppermost in the square box. The abscissa represents the clock reading of the direct reading readout system. In each case, the lower number in the square box represents the isotope component used as the internal standard. The point on the extreme lower right of the top curve represents two runs of a sample containing 5.5 per cent U^{235}. The U^{235} concentration for this sample is about 93 per cent, the remainder being other isotopes.

(2) The equipment described in this report allows the simultaneous measurement of the spectrum line intensities of interest over any convenient period of integration, so that stability of the source of excitation is of minor importance. Thus the use of time-consuming and cumbersome techniques, such as hollow cathode discharge tubes, are avoided.

(3) The fact that the spectrum lines used are perfectly "homologous" and also have identical self-reversal or absorption properties indicates that the method should be capable of high precision. This is borne out by the analytical precision obtained.

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Talanta, 1960, Vol. 6, p. 71. Pergamon Press Ltd. Printed in Northern Ireland

THE SPECTROCHEMICAL ANALYSIS OF BISMUTH USING A PHOTOELECTRIC SPECTROMETER

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Summary—In the Liquid Metal Fuel Reactor Program, a large number of Bi samples must be analyzed rapidly and accurately. A spectrochemical procedure for the determination of Mg, Zr, Fe, Cr, Mn, Ni and Mo, using a rotating-disk technique with a Baird-Atomic spectrograph and direct-reader attachment, is described.

To ensure proper performance of LMFR test loops and related engineering experiments, frequent monitoring is required of molten Bi–U alloy for Mg and Zr additives as well as corrosion products of stainless steel. During the past few years, Mg and Zr in the range of 50–700 p.p.m. were determined spectrographically by spark-excitation of an HNO_3 solution of Bi in a porous-cup electrode. In order to obtain sufficient sensitivity in the analysis of corrosion products at the 10–500 p.p.m. level, a d.c. arc procedure was utilized. This involved time-consuming sample preparation, consisting of the evaporation of Bi solutions followed by ignition, grinding, mixing and electrode packing.

With the present instrument, quicker analyses can be made on a larger number of samples. In order to take full advantage of the instrument, a procedure was developed whereby the concentration of all seven elements of interest is determined by a single exposure. A solution technique, utilizing Y as an internal standard, has been found to yield results which are satisfactory for control of the experimental loops.

Samples are prepared as a 10% (w/v) solution of Bi in 1 : 1 HNO_3. Rapid dissolution is effected by dissolving the sample in the appropriate amount of concentrated HNO_3. The solution is then diluted to constant volume with water. A 10-ml aliquot is then mixed with 1 ml of Y solution containing 0.5 mg of Y per ml. Standard solutions are similarly prepared from pure Bi and solutions of pure metals; in these solutions Y is also added as internal standard.

The prepared solution is placed in a Pyrex glass boat and excited, using a ½ × 0.200 in. rotating graphite counter electrode. Excitation conditions are as follows:

Capacitance, μF	0.005
Inductance, μH	1250
Voltage, V	18,000
Current, r.f. amp	3
Number of discharges per second	960
Analytical gap, mm	4
Entrance slit, μ	50
Time of preburn, sec	30
Time of exposure, sec	60.

Using the Baird-Atomic direct-reader attachment, condenser discharge time (in clock units) is plotted against the logarithm of concentration to give analytical working curves.

A tabulation will be presented of the spectral lines utilized for the determination of Mg, Zr, Fe, Cr, Mn, Ni and Mo, together with relative standard deviations obtained for each of these elements within specified ranges of concentration.

The method was originally developed by means of a photographic technique; therefore, this technique can also be used, providing some of the intensity levels are reduced with step filters or sectors and the period of exposure is lengthened to 3 min.

Talanta, 1960, Vol. 6, pp. 72 to 93. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF U^{235} BURN-UP IN IRRADIATED NATURAL URANIUM BY CHEMICAL AND COUNTING METHODS*

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Summary—A method was desired for determining, with a precision of 1 per cent, the U^{235} content of U samples taken lengthwise of a highly irradiated NRX natural U fuel rod. A mass spectrometric method capable of achieving this accuracy was not available at the time this work was begun.

The method chosen was based on measurements of the fission and α-counting rates of natural U samples and U samples from the fuel rod after chemical purification, in order to compare their U^{235} : U^{238} ratios.

Due to the thin sources necsssary for the counting, the time required for the direct determination of U^{238} by α-counting was too long to be practical. An indirect measure of the U^{238} content was, therefore, obtained by counting the Pu^{239} produced by neutron irradiation of the sources in a position of high flux in NRX. To ensure a valid basis for comparison of samples, all irradiation and counting was done with a source of natural U and one of depleted U placed back to back. The sources were not disturbed on changing from fission- to α-counting. This type of counting was accomplished by use of an ion chamber with a double grid, located at the opening of a thermal-neutron beam hole. Fission counting was done with the beam hole shutter open; α-counting was done with the shutter closed, a higher gas pressure in the chamber, and a higher electronic gain.

Because of difficulties caused by radiation damage to the sources, it did not appear possible to approach the precision desired for U^{235} burn-up values, and a further complexity had to be introduced into the method.

The new procedure consisted of the following steps:

(1) A set of sources and a set of targets were prepared from natural U and each depleted U sample. The sources were designed for the determination of U^{235} by fission counting; the targets, after processing, were used for the determination of U^{238} via Pu^{239}. Each set of sources and corresponding targets contained Pu^{238} which was added as a tracer. For any given U sample, sources and targets were prepared at the same time and in a manner designed to maintain the Pu^{238} : U^{238} ratio constant for both sets.

(2) Sources were fission- and α-counted in the gridded ion chamber to obtain U^{235} : Pu^{238} ratios.

(3) Targets were irradiated in the back-to-back arrangement used previously.

(4) After irradiation, the U and Pu were dissolved off the Al target backing and the Pu was carefully purified.

(5) This Pu was used to prepare sources on Pt for α pulse height analysis which gave Pu^{239} : Pu^{238} ratios directly and thus, indirectly, U^{238} : Pu^{238} ratios. From these and the U^{235} : Pu^{238} ratios obtained in (2), U^{235} : U^{238} ratios were calculated.

The use of an α-active tracer was necessary to link the two sets of counting results. The advantage of using Pu^{238} as a tracer was that the method is independent of chemical yields during the processing of irradiated samples.

The precision of the counting methods used for burn-up measurements varied from 1.3 to 2.6 per cent. Before the chemical and counting methods had been fully worked out, a satisfactory mass spectrometric method was developed and put into routine use. The precision of the mass spectrometer measurements, for samples which were analyzed by the counting techniques, varied from 0.5 to 1.4 per cent. Results obtained by analysis with the mass spectrometer and the counting methods agreed within the experimental errors listed above.

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* Contribution from A.E.C.L., Chalk River, Ontario, Canada.

INTRODUCTION

The problem

In studying the results of long irradiation of natural uranium fuel, one of the more useful pieces of information which can be obtained is the U^{235} depletion. This gives a direct measure of the integrated irradiation received by a fuel element at any point without the use of external flux monitors.

One NRX fuel rod in particular (Rod. No. 683) has been the object of a very detailed investigation.[1,2] This rod was cut up in the manner shown by the sketch in Fig. 1, and the pieces used for various measurements. The 12 in. lengths were used for reactivity measurements at ANL, and the $\frac{1}{8}$ in. discs for chemical and mass spectrometric analyses, principally at Chalk River. Among the measurements made on the discs were the radial distributions of plutonium isotopes and Cs^{137}. Also desired were the values of the U^{235} burn-up for as many samples as possible on which other measurements had been made.

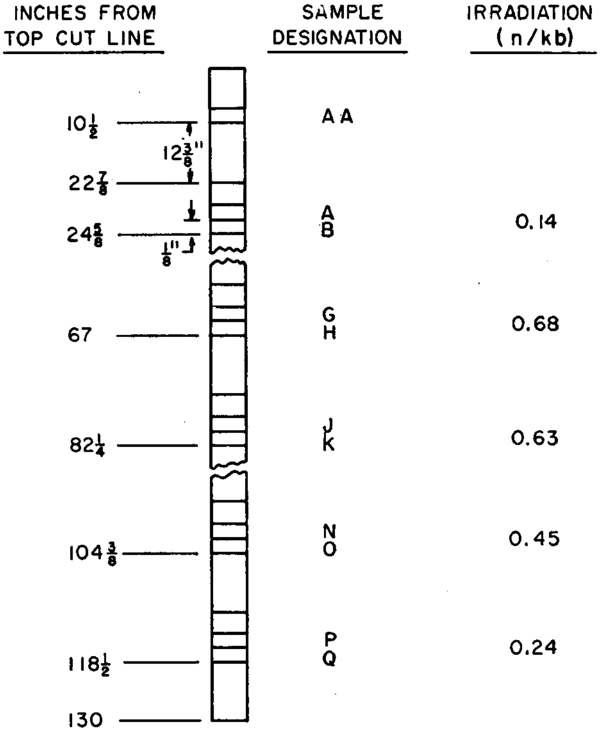

Fig. 1.—Cutting diagram of rod 683 showing location of $\frac{1}{8}$-inch disc samples.

At the irradiation levels met with in Rod. No. 683 (shown on the right of the diagram in Fig. 1), burn-up of U^{235} can readily and accurately be determined by use of a sensitive mass spectrometer to measure the ratio U^{235}/U^{238}. At the time work on this problem was started, it was understood that U^{235}/U^{238} ratios obtained with the Chalk River mass spectrometer would be subject to an error roughly 10 times greater than desired. Attempts were, therefore, made to develop a method based on α-particle and fission fragment counting, with a target accuracy of 0.1 per cent so as to give an accuracy of 1 per cent in irradiation at 10 per cent burn-up.

Subsequently, it was found that, with considerable effort, the mass spectrometer was capable of measuring U^{235}/U^{238} ratios to the required accuracy. It was, therefore, decided to use the mass spectrometer routinely for the depletion measurements, and the counting methods were abandoned while still under development. The results obtained had not met with the rather stringent accuracy requirements, and it is not possible to state what accuracy could eventually have been achieved. However, the methods merit description since, apart from any intrinsic interest they may have, the counting and chemical techniques that were developed have formed the basis for a series of precision measurements of fission cross sections[3]; the apparatus used was, in fact, turned over to these studies.

A detailed description of the apparatus and its use in the burn-up measurements, together with a thorough discussion of the requirements of various methods and the results achieved, are given by Bigham, Hanna and Tunnicliffe[4]. Although the present paper deals with the chemical problems encountered, in order to present an understandable report of the whole investigation, it seemed desirable to include modest descriptions of many of the nuclear physics aspects. For a more detailed consideration of these aspects, the reader is referred to the report of Bigham *et al.*[4]

Basis of counting methods used

Basically, what is required for a depletion measurement is a comparison of the thermal neutron fission rates per unit mass of pure natural uranium and purified depleted uranium in the same neutron flux. The fission rates in this case give a direct measure of the amounts of U^{235} in the samples. A small, easily calculable correction is required for the mass of the depleted sample to take into account the small amount of U^{238} destroyed during irradiation.

Comparison of fission counting rates can be accomplished with the required accuracy, but comparison of the masses of the samples posed several problems. It might be thought, for example, that accurate aliquots of accurately standardized solutions need only be deposited quantitatively as counting sources. However, in the first place, it is extremely difficult to mount samples quantitatively in a form suitable for precise fission counting. And even if this had been feasible in the present study, many of the depleted uranium samples were so small (some as low in weight as 15 mg) that standardization to the required accuracy by gravimetric and volumetric procedures was virtually impossible.

Conventional gravimetric and volumetric methods of uranium analysis were thus of no use, and the possibility of determining U^{238} by α-particle counting was investigated. Counting of U^{238} α-particles directly with the help of a pulse height analyzer did not seem particularly attractive because of low counting rates, and two indirect methods involving α-counting were developed. In all these methods, the α-counting rate actually observed was either that of the U^{238}, or proportional to it. Thus the U^{235}/U^{238} ratio of a given sample was arrived at through a combination of fission- and α-counting.

EXPERIMENTAL APPARATUS

Apparatus used for the chemical work in this study consisted for the most part of conventional equipment and can most conveniently be discussed along with the various procedures. Most of the counting equipment, on the other hand, was developed especially for this work and requires separate description. The individual pieces of experimental apparatus are described in detail elsewhere.[4] Only the salient feature will be given here for the sake of completeness.

Ionization chamber

In order to be certain that fission counting rates of natural and unknown uranium samples are obtained under identical conditions, the samples should be counted in the same neutron flux—in this case a collimated beam. This can best be done in a double ionization chamber with the samples mounted back-to-back and with as little backing and construction material as possible between the two sources. The effects of attenuation of the neutron beam due to scattering and absorption in the source backings can be eliminated by reversing the sources halfway through the counting. However, it was considered desirable to limit the scattering to that of 1 mm of aluminum, which is about one tenth that of a similar thickness of platinum or stainless steel.

The arrangement of the ionization chamber is shown schematically in Fig. 2. The chamber was filled with an argon–10% methane mixture to a pressure of either 20 cm of Hg, for fission counting, or 40 cm of Hg for α-counting. The gas filling the chamber was continuously purified by convection circulation through a side-tube containing calcium metal chips at 300° C.

The neutron beam

In this work, the neutron spectrum was not important, provided that the fast neutron flux was insufficient to give an appreciable U^{238} fission rate. It was necessary, however, that the beam intensity be rather uniform so that non-uniformity of sample thickness could be tolerated. Of the two beams used for this work, one was uniform to better than ± 1 per cent and the other to better than ± 2 per cent.* One of the experimental arrangements is shown in the diagram of Fig. 3.

Auxiliary equipment

In two of the methods, α pulse-height analysis was required. For this purpose, an alpha grid ionization chamber recording on an eighteen-channel 'kicksorter' was used. The design was similar to that of the system described by Harvey and Jackson[5].

In the third method, the fission counting was done after activation irradiation and it was necessary to correct for the approximately 10 per cent contribution due to Pu^{239} fission. This was done by measuring, simultaneously with the main fission counting, the fission rate of a subsidiary Pu^{239} source of known α disintegration rate. The simple 'monitor' chamber provided for this purpose was mounted in the neutron beam between the main chamber and the beam catcher. It was very similar to one half of the back-to-back chamber described by Cockcroft[6].

CHEMICAL TREATMENT OF URANIUM USED FOR SAMPLES

Natural uranium

All samples came from CP-grade starting material which was used without further purification. As a check on purity, samples supplied by two different sources were used. One source was UO_3 powder prepared several years earlier from CP-grade uranyl

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* During this work it was necessary to move from the original location (the thermal column) to another part of the reactor (experimental hole S-8).

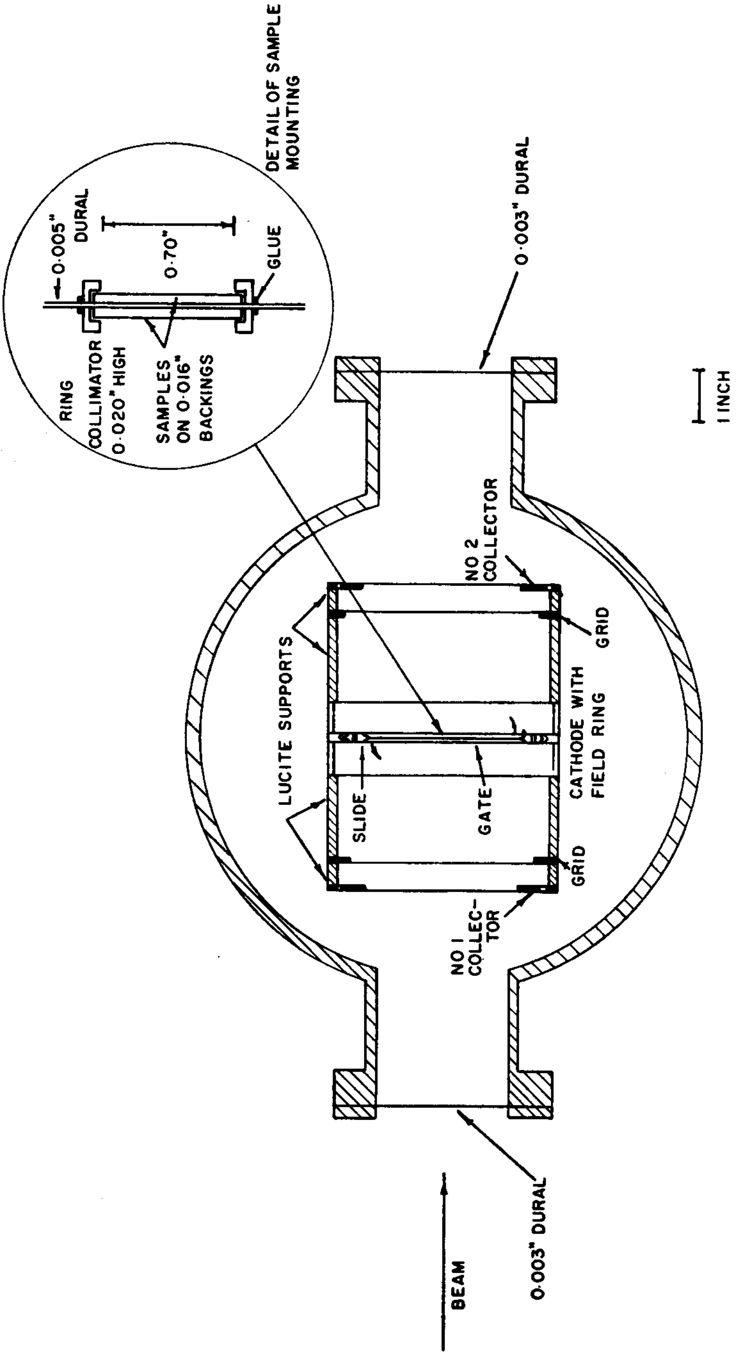

Fig. 2.—Back-to-back gridded ionization chamber.

nitrate hexahydrate; the other was CP-grade uranyl acetate. The former was dissolved in HNO_3 and the latter evaporated with concentrated HNO_3 to form the nitrate starting material. No significant difference was observed in the α/fission ratios of sources prepared from the two different starting materials.

Irradiated uranium

Degree of purity required. Since, in all of the counting methods, it was necessary to determine both fission- and α-counting rates, either all fissile and α-emitting impurities had to be removed from the irradiated uranium samples, or else corrections applied to account for their presence. Because of the high final accuracy desired, it was evident that, the fewer the corrections which were required, the more hope there would be of achieving it. Consequently, the former course was chosen. The presence of fission products was undesirable only if their β,γ-activity was high enough to cause errors in the fission- or α-counting. In any case, the purification steps used for the heavy elements thoroughly decontaminated uranium from fission products.

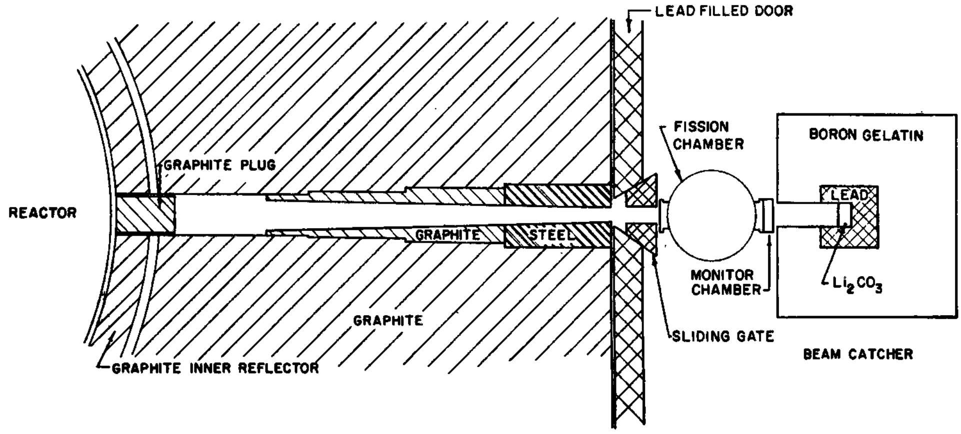

FIG. 3.—Thermal column beam assembly.

It is possible to test for the presence of plutonium and transplutonium elements in uranium by α-pulse analysis—in fact, during the purification procedure, this was done as a check and further decontamination carried out, if required. Three nuclides which could have caused errors due to difficulty of detection in the starting material were Th^{230}, Np^{237} and U^{233}, all of whose principal α-particle energies are very nearly the same as that of U^{234}.

Th^{230} was unlikely to be present, and its separation from uranium is, in any case, particularly straightforward. Although neptunium separation is not so simple, only moderate decontamination was required. The maximum Np^{237} α-activity originally present in any samples was calculated to be 3 per cent of the uranium activity, and the maximum decontamination factor required for any of the methods was somewhat less than 10^3. U^{233} could have been produced from Th^{232} impurity in the uranium rod. According to all available evidence, the thorium content was much lower than the 200 p.p.m. which would have been required to cause a significant error due to U^{233} production in Rod. No. 683.

Material for use in the direct counting method required greater decontamination from plutonium, americium and curium than did material for use in the other methods. With these nulides as impurities the α-counting would have been affected more adversely than the fission counting. In order to keep the α-counting rates of plutonium (Pu^{239} + Pu^{240}), Am^{241} and Cm^{242} to 0.1 per cent of the uranium counting rate, the maximum decontamination factors required were 3×10^5 for plutonium, 10^5 for Am^{241} and approximately 10^5 for Cm^{242}.

Purification procedure. Although requirements for the different methods varied somewhat, the most stringent were invariably the objective since starting material purified to such a degree could then be used for any method. The sequence of steps was: (1) ether extraction from saturated $Mg(NO_3)_2$ solution 0.1 *M* in HNO_3 to separate uranium from Np, Am, Cm, the bulk of the fission products, and some Pu, (2) adsorption on an anion-exchange column (Dowex-1) from 12 *M* HCl solution to further decontaminate from Pu, Am and Cm, and (3) passage through a Dowex-1 column in 9 *M* HNO_3 to remove the remainder of the Pu.

Two single volume ether extractions were normally carried out to ensure sufficient decontamination from Np^{237}, since its detection was not possible by α-pulse analysis. In the second step, after washing Am and Cm through the column, 5–10 column volumes of 1 per cent NH_4I solution in 12 *M* HCl were passed through to elute Pu as Pu^{III}. The uranium was then eluted with distilled water. In the third step, uranium passed rapidly through the column in 9 *M* HNO_3 while the plutonium was strongly adsorbed. Normally, these steps reduced all contaminants to a satisfactorily low level, but in one instance a repetition of the third step was required to give sufficient decontamination from Pu.

METHODS

Three distinct methods were used in this work. As pointed out earlier, they all depended on fission counting for the determination of U^{235} and α-counting for the determination of U^{238}. In Method A* fission and α-counting were done directly on purified uranium samples. In Method B, both fission and α-counting were done on samples which had been neutron activated in the NRX in order to increase their α-counting rates via Pu^{239} production. In Method C, fission counting was done on separate sources, and an even more indirect procedure than in Method B was used to arrive at the U^{238} contents of samples.

Method A

From the standpoint of the number of operations required, this method was the simplest of the three which were tried. It consisted of (1) mounting a source of natural uranium back to back with one of depleted uranium in the double ionization chamber already described, (2) determining the ratio of their fission counting rates in the neutron beam, (3) closing the beam shutter, doubling the gas pressure and determining the ratio of their α-counting rates.

Since the relative amounts of the uranium isotopes are different in the depleted and natural samples, for the determination of the U^{238} content of depleted uranium by α-counting, a knowledge of its specific α-activity is required. The determined U^{238} content of depleted samples must be corrected for U^{238} destroyed during irradiation, in

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* The methods will be given the same identifying letters as used by Bigham *et al.*[4]

order to determine the U^{238} initially present; however, this is a small and easily calculable correction. In order to determine the specific activity, on the other hand, an analysis of the α-spectrum is required in order to determine the fraction of total α-counts in the U^{238} peak and correct this for the contributions of the other α-particles.

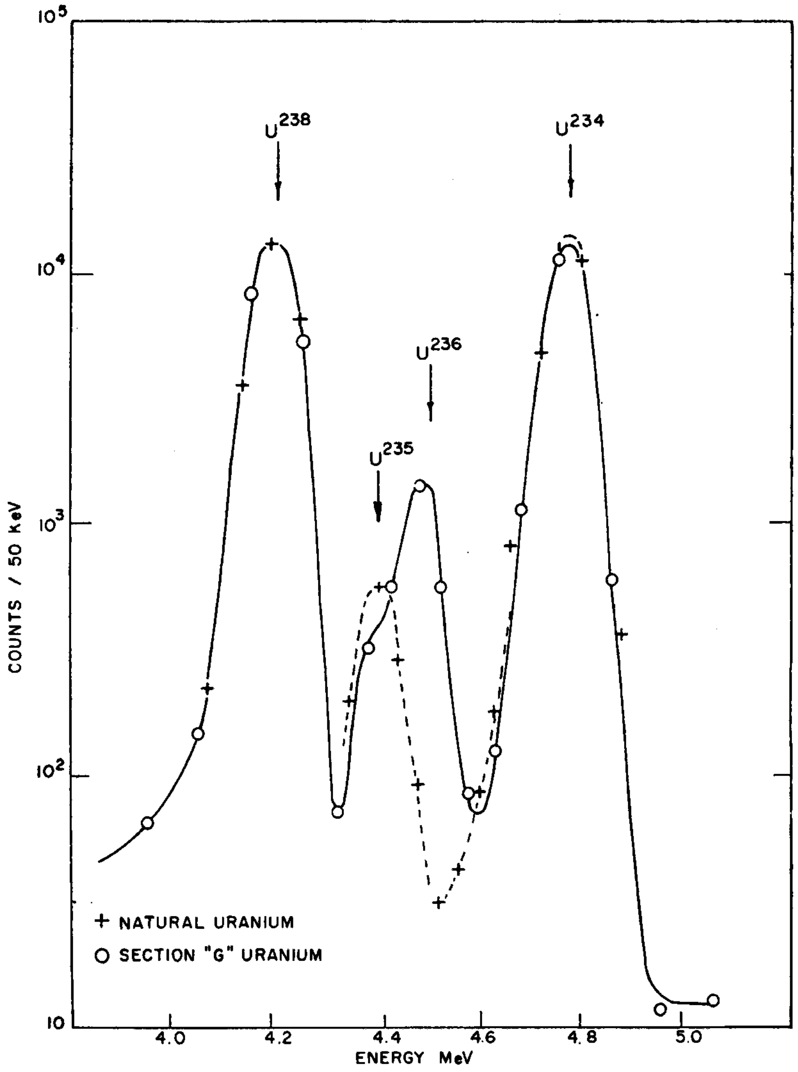

FIG. 4.—Alpha spectra of natural and Section "G" uranium.

The α-spectra were obtained by use of the grid ion chamber and 'kicksorter' described previously. In Fig. 4, the spectra for natural and Section G uranium are shown normalized to give the same intensity in the U^{238} peak at 4.20 MeV. Results of the analysis are given in Table I in terms of the relative α-particle specific activities per initial U^{238} atom.

Sources used for these subsidiary measurements contained about 100 μg of U spread over mirror-finish platinum discs $1\frac{1}{8}$ in. in diameter. These were prepared in two ways—electrodeposition, using the method of McAuliffe[7], and lacquer spreading, according to the method of Glover[8] as developed by the author.[9] Basically, the latter method consists of either pipetting or brushing a lacquer solution containing dissolved $UO_2(NO_3)_2$ over the metal surface to be coated, allowing the solvent to evaporate, and then flaming to burn off the lacquer residue and convert the uranyl nitrate to oxide. For the spectral analysis, the sources prepared by the lacquer technique proved to be the more suitable, and were used to obtain the results given above (Fig. 4, Table I).

For depletion measurements, Method A was very tedious. Because of the low specific α-activity of uranium, a 100 μg sample requires counting for about 10 days to achieve the necessary statistical accuracy. At the same time, the background and spurious rates have to be known and held constant to within about 3 counts/hr. Because of this, the method was not considered practical at first; instead, Method B was planned and the double ionization chamber designed with that method in mind. In fact, Method A was not tried until trouble was experienced with Method B. As a consequence, sources prepared by procedures developed for Method B were used for Method A, and these preparative methods are described in a separate section.

Table I.—Relative α-particle specific activities per initial U^{238} atom

Isotope	Energy, MeV	Natural	G
U^{238}	4.20	1	0.9975
U^{234}	4.76	1	0.9070 ± 0.0043
U^{235}	All groups	0.046 ± 0.001	0.0293 ± 0.0007
U^{236}	4.50	0	0.0768 ± 0.0008
Total		2.046 ± 0.001	2.0106 ± 0.0045
Ratio: $\frac{\text{natural}}{\text{depleted}}$		1	1.0176 ± 0.0022
U^{235} Burn-up value assumed		0	36.3%

Method B

This method was designed to reduce times required for α-counting by a factor of 50 to 100 over those required by Method A. If a thin sample of natural uranium is irradiated for one month, for example, in a high-flux irradiation position of NRX, the resulting Pu^{239} α-disintegration rate will be about 100 times greater than that of the natural uranium. Irradiations were carried out with a natural sample back to back with each unknown sample. Since natural and unknown samples were irradiated in the same flux, a comparison of their α-counting rates was equivalent to a comparison of their U^{238} contents. Similarly, comparison of their fission rates was equivalent to comparison of their U^{235} contents, after applying a suitable correction for the fission rates due to plutonium by the method described previously.

Because of a combination of two effects, the results obtained by Method B were less accurate than had been hoped for. One of these was the deterioration of sources due to irradiation; the other was the persistent and variable contamination of the sources with Po^{210}. The latter affected only the α-counting, the former mainly the fission counting. Although the better sources after irradiation were hardly distinguishable visually from unirradiated sources, marked deterioration of their fission counting plateaus showed that they had, indeed, been thickened by irradiation. This drawback might perhaps have been tolerated but the Po^{210} contamination could not be. Although all materials used in the irradiations (aluminum irradiation capsules, blank discs and spacers, as well as the source disc material) were given various hot acid cleaning treatments to remove traces of surface bismuth, small but significant and uncontrollable amounts of Po^{210} persisted.

Method C

In order to avoid the contamination and irradiation damage problems encountered in Method B, a more complicated method involving the use of Pu^{238} as a tracer was investigated. The procedure for this method (Method C) consisted of the following steps:

(1) A set of sources and also a set of targets were prepared from natural uranium and each depleted uranium sample. The sources were designed for U^{235} determination by fission counting; the targets, after processing, were used for U^{238} determination via Pu^{239}. Each set of sources and corresponding targets contained Pu^{238} added as a tracer. The amount of tracer was so chosen that its α-activity was about equal to that of the Pu^{239} produced in the irradiation.

(2) For any given uranium sample, sources and targets were prepared at the same time and in a manner designed to maintain the $Pu^{238} : U^{238}$ ratio constant for both sets.

(3) Sources were fission and α-counted in the double gridded ion chamber to obtain $U^{235} : Pu^{238}$ ratios.

(4) Targets were irradiated in a manner similar to the back-to-back arrangement used previously.

(5) After irradiation, the uranium and plutonium were dissolved off the aluminum target-backing and the plutonium was carefully purified.

(6) This plutonium was used to prepare sources on platinum for α-pulse-height analysis, which gave $Pu^{239} : Pu^{238}$ ratios directly and thus, indirectly, $U^{238} : Pu^{238}$ ratios. From these and the $U^{235} : Pu^{238}$ ratios obtained in (3), $U^{235} : U^{238}$ ratios were calculated.

The use of an α-active tracer was necessary to link the two sets of counting results. As the tracer, Pu^{238} had the advantage over a non-plutonium isotope in that the method was independent of chemical yields during target processing.

Although Method C eliminated all the problems it was supposed to, a new and unexpected difficulty arose which prevented the method from achieving the high final accuracy expected on the basis of the counting results. This difficulty will be described during the discussion of the various methods and the results obtained by them.

SOURCE PREPARATION AND CHEMICAL PROCESSING

General requirements

Regardless of method, certain general principles had to be observed throughout the chemical work in an effort to prevent contamination, especially cross contamination, of the samples. The strictness of the precautions required in this work cannot be too greatly stressed. Reagents were checked for α-activity and fissile material. Whenever possible, a separate fume hood was kept for natural uranium and each of the two depleted materials used. All pieces of apparatus, such as electrodeposition cells, were used for only one type of uranium. The one exception to this was the muffle furnace which was used for igniting all sources prepared by the lacquer technique; in this case, it was considered satisfactory to rest each sample on its own insulator during its time in the furnace.

One of the most important requirements for satisfactory fission and α-counting is a uniformly thin source. Coupled with this must be a very smooth backing surface which is reasonably level. Although the neutron beams used were quite uniform, to avoid any adverse effects from even slight nonuniformity, the sources should be reasonably uniform over their whole area. The tolerance was set at ±10 per cent which was unnecessarily strict in view of the neutron beam uniformity attained. Another requirement of the sources was that they be adherent; this was particularly important for sources which had to undergo relatively long irradiations before being counted.

From the point of view of the counting, it was very desirable to use source backing material which affected the measurement of neutron flux as little as possible. This meant that it had to have rather a low absorption cross section, and also be thin to keep scattering effects small. It was preferable, too, that during in-pile irradiation, either low-level or short-lived activity be produced. From the point of view of source preparation, a material capable of withstanding temperatures of ca. 500° C was desirable in case ignition of the source was required. Aluminum was considered the most suitable backing material on all counts, and pure aluminum sheet (grade 1S) 0.016 in. thick was used.

Source preparation for Method B

At the time the work was started, it was not known how uniform the collimated neutron beam would be. Consequently, much stricter limits were set on source uniformity than later proved to be necessary. For the achievement of such uniformity, it was felt that electrodeposition offered more hope of success than did lacquer painting or pipetting. Also, provided the electrodeposition could be made quantitative, or its rate controlled, the average thickness of the uranium oxide deposit could be closely controlled. Actually, electrodeposition methods were not invariably satisfactory, although a number of suitable sources were obtained; the lacquer method, on the other hand, proved capable of producing at least as good sources, if not slightly better. It should be noted that 'suitable' here is used with reference to sources before irradiation. None of the sources stood up to irradiation quite as well as had been hoped, but again, the lacquer sources were somewhat better.

Electrodeposition directly on aluminum

In applying almost all the methods for electrodepositing uranium oxide adherently on any metal from aqueous solution, a temperature of 70–80° C is required (see, for example, McAuliffe[7]). McAuliffe was not successful in depositing uranium oxide on aluminum, but Wilson and Langer[10] succeeded in depositing thick films of oxide (ca. 2 mg/cm^2) at 80° C, using a very thin subcoat of zinc on the aluminum and essentially the same ammonium oxalate electrolyte as recommended by McAuliffe.

The method of Wilson and Langer was found to be of no use in depositing uranium oxide in the range of thickness, 20–50 μg/cm^2, required for this work. It has since been shown by the author[11] that below a critical average deposition rate no uranium is deposited, but instead the aluminum cathode surface is attacked and a floc of $Al(OH)_3$ is formed in the electrolyte. The critical rate varies somewhat for different surface preparations of the aluminum (such as zinc subcoating[10] surface abrading[12] or HNO_3-HF etching[13]) and is such that a minimum thickness of the order of 200 μg U/cm^2 can be deposited when aiming for quantitative deposition. Thinner deposits than this can, of course, be obtained by aiming at thick sources and stopping the deposition in its early stages. However, due to variable induction periods and relatively high initial rates of deposition, control of the amount deposited is difficult.

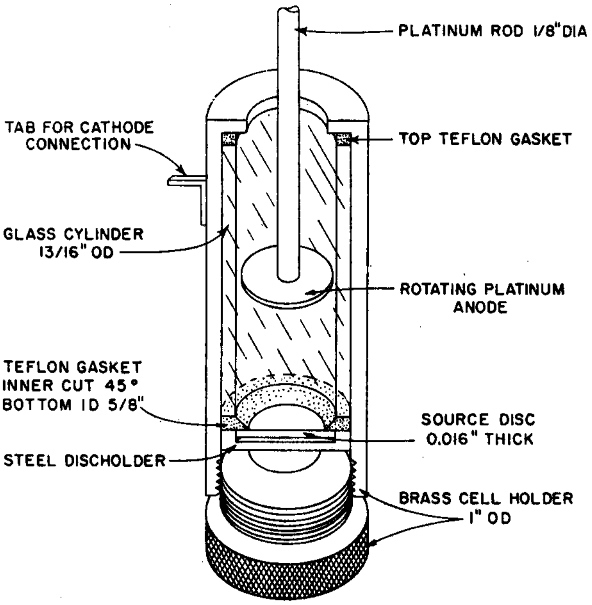

FIG. 5.—Sketch of electrodeposition cell.

In any case, the nature of the deposition process on aluminum appears to be such that roughened surfaces (by etching or abrading) are required for adherent deposits. Since, for precise fission and α-counting, very smooth surfaces are required, no further effort was expended on straight aluminum; instead, the use of thin copper and nickel plates on the aluminum was investigated.

Electrodeposition on copper and nickel plated aluminum

Both copper and nickel can be plated directly on aluminum after the proper pretreatment of the surface, and both elements have low enough neutron absorption cross sections (approximately 4 b) that a plate 0.001 in. thick, for example, can be tolerated by the counting methods. Also, the only activities induced to an appreciable extent (Cu^{64} and Ni^{65}) have short enough half-lives to cause no trouble. There appeared to be no doubt that McAuliffe's method[7] would work well for both metal plates, and the principal problems were to obtain adherent sources on adequately smooth and adherent metal plates.

The cells used for electrodeposition were similar to those used by numerous other investigators.[7] One arrangement is shown in the sketch of Fig. 5, in which the parts of the cell were held in place by a brass container with threaded bottom plug. At first, an ordinary washer-shaped gasket had been used at the bottom of the cell and the anode stirrer was moved up and down, rather than rotated, in an effort to prevent an area of light deposition around the center of the cathode which appeared to result from rotational stirring.[7] When this procedure was used, the uniformity was quite good over most of the area, but the edges were markedly scalloped. The same effect was observed with rotational stirring at speeds of 2–600 r.p.m. Several arrangements were tried with subsidiary copper gaskets of different shapes next to the copper plated cathode source discs; none were satisfactory. The most satisfactory arrangement found was that shown in the sketch, with the Teflon gasket cut at a 45° angle. Although, with this arrangement, quite uniform sources were prepared with a reasonably sharp cut-off at the edge of the Teflon gasket, a fairly large fraction had small spots of heavy deposition or small areas of almost no deposition, apparently due to formation of gas bubbles. These effects were observed even on pure copper discs, and serve to illustrate the fact that phenomena observed during electrodeposition are very dependent on the surface properties of the base metal, being particularly affected by those irregularities which are not apparent to the eye.

Conditions used for electrodeposition were all within the ranges found most satisfactory by McAuliffe[7]. Those which gave the best results are listed below.

Temperature	80° C
Current density	125 mA/cm^2
$(NH_4)_2C_2O_4$ concentration	0.15 *M*
Initial pH	8 ± 0.5
Stirring rate	6–700 r.p.m.

Electroplating

Aluminum sheets were prepared for plating by the anodic treatment of Bengston[14] after preliminary cleaning and a 0.5 *M* HF etch at room temperature. After the anodic treatment at 32° C for 10 min, the sheets were immediately transferred to the copper or nickel plating baths. The nickel plating bath was of the high sulfate type used for plating aluminum which has been given a zincate pretreatment. The copper plating process employed was the Unichrome process described by Coyle[15], in which a bath is used of $Cu_2P_2O_7$ dissolved in a $Na_4P_2O_7$ solution and the electrodeposition is made at fairly high current densities at 40 to 60° C.

Because of the surface roughening caused by the reported pretreatment of aluminum for direct copper and nickel plating, it did not seem worthwhile to attempt "mirror finish" plating. Instead, after plating, the sheets were buffed to a mirror finish on a high speed buffing wheel and cut into discs. These were thoroughly cleaned by boiling in "Alconox" solution before they were used in the electrodeposition process. Since the original etched aluminum surfaces were rough, the metal plates were also rough, and plates of the order of 0.001 in. in thickness were required to allow mirror polishing without going through to the base metal. Almost invariably, blisters formed on copper plates originally 0.002 in. thick after they were polished and boiled in "Alconox" solution, and nickel plates of 0.001 in. often suffered the same fate. While nickel plates around 0.0005 in. in thickness were usually adherent, they were not easily polished without going through to the aluminum; consequently, most of the sources were prepared on copper plated discs. If the latter survived the boiling treatment and the 30–40 min electrodeposition at 80° C without any signs of blistering, it was observed that they did not blister under irradiation.

Sources by lacquer method

The basic steps in the lacquer method for depositing thin films of uranium oxide (and many other medium and heavy metal oxides) have already been outlined. Lacquer solution containing dissolved $UO_2(NO_3)_2$ was prepared as follows. A strong nitric acid solution of $UO_2(NO_3)_2$ was evaporated just to dryness under an infra-red lamp, avoiding too strong heating. The residue was dissolved in a small volume of acetone and transferred to the required volume of a solution of cellulose nitrate in amyl acetate. The volumes were calculated so that the final solution would have the correct uranium concentration for the particular purpose for which it was required, and the proper cellulose nitrate and acetone concentrations for either painting on with a brush or applying with a pipette. For example, a solution containing 3–3.5 g of cellulose nitrate per 100 ml was most suitable for pipetting, but this was too viscous for painting, becoming tacky before it could be completely brushed out. Solutions containing around 2 g/100 ml were most suitable for painting.

At first, sources were prepared by pipetting onto the counting discs the amounts of uranium solution required to give the desired counting rates. Since there were still some doubts about the uniformity required, it was felt that such sources might not be uniform enough. Accordingly, it was decided to switch to the painting technique. In this procedure, about ten successive coats were applied to a relatively large sheet (2 in. × 3 in.) and discs were punched out from the areas that appeared by visual inspection to be uniform. For macroscopic uniformity, such inspection was adequate since layers of all thicknesses above about 10 μg U/cm^2 were colored (interference effects) and, in the range of thickness of sources used (20–40 μg/cm^2), the color varied rather rapidly with thickness. Thus, it was only necessary to select areas of a sheet where the color did not vary in order to obtain uniform sources. By means of the color, the film thickness could also be estimated quite closely and, hence, the weight of uranium on the disc.

For successful application of the lacquer technique, it was required that the sheets be flat and level during painting. To keep them level they were placed on a small plate with a bubble levelling device. Each polished sheet for painting was heated at 500° C for a few minutes to soften it, then flattened by passing it through a small pair of rolls while sandwiched between two sheets of polythene (to avoid roll marks).

For successful counting, very smooth surfaces were desirable. With a little practice a mirror finish on small areas ($\leqslant$ 1 in.^{2}) can be obtained by electropolishing. Quite a lot of effort was put into developing methods for electropolishing the 0.016 in. 1S aluminum sheet in areas of 5–6 in.^{2}, with only modest success. It was found that chemical polishing produced surfaces which were satisfactorily smooth for counting, and 2 in. by 3 in. pieces could easily be handled, so all subsequent polishing was done chemically. The baths used were the R5 polishing bath[16] containing phosphoric, acetic and nitric acids, and one due to Jumer[17] which was largely phosphoric acid with small amounts of Na_2SO_4 and $NaNO_3$. Both baths were operated at around 100° C or a slightly higher temperature.

Chemical work associated with Method C

Sources were all prepared by the lacquer technique in the same manner as described in the preceding section. Successive coats of lacquer were applied to and burnt off chemically polished aluminum sheets 0.016 in. in thickness, and source discs were punched out in areas where the uranium oxide deposit was uniform.

Target foils were also prepared by lacquer painting; for this purpose, however, 2 in. squares of 1S aluminum foil 0.005 in. in thickness were used. For each irradiation three foils were prepared, one containing approximately 10 μg/cm^2 of depleted uranium and Pu^{238} tracer, and two containing approximately 5 μg/cm^2 of natural uranium and Pu^{238}. These foils were wrapped in 0.001 in. aluminum foil to prevent cross contamination during irradiation, rolled into cylinders and placed inside an irradiation capsule. The depleted foil was sandwiched between the two natural foils. This arrangement was chosen to minimize differential attenuation of resonance neutron flux by averaging the effect between the natural and depleted samples.

For each irradiation, a set of foils prepared in exactly the same manner, except that the uranium was not 'spiked' with Pu^{238}, was included with the 'spiked' set. These were used to measure the production of Pu^{238} from uranium, since the rates of production were different for the natural and depleted samples due to the presence of U^{236} in the depleted material.

Chemical treatment of irradiated targets

After removal of the samples from the reactor, a waiting period of about 2 weeks was allowed for the bulk of the Pu^{239} to grow in from the Np^{239} remaining at the end of the irradiation. About 0.3 μg of plutonium was produced in each irradiated sample. Chemical separations were carried out simultaneously on the natural and depleted material. The steps of the separation procedure outlined below were all given thorough preliminary tests, using unirradiated target foils and (particularly to check on decontamination from Po^{210}) irradiated sources from Method B. The steps were:

1. Dissolving the deposit off the target foils and their 0.001 in. wrappers with hot 1 : 1 HNO_3. This dissolved appreciable amounts of aluminum, but weaker acid did not satisfactorily dissolve the deposit.
2. Adsorption of plutonium from $9M$ HNO_3 on 'large' Dowex-1 resin columns and washing uranium, aluminum, neptunium and polonium through with 15 column volumes of $9M$ HNO_3.
3. Elution of plutonium by means of $0.5M$ $NH_2OH{\cdot}HNO_3$.
4. Repetition of steps 2 and 3, using 'small' Dowex-1 resin columns.

The 'large' columns were approximately 1 cm in diameter and 5–6 cm in length to allow reasonable flow rates for the relatively large volumes of viscous aluminum nitrate solution. The small columns were approximately 1½ mm in diameter by 4 cm in length. They were designed to give a final decontamination from traces of uranium and aluminum which might have come through the large columns. This was necessary because no visible solid residue could be tolerated in the final plutonium sources.

Plutonium source preparation

The lacquer method of depositing plutonium after the above purification was useless because, in fact, there was invariably a visible residue on the platinum discs after preparation of the sources. This residue was inorganic (since flaming did not remove it) and was definitely associated with the plutonium and not the lacquer solution. Later experience in the preparation of thin β-sources[18] has shown that virtual elimination of solid residues from source materials purified by ion-exchange can only be achieved by special purification of reagents and working in polythene instead of glass to avoid pick-up of inorganic matter.*

The use of electrodeposition promised to overcome the residue problem since the conditions required are not favorable for deposition of cations such as the alkali and alkaline earth elements which might have come from the glassware and reagents. In the method of Miller and Brouns[19], provision is made for the oxidation of plutonium to the plutonyl state, using ozone to avoid the introduction of interfering cations. Since an ozonator was not available, a method of oxidizing the plutonium with the aid of persulfate was developed.[20] Any alkali (or ammonium) persulfate may be used since the Miller and Brouns electrolyte is a 1–2M KOH solution. One ml portions of 0.2M nitric acid solution containing 0.3 μg Pu were placed in a boiling water bath, a few small crystals of an alkali persulfate was added with stirring, and the solutions were heated for about five more minutes. After transfer to the 1.2M NaOH electrolyte in electrodeposition cells of the same type as shown in Fig. 5, plutonium was deposited on mirror-finish platinum discs 1 in. in diameter in a circle 1 cm in diameter at the center of the disc. The sources were invisible until after they had been flamed, at which time a faint brown shadow appeared. This was attributed to the presence of traces of iron in the caustic electrolyte.

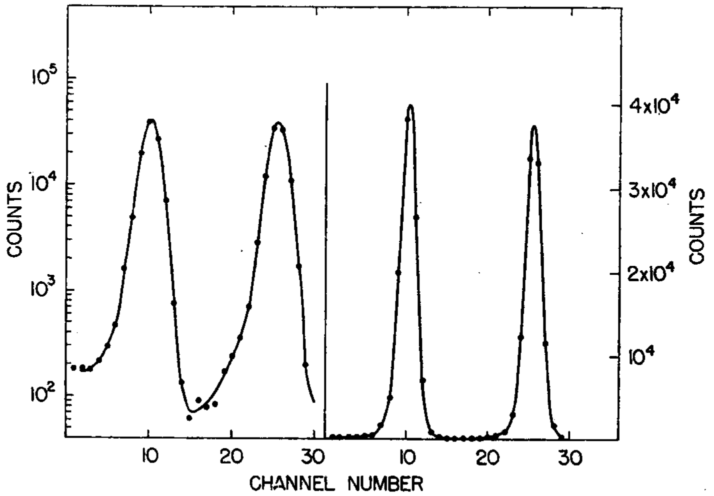

FIG. 6.—Pulse analysis of Pu^{238}–Pu^{239} peaks using source SP-15.

Pu^{238}–Pu^{239} pulse-height analysis was performed, using the grid ion chamber and eighteen-channel 'kicksorter'. For the "spiked' samples, in which counting rates of the two isotopes were roughly equal, a correction of about 0.4 per cent had to be applied for the contribution which the tail of the Pu^{238} peak made to the Pu^{239} peak. Fig. 6 shows an α-spectrum obtained for source SP-15, using a 'kicksorter'–ion chamber

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* One exception is the method of Børnholm *et al.*, *Nature* 1956, **178,** 1110 using what might be called microcolumns in glass capillaries and only a very few λ of extremely pure eluting solutions.

combination very similar to that described earlier. Correction for the Pu^{238} tail in this case amounts to about 0.3 per cent, and Po^{210} activity is undetectable (<0.1 per cent of either peak).

EXPERIMENTAL RESULTS

Of the measurements by Method A, three were made on Section G material, using two pairs of electrodeposited sources, and one on Section P material, using lacquer sources (refer to Fig. 1 for location of discs *P* and *G*.)

The results are given in Table II, and represent about 800 hr of counting for the G and about 80 hr for P data. Typical rates in the experiments with material from section G were 30 α counts/min with a background of 2.5 counts/min and about 3000 fission counts/min with a background of about 2 counts/min. The results show a deviation from the mean considerably larger than expected from the statistical errors. The one result for P material was obtained from sources with counting rates about three times those used for the G material, and is in good agreement with the mass spectrometer result (see Table V).

Table II.—Depletion measurements by Method A

Samples	Burn-up, %	Deviation from mean
G14/U14	38.47 ±0.23	1.48
G15/U15	36.68 ±0.28	0.31
G15/U15	35.81 ±0.28	1.18
	Mean value 36.99 ± 0.64*	
P90/U90	15.00 ±0.23	

Note: Errors given are statistical errors of counting except for that marked with an asterisk, which is the root mean square deviation.

The same sort of scatter obtained for results from the analysis of material from Section G, using Method A, is observed in the results by Methods B and C. These results are summarized in Tables III and IV, respectively. Using Method B, seven pairs of sources were measured, including one natural uranium pair which was included as a check. Of the other six results, one was rejected as an obvious 'flier'. The root mean square deviation of the set of five 'good' determinations was 2.3 per cent, which is 15 times that expected from statistics.

Considering Method C, the fission/α-count ratio measurements on the unirradiated sources were straightforward, with counting rates of a few thousand per minute. The measurement of Pu^{238}/Pu^{239} activity ratios in the plutonium separated from the irradiated targets also presented no problems. However, the result for material from the G Section was quite wide of the mark, and deviation of the results for material from the P Section was considerably higher than would be expected from the purely statistical errors in the counting.

In Table V, the collected results of depletion measurements by the three counting methods are compared with the mass spectrometer results. Except for the isolated

TABLE III.—DEPLETION MEASUREMENTS BY METHOD B

Capsule number	Sample numbers	Prepared by	$\frac{(235/238)\ \text{Depleted}}{(235/238)\ \text{natural}}$	Statistical error	Deviation from mean
C 79	U41/G41	Painting	0.6606	0.0015	0.0208
C 79	U40/G40	Painting	0.5438	0.0009	Rejected
C 80	U14/G14	Electrolysis	0.6348	0.0006	0.0050
C 80	U42/G44	Electrolysis	0.6526	0.0012	0.0128
D 70	U68/G66	Painting	0.6190	0.0016	0.0208
D 70	U65/G65	Painting	0.6322	0.0016	0.0076
D 70	U66/U67	Painting	1.0014	0.0018	—

Notes: Mean of G/U comparisons, 0.6398 ± 0.0067.
Root mean square deviation of a single measurement, 0.0149 = 2.3 per cent.

TABLE IV.—DEPLETION MEASUREMENTS BY METHOD C

Number	Pu source number	$\frac{(\alpha_9/\alpha_8)_D}{(\alpha_9/\alpha_8)_N}$	Error, %	Fission source number	$\frac{(F/\alpha_8)_D}{(F/\alpha_8)_N}$	$\frac{(N_{235}/N_{238})_D}{(N_{235}/N_{238})_N}$	Error, %	Burn-up, %
I	$\frac{\mathrm{SG2}}{\mathrm{SU2}}$	0.9784	0.14	GS1/US1 GS2/US2	0.5872 0.6010	0.6000 0.6134	0.16 0.17	39.5 ± 0.4
II	$\frac{\mathrm{SP6,7}}{\mathrm{SU6,7}}$	0.9511	0.14	PS5/US5 PS6/US6	0.8063 0.8151	0.8474 0.8570	0.16 0.18	14.9 ± 0.4
III	$\frac{\mathrm{SP12,13}}{\mathrm{SU12,13}}$	0.9332	0.11	PS10/US10 PS11/US11	0.8004 0.8051	0.8577 0.8628	0.13 0.18	14.1 ± 0.3

Note: D = depleted; N = natural.

TABLE V.—COLLECTED RESULTS

Method	Burn-up, %	
	G	P
A. Alpha and fission counting of unirradiated samples	37.0 ±0.6	15.0* ±0.2
B. Alpha and fission counting of irradiated samples	36.0 ±0.7	
C. Pu^{238} tracer method	(39.5)†	14.5‡ ±0.4
Mass spectrometer analysis (Lounsbury[1])	36.3 ±0.16	14.96 ±0.21

* Isolated measurement; accuracy quoted is statistical.
† Isolated measurement; probably invalidated by bad mixing of tracer.
‡ Mean of two; error corresponds to the difference between them.

measurement of G material by Method C, the counting results agree with the mass spectrometer results within the accuracy claimed. However, the accuracy achieved with any of the counting methods did not reach the ±1 per cent desired.

DISCUSSION AND CONCLUSIONS

It was emphasized in the last section that the scatter in the counting results was disappointingly large, considering the relatively small errors arising in the counting itself and in the corrections (mostly small) which were required in the various methods. The reasons for this, insofar as they are known, were different for each method, and thus would require different treatment for their reduction or elimination.

In the case of the results for G material by Method A, the scatter is believed to be due primarily to fluctuations in background during the lengthy periods of α-counting. Trouble from this source can be greatly alleviated simply by increasing the counting rates of the samples used. In fact, the counting rates used in the analysis of P material were three times those used in the analysis of G material. By designing a chamber to take larger source discs, sources of still higher counting rate could be used.

The scatter in Method B results was probably due partly to uncertainties in the counting (particularly fission counting) resulting from irradiation damage to the sources. However, a larger uncertainty was introduced by the random polonium contamination mentioned earlier. Although the presence of Po^{210} on the sources was not directly proven, it was found as a surface deposit on the blank spacing discs which had faced the sources at a distance of about 5 mm during irradiations. Small amounts of plutonium, very variable, but averaging about 0.2 per cent of the sample, were also found on the blank discs, so that it is completely reasonable to expect that the polonium, which is notorious for migrating, had been transferred from the sources to the blank discs during irradiation.

The amounts of bismuth required to give the observed Po^{210} activities were very small, being about 5×10^{-10} g for the activities on the blank discs. A random variation of about 2×10^{-9} g between sources would account for the observed scatter of the results, so that amounts of the order of 10^{-8} g were probably present on the sources. Since surfaces of source discs were cleaned (e.g. by chemical polishing) before source deposition, it appears that the bismuth found its way to the sources during deposition. Indeed, it is not surprising that millimicrogram amounts might have been present in the chemical reagents and in apparatus which could not be given standard acid cleaning treatment such as the brushes used for lacquer painting. It should be feasible to decrease this trace of bismuth contamination by a factor of 10 or so without expending too great an effort, especially once the source or sources of contamination have been discovered. However, in dealing with such small amounts there is always the worry that, having sufficiently cleaned up all reagents and apparatus, contamination will sooner or later creep in from some unexpected source.

One obvious way of solving the problem without preliminary decontamination from traces of bismuth would be to determine the exact amounts of Po^{210} contamination by radiochemical and counting methods after the samples had been counted. This course of action, however, it not too attractive because it adds two more steps to the already lengthy procedure.

In the case of Method C results, the lack of constancy was apparently largely due to lack of constancy of the Pu^{238}/U^{238} ratio on the targets and foils. Detailed examination of the results showed that those obtained with different pairs of samples did not agree; for example, in measurement I there was a discrepancy of 2.2 per cent between the F/α ratios from GS1 and US1 and those from GS2 and US2. This implies that the Pu^{238}/U ratio was not constant over the aluminum sheets from which source discs were punched.

Although it was felt that during preparation of 'spiked' lacquer solutions the Pu^{238} tracer was thoroughly mixed with the uranium, some doubt existed because of the high viscosity of the solutions. Special precautions were, therefore, taken with the mixing of the tracer in the third series of measurements. Although the discrepancy between results from the two sets of sources was only 0.6 per cent, the burn-up value obtained still differed considerably from the mass spectrometer value. This leads one to suspect that, regardless of constancy of Pu^{238}/U ratio on the source sheets, this ratio for the sources was different from that of the targets.

Another possibility is that, regardless of the constancy of the Pu^{238}/U ratio on both the sources and targets, the Pu^{238}/Pu^{239} ratio was altered during treatment of the irradiated targets. During the dissolution of the target material off the aluminum backings, this could happen only if the target material were incompletely dissolved and one of the isotopes (presumably Pu^{239} because of recoil from neutron capture in the parent uranium) tended to be imbedded in the backing to a greater extent than the other. Certainly no large effect could be attributed to this cause since a fair depth of aluminum was dissolved from the backing at the same time as the target material. However, it is possible that a small error could have arisen from this cause, especially since attack of the aluminum backing was not uniform on a micro scale.

If it is assumed that any such error was too small to be significant, we are left with the alternative that the Pu^{238}/U ratios had not in fact been maintained constant. This effect must then have been due to some phenomenon occurring in the lacquer solutions themselves, or in the process of target preparation.

Regarding the former possibility, it is well known that trace amounts of inorganic ions are adsorbed from aqueous solutions on the walls of glass containers. For example, in standardization of solutions of radioisotopes, small amounts of inactive carrier are added and solutions are kept acidic to minimize adsorption. In our situation, it is conceivable that slow adsorption of Pu^{238} tracer on the glass container walls was occurring during the course of source and target preparation. A similar type of occurrence, involving Pu^{238} tracer, was observed by Hart[21] in nitric acid solution. He found that, after thorough mixing, considerable time had to elapse before the ratio of Pu^{238} tracer to other plutonium isotopes would remain constant.

In our procedure of lacquer painting, adsorption of the tracer would probably have caused the most trouble in the mechanics of source and target deposition. For example, adsorption might have occurred on particles of material from the brushes, or even in the brushes themselves, in such a way as to progressively change the Pu^{238}/U ratios. Then, since more coats were required for sources than for target foils, the final ratios on the two would have been different.

If adsorption on the glass were the only problem, it probably could be solved by allowing the adsorption process to come to equilibrium before beginning lacquer application. However, if adsorption in the brushes was involved, probably the only solution would be to throw away the brushes and develop the technique of applying lacquer with a micropipet. This undoubtedly can be done on the size of sheet used in this work, since it was done successfully[22] on extremely thin foil over an area roughly half this size during the course of another investigation.[23]

Comparison of Methods A, B and C can be made from both the counting and the chemical point of view. The 'chemical' comparison is the critical one in deciding on a method to use, since counting techniques have been mastered or, in the case of the troublesome α-background in Method A, almost certainly can be without to much effort.

From the chemical point of view, Method A presents no problems at all, and in terms of effort is much simpler than either Method B or C. The chemical problems of both Methods B and C could be, with considerable effort, either solved or circumvented, but both are long and C in particular is rather complicated. By comparison, the chemical work required for preparation of mass spectrometer samples is simple, since Pu and other α-activities many times that of the uranium can be tolerated. Of the three counting methods, Method A most nearly corresponds to the mass spectrometric method as far as overall effort is concerned, although the chemical effort is greater for the counting method.

Two more things should be pointed out. The first is that any of the counting methods, even at the stage of development which was attained in this work, would be applicable where accuracies of only a few per cent are needed. Under such conditions, the large total number of counts taken for each determination in the present work would not be required, and Method A would become quite attractive. The other point to be made is that the accuracy achievable by counting methods increases progressively as the burn-up increases, basically because the fission rate is a good measure of U^{235} even at very low concentrations. Since this is unlikely to be true of mass spectrometric determinations, counting methods, particularly method A, may be very useful in the concentration region encountered in very high burn-ups.

This paper should give some idea of the complexity of the type of analytical problem which is often encountered in the determination of specific reactor constants and more general nuclear data. The problem discussed in the present paper proved to be more difficult than most, and was not completely solved before work had to be stopped, although it probably could eventually have been solved. However, the description of our attempts at its solution will serve to illustrate the wide variety of techniques and meticulous attention to detail required for successful solution of such complex problems.

ACKNOWLEDGEMENTS

The experiments described in this paper represent a joint effort of several people. The author is responsible only for the chemical aspects. Dr. C. B. Bigham, G. C. Hanna and P. R. Tunnicliffe were responsible for the conception and design of the physical aspects of the experiments and made most of the physical measurements. Their report has been referred to earlier.[4] I am greatly indebted to them for helpful comments on the content of this paper and for permission to reproduce Figs. 2, 3 and 4.

Dr. J. P. Butler and Mrs. J. S. Merritt kindly supplied the Pu^{238} tracer used.

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ANALYTICAL METHODS USED IN A STUDY OF REACTIVITY CHANGES WITH LONG IRRADIATIONS

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Summary—A number of samples of natural U have been irradiated to various levels, up to 6200 MWD/t, in the NRX reactor at Chalk River for studies of the variation of reactivity with neutron irradiation. Measurements of the reactivity of the samples before and after irradiation have been made in the GLEEP reactor at Harwell. Chemical and mass spectrometric analyses of the samples have been made at Chalk River. A comparison of some of the results with theoretical predictions, based on the latest BNL cross-section data, was presented at the 1959 Annual Meeting of the American Nuclear Society, 15–17 June, by Kushneriuk[9]. A discussion and interpretation of all the results will be given in subsequent papers by D. S. Craig, R. G. Hart, M. Lounsbury, and A. G. Ward. The analytical methods used are discussed in the present paper.

The U was determined gravimetrically by diuranate precipitation and volumetrically by $Ce(SO_4)_2$ titration. These methods are straightforward and are mentioned only briefly. Plutonium was determined by four different methods: spectrophotometric, direct low-geometry α-counting, isotopic dilution with highly irradiated Pu, and isotopic dilution with Pu^{238}. A comparison of these methods is the primary concern of this paper.

Some brief comments are also given on reactivity changes with long periods of irradiation.

INTRODUCTION

THE Canadian approach to atomic power is based on the heavy-water moderated reactor fueled with natural uranium. To achieve economic generation of power in such a reactor, an energy yield of 8000 thermal megawatt days (MWD) or more per ton of uranium must be attained without reprocessing. Consequently, an integral part of the research program at Chalk River has been an examination of the overall credit and debit balance of neutrons over the lifetime of the fuel and a correlation of this balance with theory.

The important changes in the fuel during irradiation are the depletion of U^{235} and the ingrowth of the successive plutonium isotopes 239, 240 and 241, and also the fission products. Such a program, therefore, is inherently dependent upon accurate analytical methods for uranium and its isotopes, and plutonium and its isotopes. In this paper, the determination of uranium will be discussed only briefly because the methods used are well known. The principal topic for discussion will be the analysis of plutonium as the methods we used are unique. The mass spectrometric aspects of the program will not be discussed, outside of outlining some of the results. Those particularly interested in this subject are referred to a paper by Lounsbury in the 1956 issue of the *Canadian Journal of Chemistry.*

URANIUM ANALYSIS

First of all, methods for uranium analysis will be mentioned briefly . These can only be defined as brute force methods as a certain amount of radiation exposure was accepted in order to achieve the accuracy required. The standard gravimetric method[1] involving ammonium diuranate precipitation and ignition to U_3O_8 was used on the lower irradiated samples. The higher irradiated samples were analyzed volumetrically[2], using ceric sulfate oxidation of U^{IV} to U^{VI} after reduction by means of a Jones reductor. Approximately 500 mg of U was taken for each gravimetric analysis and approximately 50 mg of U was taken for each volumetric analysis. A correction for a small amount of corrosion-product iron was required in both methods. This correction was based on results obtained by colorimetric analysis, using the *o*-phenanthroline method, and normally amounted to a fraction of a per cent.

The precision of a single gravimetric analysis at the 95 per cent confidence level was ±0.39 per cent, while that of a single volumetric analysis was ±0.38 per cent at the same confidence level. By following the usual practice of analyzing each sample in duplicate, the mean error was reduced to below 0.3 per cent. Results for some of the samples which were analyzed by both methods are given in Table I. The cross-checks obtained give us confidence that there is no bias in either method.

TABLE I.—COMPARISON BETWEEN GRAVIMETRIC AND VOLUMETRIC URANIUM ANALYSES

Slug No.	Total U, *mg/ml* (gravimetric)	Total U, *mg/ml* (volumetric)	Atom ratio U^{235}/U^{238}
AGW-1-8	241.8 ± 0.7	241.5 ± 0.7	$(0.7116 \pm 0.0010) \times 10^{-2}$
AGW-1-5	238.0 ± 0.7	238.9 ± 0.6	$(0.6841 \pm 0.0010) \times 10^{-2}$
AGW-1-9	254.8 ± 0.7	254.7 ± 0.7	$(0.6218 \pm 0.0010) \times 10^{-2}$
AGW-1-11	242.4 ± 0.7	242.7 ± 0.7	$(0.5671 \pm 0.0016) \times 10^{-2}$
AGW-1-4	277.2 ± 0.8	277.7 ± 0.7	$(0.4764 \pm 0.0012) \times 10^{-2}$

PLUTONIUM ANALYSIS

All samples were analyzed for plutonium by two different methods, a spectrophotometric method and a direct α-counting method.

The spectrophotometric method was developed by Allison at Chalk River[3] and has been used there routinely since that time. An aliquot of dissolver solution containing 1.5–4 mg of plutonium is adjusted to 8*M* with nitric acid and is then passed through a 2-ml column of 250 to 350 mesh Dowex-1 in the nitrate form. The plutonium is absorbed while the uranium and fission products pass through the column. The column is then washed with 5 column volumes of 10*M* nitric acid. The 10*M* nitric acid is then displaced with 1 column volume of 1*M* nitric acid and the purified plutonium is eluted with 5 ml of 10-per cent hydroxylamine nitrate. The eluate is is collected in a 5-ml volumetric flask, centrifuged and transferred to a 5-cm spectrophotometer cell. Absorbancy measurements are then made with a Beckman Model DU spectrophotometer at a wavelength of 602 mμ. A schematic diagram of the apparatus is given in Fig. 1. There is always a small loss of plutonium to the aqueous raffinate. This loss is normally of the order of 0.2–0.3 per cent, but can go higher if dissolving conditions are abnormal. The loss is determined by α-counting an Am- and Cm-free source and is added to the spectrophotometric result. The precision of a single analysis at the 95 per cent confidence level is ±1.4 per cent. The usual practice of analyzing each sample in duplicate reduces the error to ±1.0 per cent. The method is readily adaptable to remote operation. The scheme used at Chalk River is described in the literature.[4]

The direct α-counting method for plutonium[5] was developed primarily for the analysis of radial samples taken from a cross section of an irradiated uranium rod.

These samples, taken to provide a knowledge of the variation of cross sections across the diameter of a rod, contain too little plutonium to be analyzed spectrophotometrically. A sample containing approximately 50 μg of uranium is accurately pipetted onto a stainless-steel source tray. The micropipet used is washed three times with a solution of tetraethylene glycol in dilute nitric acid (four drops of TEG in 10 ml of $1M$ nitric acid). The solution on the source tray is then evaporated to dryness under an infrared lamp and the source tray is ignited to redness. The evaporation must take place very slowly in order to avoid decomposition of TEG by hot nitric acid. Two to three hours are necessary for the drying. The total α-distintegration rate is measured in a Ward-type low-geometry chamber[6] and the α-spectrum is measured in a Frisch gridded ion chamber[7] using an AECL-2230 pulse analyser[8] and preamplifier described by Harvey *et al.*[7] A typical spectrum is shown in Fig. 2. From the total count rate, the α-spectrum, a mass analysis of the plutonium and the specific α-activities of Pu^{239} and Pu^{240}, the amount of plutonium in the sample can be calculated. The precision of a single analysis at the 95 per cent confidence level is ±1.9 per cent. The usual practice of analyzing each sample in duplicate and taking the mean reduces the error to ±1.3 per cent.

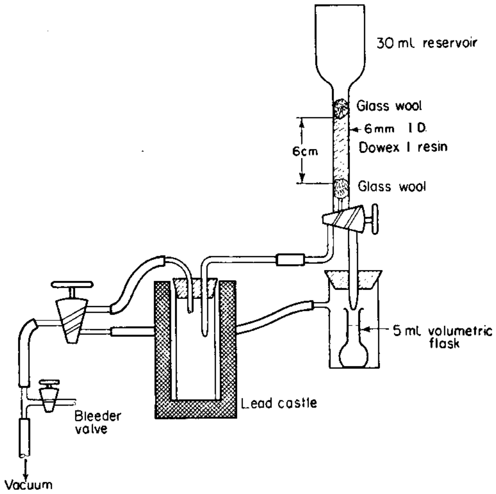

FIG. 1.—Ion exchange apparatus for Method B.

The results for a number of samples analyzed by both methods are given in Table II. Again the cross checks obtained give us confidence that there is no bias in either method.

A limited amount of work has been done on two isotopic dilution methods for plutonium; one involves isotopic dilution with Pu^{238},[5] the second isotopic dilution with plutonium rich in Pu^{240}.[5] The former method is based on an α-count of the purified product while, in the latter method, a mass analysis is made of the product. Since a sufficient number of analyses are not available to establish the precision of these methods in the usual manner, an attempt has been made to arrive at an evaluation of the error by considering all the possible contributing errors. In this manner, it was estimated that the precisions for single analyses at the 95 per cent confidence level is ±1.8 per cent for the Pu^{238} dilution method and ±2.2 per cent for the Pu^{240}

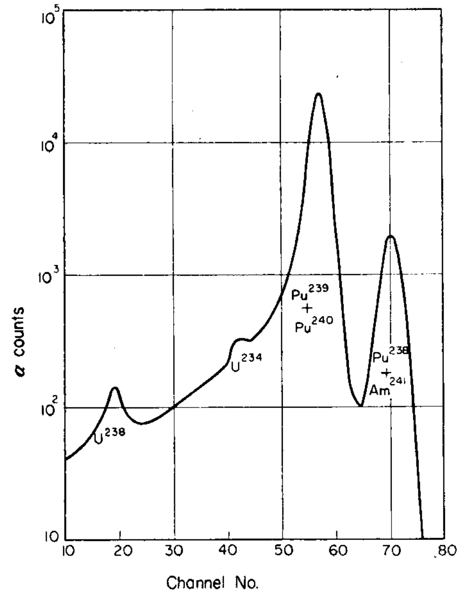

FIG. 2.—Typical α-spectrum of a plutonium sample.

TABLE II.—COMPARISON BETWEEN SPECTROPHOTOMETRIC AND DIRECT α-COUNTING PLUTONIUM ANALYSES

Slug No.	Total Pu, *mg/l.* (spectrophotometric)	Total Pu, *mg/l.* (direct α-counting)
AGW-1-9	195 ± 2	194 ± 3
AGW-1-11	295 ± 3	293 ± 4
AGW-1-4	505 ± 5	498 ± 6
42-1	455 ± 5	455 ± 6
42-2	519 ± 5	529 ± 7
42-3	558 ± 6	567 ± 7
42-4	517 ± 5	516 ± 7
42-5	423 ± 4	426 ± 5
42-6	278 ± 3	280 ± 4

dilution method. The cross checks obtained between the four methods on the few samples analyzed by isotopic dilution are shown in Table III. One further point

TABLE III.—COMPARISON BETWEEN SPECTROPHOTOMETRIC, DIRECT α-COUNTING AND ISOTOPIC DILUTION ANALYSES

Slug No.	Total Pu, *mg/l.* (spectro-photometric)	Total Pu, *mg/l.* (direct α-counting)	Total Pu, *mg/l.* (Pu^{238} dilution)	Total Pu, *mg/l.* (Pu^{240} dilution)
AGW-1-5	80.6 ± 0.8	—	77.3 ± 1.4	79.7 ± 1.6
AGW-1-9	195 ± 2	194 ± 3	195 ± 4	(199 ± 4)
AGW-1-11	295 ± 3	293 ± 4	301 ± 6	(303 ± 6)
AGW-1-4	505 ± 5	498 ± 6	514 ± 10	513 ± 14

Note: ( )—isotopic equilibrium not certain.

requires mention. We have definite evidence that isotopic equilibrium is not attained immediately after spiking. Sample 4 gave a result of 579 mg/l. when separated shortly after spiking. This factor should be studied in detail before too much faith is put in either of these methods. We have as yet not found time to make this study.

CORRELATION WITH THEORY

Finally, the correlation achieved between experiment and theory will be indicated. Figures 3 and 4 are taken from a paper[9] presented by Kushneriuk, of our theoretical physics branch, at the 1959 Annual Meeting of the American Nuclear Society, in June of this year. Figure 3 shows the correlation between U^{235} burn-up and grams of plutonium produced per kilogram of uranium. The solid line is calculated, using the latest BNL cross sections for a moderator temperature of 38° C. The slightly high value for the rod 42 point is attributed to a slightly different environment than that assumed in the calculation. Figure 4 shows the correlation between grams of plutonium per kilogram of uranium and the isotopic composition of the plutonium. The dotted curves are elementary approximations based on the assumption of constant cross sections. The solid curves take into account self shielding of the plutonium isotopes. The excellent agreement between experiment and theory gives us confidence that our reactivity predictions contain no very significant unknowns and that our predictions of the burn-up attainable in our power reactors are correct.

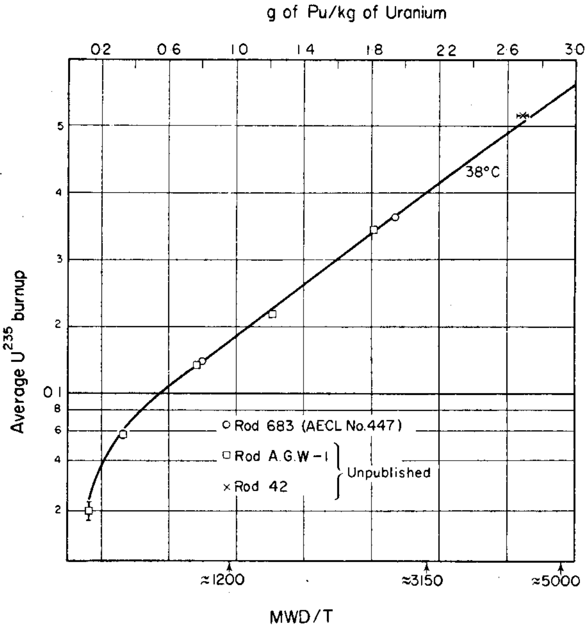

FIG. 3.—Correlation between U^{235} burnup and grams of plutonium per kilogram of uranium

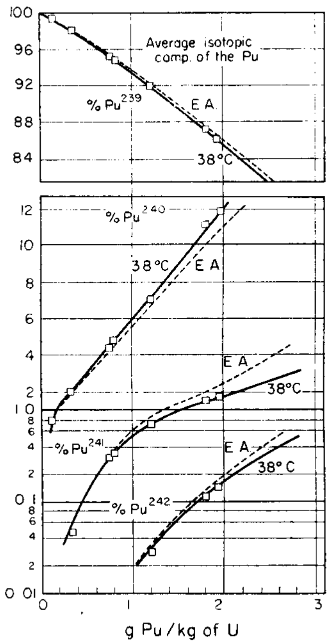

FIG. 4.—Correlation between grams of plutonium per kilogram of uranium and the isotopic composition of the plutonium.

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Talanta, 1960, Vol. 6, pp. 100 to 104. Pergamon Press Ltd. Printed in Northern Ireland

THE COLORIMETRIC DETERMINATION OF ZIRCONIUM IN PLUTONIUM-URANIUM-'FISSIUM' ALLOYS*

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Summary—This method was developed for the determination of zirconium in plutonium-uranium-'fissium' alloys. A sample of the alloy containing 40–100 μg of zirconium in 10*N* nitric acid is separated from plutonium and from some of the palladium by anion exchange. The effluent is analyzed for plutonium since more than 60 μg will interfere. The ruthenium is removed by fuming with perchloric acid. The uranium and molybdenum do not interfere in reasonable quantities as they exist in this alloy. The alizarin red-S lake is formed in 0·1*N* nitric acid, and its absorbancy is measured by means of the Beckman Model B spectrophotometer at 520 mμ. The color is stable for several hours and reproducible within 3–5 per cent of the amount present. The interference of the alloying constituents and reagents are given. The time required for duplicate analyses is about 3½ hr, and the equipment and techniques used are standard.

INTRODUCTION

'FISSIUM' (Fs)[1] is the name that has been applied to all the alloys of uranium, plutonium and fission products coming from the work on pyrometallurgical processing.

The problems introduced by starting a reactor cycle on pure uranium or plutonium and then processing and fabricating a slightly different alloy with every cycle are tremendous. As a result, it has been planned to load the reactor with an alloy approaching one of the equilibrium alloys in composition. The change in composition per cycle in this case is slight and changes in properties are expected to be negligible.

A novel feature of the Experimental Breeder Reactor-II (EBR-II) is that the fuel processing is an integral part of the reactor cycle.[2] The metallurgical refining process and the fabrication methods that will be used involve very short cooling times and incomplete decontamination of the fuel. Chemical methods of processing are much more expensive than the pyrometallurgical processing because they require a longer cooling period, and thus a larger fuel inventory, and much more elaborate processing equipment. After a few cycles in the reactor and through the pyrometallurgical process, the equilibrium alloy will vary according to the original fuel composition. A few typical reference alloys have been set up for test purposes; however, the Pu-U-Fs experimental alloys submitted for analyses have been quite variable, as is shown in Table I.[3] The variations in weight per cent of the U–Pu-Fs encountered in our analysis is indicated in the last column of Table I.

Our basic philosophy in analyzing plutonium-bearing samples is to use a method which calls for the smallest sample size as long as the accuracy obtained is adequate for the problem. Consequently, this method with an accuracy of about 3 per cent standard deviation serves the purpose very well for the present state of fuel development with 'fissium' alloys.

It was obvious from some work reported earlier[4,5] on the analytical application of the nitric acid anion exchange system to plutonium-'fissium' alloys and on the

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* Work performed under contract with the U.S. Atomic Energy Commission.

TABLE I.—TYPICAL REFERENCE FISSIUM ALLOYS

Element	U-'Fissium'	Pu–U-'Fissium'	Variations in Pu–U-'Fissium'
Uranium	95.0	69.2	50–75
Plutonium	—	20.0	20–40
Zirconium	0.2	0.5	0.05–4.5
Molybdenum	2.5	2.8	1.25–6.0
Ruthenium	1.5	4.3	1.25–6.0
Rhodium	0.3	0.7	0.25–0.9
Palladium	0.5	2.5	0.7 -2.5

determination of neptunium, using anion exchange, that the plutonium interference could be removed. In 10*N* nitric acid, the Pu^{4+} has a distribution coefficient of about 2500 while that for Zr^{4+} is only 0.7.[5] Some of the palladium is removed and ruthenium, the only other interfering element, can be removed by fuming with perchloric acid after the anion exchange. The complete recovery of the zirconium after fuming was difficult but was found to be quantitative after refluxing with nitric acid.

EXPERIMENTAL

The alizarin lake was found to be stable[6] in 0.1*N* nitric acid for several hours if the waiting period after the addition was at least 1½ hr.

If hydrofluoric or sulfuric acid was used in the dissolution of the alloy, complete removal was necessary. If these acids are present, the procedure should be modified. The fuming with perchloric acid after elution from the anion resin column should be continued until the sample has evaporated to dryness. Traces of these acids either inhibited or prevented the formation of the lake. However, the only alloying constituents which did interfere were plutonium and ruthenium. The rhodium, molybdenum and palladium gave no interference when the ratio of each to zirconium was 1 to 1. The uranium did not interfere when it was 2000 to 1.[6]

The nitric acid did not affect the slope up to 0.15*N* but above that the optical density decreased. Mixtures of nitric and hydrochloric acids gave the same slope as long as the total acidity did not exceed 0.15*N*.

A perchloric acid medium for the development of the alizarin lake would probably work just as well as the nitric acid.[7]

The plutonium content in excess of 60 μg in a final volume of 25 ml was found to interfere. Excess plutonium caused the slope to decrease as is shown in Fig. 1.

Even though the distribution coefficient for the Pu^{4+} was stated to be about 2500, the decontamination factor varied from 60 to 2500. The erratic decontamination factor may be due to either polymerization or disproportionation in the 10*N* nitric acid.[8,9] In all cases, the decontamination was more than adequate to prevent the interference of plutonium (Table II).

The volume of 10*N* nitric acid necessary for complete elution of the zirconium from a resin column (6 mm × 6 cm) is less than 25 ml.[4] An aliquot from a standard solution containing zirconium was eluted from the resin column and compared to a like aliquot from the same solution. Quantitative recovery was indicated by comparison of spectrophotometric measurements.

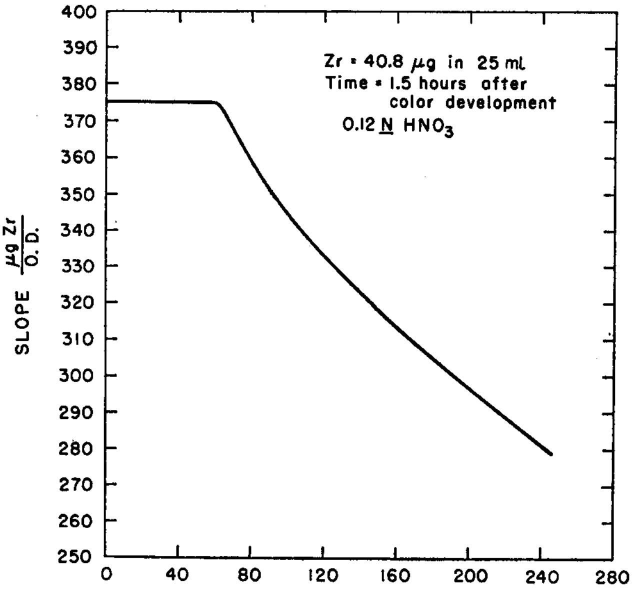

FIG. 1.—Plutonium interference.

Some experimental data indicated that the zirconium in 0.1N nitric acid could be accurately determined in the presence of as much as 200 µg of plutonium if the solution is allowed to stand for at least 12 hr before the addition of sodium alizarin sulfonate.

TABLE II.—Pu DECONTAMINATION BY ANION EXCHANGE—10N HNO$_3$

Sample number	Sample weight in aliquot, *mg*	Pu, %	Pu in sample, µg	Pu left, µg,	D.F.
3305-A	1.70	19.4	330	0.7	470
3306	4.90	20.1	985	2.7	365
3307	2.07	20.2	420	5.6	75
3308	1.57	20.7	325	5.3	60
3309-A	1.33	19.3	255	0.1	2550
3310-A	2.58	19.8	510	1.4	365
3311	2.60	41.5	1080	9.0	120

PROCEDURE

Reagents.

Nitric acid: 10N

Analytical Grade AG 1 × 10 Anion Exchange Resin.*
(Processed from Dowex-1 × 10).
Moisture 33–39 per cent.
Total capacity—3 mequiv./dry gram.
Mesh size—200–400.
Supplied in the chloride form.

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* Supplier: Bio-Rad Laboratories, 800 Delaware, Berkeley, California.

Concentrated perchloric acid (70%).
Concentrated nitric acid.
Distilled water.
Sodium alizarin sulfonate: 0.0125% in H_2O
Hydrochloric acid: 6*N*.
Hydrogen peroxide 30%.
Hydrofluoric acid: 1*N*.

The Pu–U-Fs alloy was dissolved in 6*N* hydrochloric acid, hydrogen peroxide and a drop or two of 1*N* hydrofluoric acid when necessary. The sample was diluted to a convenient volume and an aliquot containing 40–100 μg of zirconium was transferred to a small beaker or centrifuge tube. Enough concentrated nitric acid was added to make the solution 10*N* and it was allowed to stand overnight. The anion column (6 mm × 6 cm) was prepared by washing it alternately with 5 ml portions of 10*N* nitric acid and water, the final wash solution being 10*N* nitric acid. The total volume of wash solution was 25–30 ml. The solution of the alloy was transferred to the column by gravity with an elution rate of about 1–2 ml/min. The column was washed with 25–30 ml of 10*N* nitric acid (using a vacuum) with an elution rate of about 6 ml/min. The eluant collected was sampled for α-assay to determine the $Pu^{239,240}$ plus Am^{241} content.* If the total plutonium was less than 60 μg, there was no interference.

The eluant was evaporated to 5–10 ml, cooled, and five drops of concentrated perchloric acid were added. The sample was then fumed in perchloric acid for about 5 min to remove the ruthenium after which it was allowed to cool. Two hundred μl. of concentrated nitric acid were added and the solution refluxed for about 20–30 min to insure complete dissolution of the zirconium. The solution was cooled, transferred to a 25-ml volumetric flask and diluted to about 15 ml with water. Five millilitres of 0.0125% sodium alizarin sulfonate were added and the solution was mixed. Final dilution to the mark was made with water, following which the contents were mixed again and allowed to stand 1½ hr.

A portion of the solution was transferred to a 1-cm Corex cell, compared to a blank of 0.12*N* nitric acid containing sodium alizarin sulfonate and the optical density at 520 mμ determined. The concentration was then determined by use of a previously established calibration factor, μg zirconium/O.D. The color remained stable for several hr.[6]

RESULTS AND DISCUSSION

Duplicate test results for a set of four samples ranging from 1.5 to 4.5 per cent zirconium are shown in Table III.

Three standards were prepared from Pu–U-Fs alloys which contained a nominal composition of 0.05–0.15 per cent zirconium. A standard solution of zirconium was added to these alloys to make the percentages equivalent to 2.96, 4.62 and 6.01 zirconium. It was assumed that the nominal composition was correct. The analytical values were biased on the low side (Table IV). Most of the determinations were made about two months after the preparation of the standards. Zirconium is known to hydrolyze readily even in strong acid solutions. In view of this, it is desirable to make the zirconium determinations within a few days of the dissolution of the sample.

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* The Am^{241} is the daughter of Pu^{241} which is normally found in the plutonium that we have used.

Table III.—Duplicate test results for unknown samples

Sample number	Zr, % (nominal composition)	Zr, % (found)	Average Zr, % (found)
3306	1.5	1.46 1.51	1.48
3307	3.0	2.96 2.88	2.92
3308	4.5	4.51 4.40	4.46
3311*	3.0	2.87 2.93	2.90

*Sample number 3311 contained 40 per cent plutonium in the Pu–U-Fs alloy while the others contained only 20 per cent plutonium.

Table IV.—Zr analyses on standard Pu–U-Fs alloys

Sample number	Zr added, %	Zr recovered, %	Average Zr found, %	Std. Dev., %	Error, %
3305A	4.62	4.72 4.50 4.50 4.32 4.49	4.51	3.6	−2.4
3309A	6.01 ?	5.42 5.76 5.64	5.61	3.1	−7.1
3310A	2.96	3.00 2.88 2.88	2.92	2.4	−1.4

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Talanta, 1960, Vol. 6, pp. 105 to 111. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL PROGRAM FOR PROCESSING STAINLESS STEEL–URANIUM DIOXIDE REACTOR FUEL ELEMENTS*

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Summary—Analytical programs have been described for uranium recovery processes for aluminum–uranium and zirconium–uranium reactor fuel elements. It is the purpose of this paper to describe the analytical program for the uranium recovery process involving stainless-steel–uranium-reactor fuel elements.

The recovery process consists of a two-step dissolution and the regular liquid–liquid solvent extraction using TBP in kerosene. Sulfuric acid is used to dissolve the stainless steel. As a result of the sulfuric acid dissolution, the uranium is converted to a slurry. The uranium slurry is then dissolved in nitric acid. After the nitric acid dissolution, the feed material is compatible with the extraction columns used at the Idaho Chemical Processing Plant for other type fuel elements previously described.

In order to analyze samples of dissolver solutions for constituents necessary for plant operation, three new analytical methods were developed. These methods are a rapid method for determining uranium, one for nitrate and one for sulfate. Methods are described for uranium, acidity, specific gravity, nitrate and sulphate in the dissolver solution, and for small amounts of uranium in the extraction column raffinates. Samples of dissolver solution and first cycle aqueous raffinate contain large amounts of fission products. These samples require shielded facilities for analytical work. The remote analytical facility described by Dykes and his co-workers was used for this work.

Precision and accuracy data are given for the analytical methods described.

INTRODUCTION

ANALYTICAL programs have been described for uranium recovery processes for aluminum–uranium[1] and zirconium–uranium[2] reactor fuel elements. It is the purpose of this paper to describe the analytical program for the uranium recovery process of stainless-steel–uranium dioxide reactor fuel elements.

Figure 1 shows a simplified flowsheet of the recovery process used. The scheme consists of a two-step dissolution and the conventional liquid–liquid solvent extraction

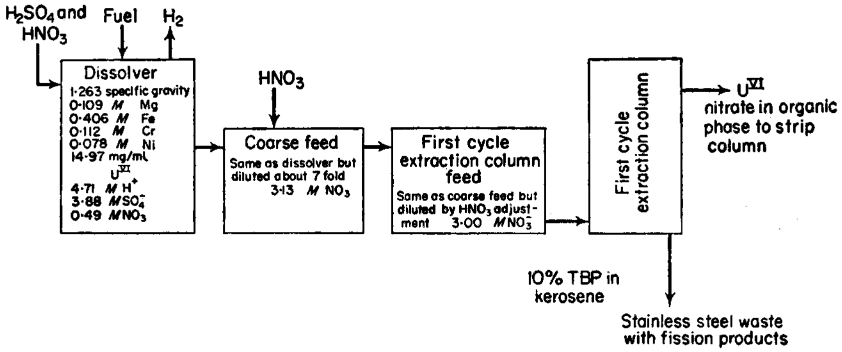

FIG. 1.—Stainless-steel fuel dissolution and extraction column feed preparation.

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* Work done under Contract AT(10–1)-205 to the U.S. Atomic Energy Commission.

using tributylphosphate in kerosene. Sulfuric acid is used to dissolve the stainless steel. As a result of the sulfuric acid dissolution, the uranium dioxide is converted to a slurry. The uranium dioxide slurry is then dissolved in nitric acid. After the nitric acid dissolution, the feed material is compatible with the extraction columns used at the Idaho Chemical Processing Plant for other type fuel elements previously described.

SAMPLES ANALYZED

The more important routine samples, constituents determined and analytical techniques are summarized in Table 1.

In order to analyze samples of dissolver solutions for constituents necessary for plant operation, three new analytical methods were developed. These methods are a rapid method for determining uranium, one for nitrate and one for sulfate.

Samples of dissolver solution and first cycle aqueous raffinate contain large amounts of fission products. These samples require shielded facilities for analytical work. The remote analytical facility described by Dykes *et al.*[3] was used for this work.

ANALYTICAL METHODS

Uranium in dissolver, coarse feed, first cycle extraction column feed and first cycle extraction column product

From the composition listed in Table 1, it can be seen that these samples, with exception of the first cycle extraction column product, contain constituents which interfere with analytical procedures. Liquid–liquid solvent extraction has been used successfully in separating uranium from fission products and other interfering impurities. After separation, samples readily lend themselves to the isotopic dilution mass spectrometric method. This technique was proposed by Ingram[4] and further developed for uranium by Duffy and Tingey[5], and Goris and Tingey.[6] This is an excellent method since quantitative recovery from the extraction is not required and concentration as well as isotope ratio are obtained at the same time. This method is used for the plant input measurement.

The separation procedure is as follows.

To a test tube is added 0.5 ml of a 1.0 mg/ml uranium-233 standard solution and 4.0 ml of $1N^B$, $2.0M$ aluminum nitrate salting solution. The test tube is transferred to the remote facility (Figs. 2 and 3) where 0.5 ml of the sample is added from a remote pipetter (Figs. 4 and 5). This pipetter was discussed at the Second Conference on Analytical Chemistry in Nuclear Reactor Technology in 1958. Details on the apparatus are given by Dykes.[7] The test tube is then stoppered and the aqueous solution is mixed by shaking to obtain homogeneity. A manipulator (Fig. 6) is used to shake the tube. Two milliliters of organic extractant, hexane, are added and the mixture is stoppered and shaken for 1 min. As much of the organic as possible is poured into a clean centrifuge tube. The tube is transferred from the remote facility to the conventional laboratory. The uranium is simultaneously stripped from the organic phase and precipitated as the peroxide by contacting with 1 ml of 30% hydrogen peroxide.

After centrifuging and decanting, the precipitate is washed with 1 to 1 water–acetone mixture and transferred to the Mass Laboratory.

The peroxide is dissolved in a minimum amount of nitric acid and evaporated on a tantalum filament. Details of the operation of the mass spectrometer and of the

TABLE I.—IMPORTANT ROUTINE SAMPLES, CONSTITUENTS DETERMINED AND ANALYTICAL TECHNIQUES

Sample	Composition		Constituent determined	Analytical technique
Dissolver	Specific gravity	1·263	Uranium	Isotope dilution Mass spectrometer
	Mg	$0{\cdot}109M$		
	Fe	$0{\cdot}406M$	Uranium	Spectrophotometric
	Cr	$0{\cdot}112M$	Nitrate	Spectrophotometric
	Ni	$0{\cdot}078M$		
	U	14·97 g/l. U^{VI}		
	H^+	$4{\cdot}71M$		
	SO_4^{2-}	$3{\cdot}08M$		
	NO_3^-	$0{\cdot}496M$		
Dissolver wash	$H_2O < 0{\cdot}01M\ NO_3^-$		Nitrate	Acid–base titration and spectrophotometric
Coarse feed	As dissolver, but diluted about seven-fold and $3.13M\ NO_3^-$		As dissolver plus	
			Specific gravity	Falling drop
			Acidity	pH titration with oxalate complexing
			Sulfate	Amperometric
			Fission products	Total β- and γ-counting
First cycle extraction column feed	As coarse feed but diluted by nitric acid adjustment NO_3^- $3.00M$		Nitrate	Spectrophotometer
First cycle extraction column raffinate	As first cycle feed but with less than 1×10^{-3} mg/ml of U^{VI}		Uranium	Pellet fluorophotometric
First cycle extraction column product	$1M$ U^{VI} nitrate $0.81M\ HNO_3$		Uranium	Isotope dilution Mass spectrometer
			Specific gravity	Falling drop
			Fission products	Total β and γ

determination are given by Duffy *et al.*[8] Results are reported for total uranium concentration and percentages of each isotope.

The isotopic dilution mass spectrometric method is time consuming and is not a method to be used if production schedules are critical. In order to obtain rapid data for uranium concentration, a spectrophotometric method was developed. The procedure is as follows.

To a test tube is added 6 ml of $2.8M$ aluminum nitrate ($2N^B$, $0.025M$ in TPAN) and 3 ml of hexone. The tube is transferred to the remote line where 0.750 ml of sample is added. A polyethylene stopper is used to stopper the tube and it is transferred to the special tumbler (Fig. 7) and mixed for 3 min. As much of the organic as possible is poured off and transferred to the conventional laboratory. The sample is centrifuged and as much of the organic as possible is transferred to a 1-cm Corex absorption cell. The spectrum of the material is scanned from 500 to 400 mμ on a Cary Model 14 recording spectrophotometer at a scan speed of 5 A/sec.

Details on this method are given by Maeck *et al.*[9]

Uranium in first cycle extraction column raffinate.

These samples are very low in uranium ($<1.0 \times 10^{-3}$ mg U/ml) and pellet fluorophotometry is used to analyze them. They contain large amounts of fission products which create radiation problems. Also, they contain foreign ions which quench fluorescence. In order to separate the uranium from fission products and other interfering ions, a liquid–liquid extraction is made in the Remote Analytical Facility. The uranium, which is contained in the organic phase, is transferred to the conventional laboratory where pellets are prepared and the fluorescence measured.

The procedure is as follows.

To a test tube is added 0.5 ml of sample and 1.5 ml of solution, 1.5M in aluminum nitrate, 5 per cent in citric acid, 1M in nitric acid and 2 ml of 1 per cent tributylphosphate in n-hexane. After extracting for 1 min, as much of the organic as possible is transferred to the conventional laboratory. Sodium fluoride pellets are prepared in platinum dishes and 0.2 ml aliquots are pipetted onto each pellet. The pellets are dried under infrared lamps, fused in a gas–air flame and the fluorescence is measured in a high-sensitivity fluorophotometer. Uranium concentration is then read from a working curve prepared from processed standards.

Acid in coarse feed

The coarse feed sample contains hydrolyzable ions which require complexing before acidity is measured. A pH titrimetric method is used to determine free acid (or base) in solutions of this nature. Oxalate, as the potassium salt, is used as the complexing agent. The potassium oxalate is adjusted to a reference pH of 5.80. This pH minimizes hydrolysis in a stainless-steel matrix. The method is described by Booman *et al.*[10]

The procedure is as follows.

Fifteen ml of an 8% potassium oxalate solution adjusted to a pH of 5.80, is added to a 50-ml beaker. If the sample is known to be nearly neutral or slightly basic, an acid "spike" is added. The beaker is transferred to the Remote Analytical Facility where 0.200 ml of sample is added by the pipetter. The beaker is then transferred to a titration apparatus (Figs. 7 and 8) and allowed to digest for 2 hr. This digestion time is required for chromium to complex. After digestion, the sample is titrated with standard 0.2N sodium hydroxide until the exact reference pH is obtained. Acidity is calculated from the base titer, sample volume and volume and normality of acid "spike".

Specific gravity in coarse feed and first cycle extraction column product

These samples contain fission products; therefore, they require remote handling. Specific gravity is determined by the falling drop method. A small, known volume

FIG. 2.—Operating aisle of remote laboratory.

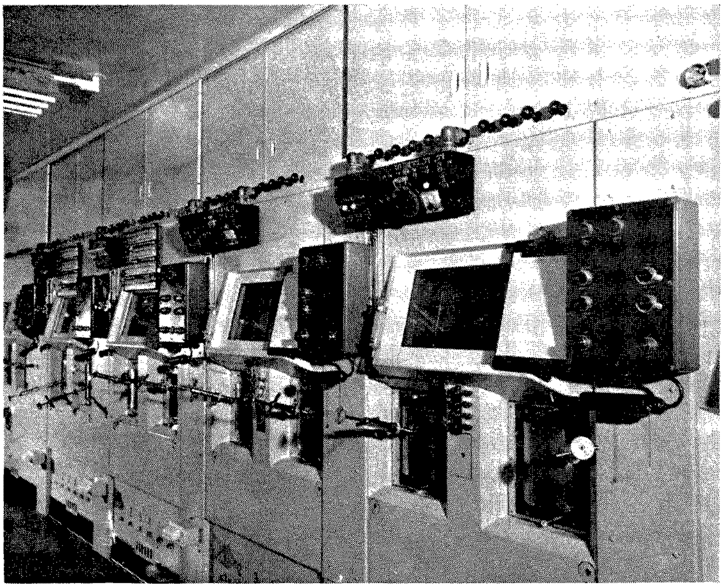

FIG. 3.—Remote line.

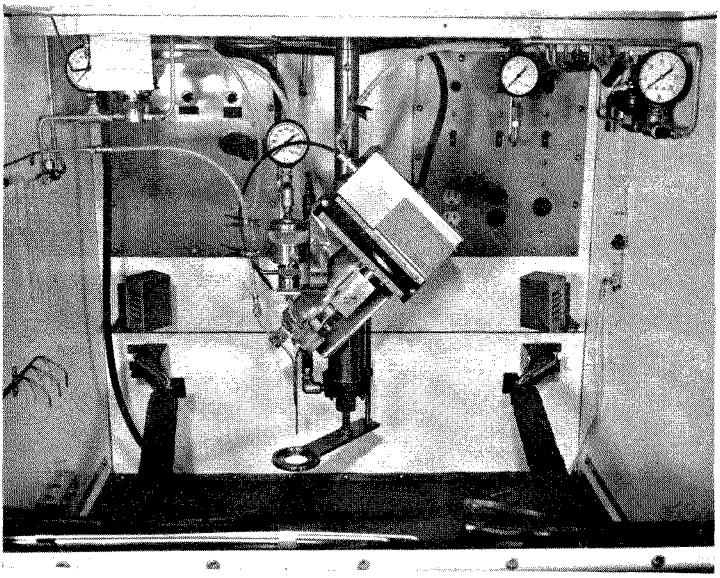

FIG. 4.—Remote analytical facility Model B pipet box installation.

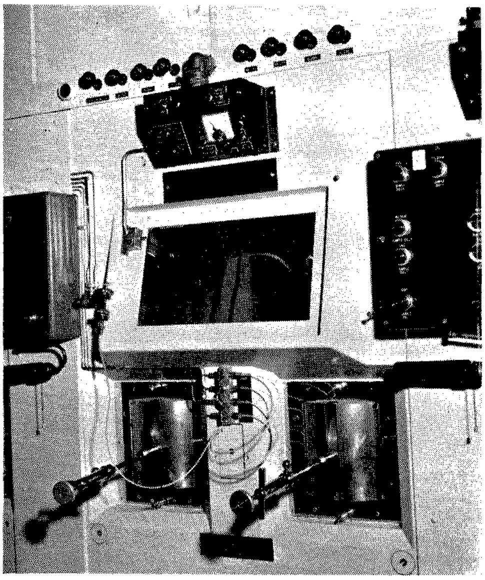

FIG. 5.—Remote analytical facility Model B pipetter.

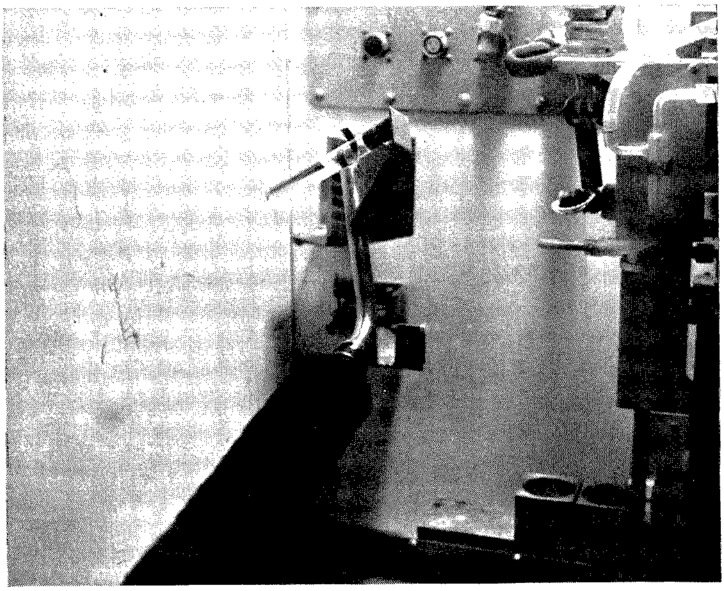

FIG. 6.—Remote analytical facility manual extraction apparatus.

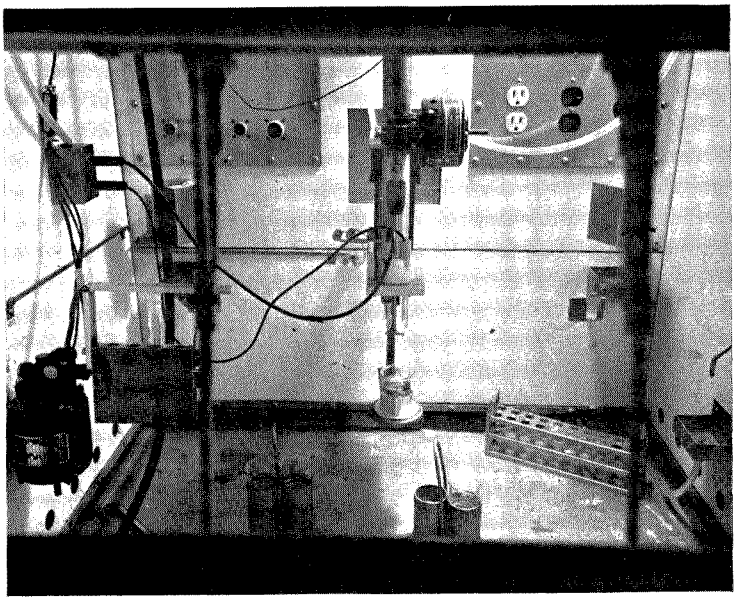

FIG. 7.—Remote analytical facility mechanical extraction apparatus.

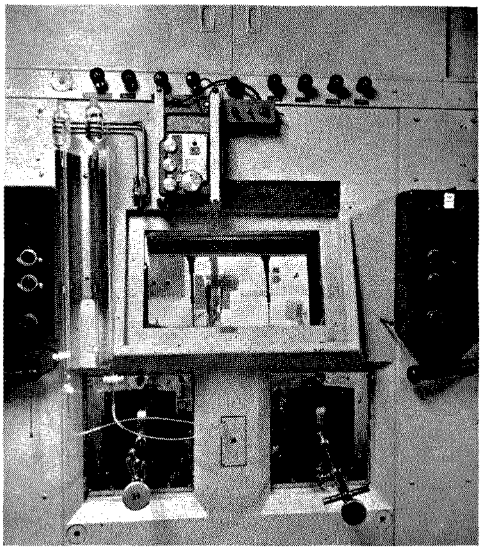

FIG. 8.—Acid titrator.

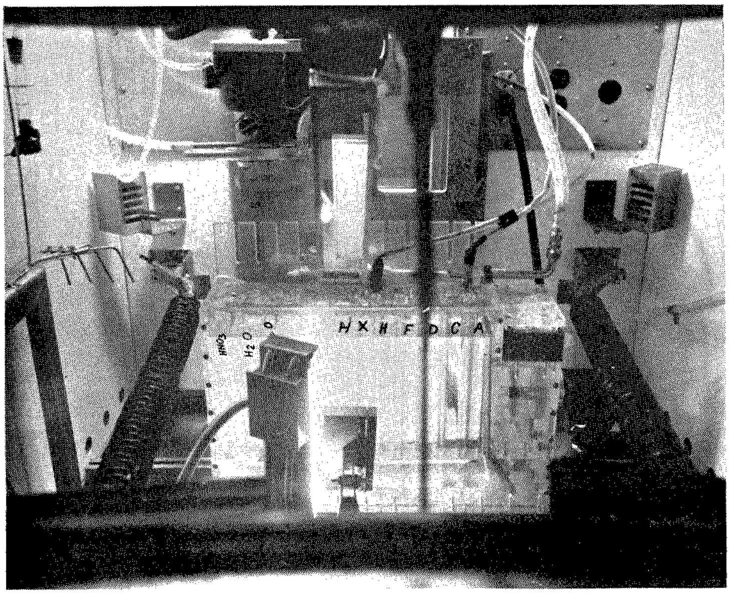

FIG. 9.—Falling drop specific gravity apparatus box installation.

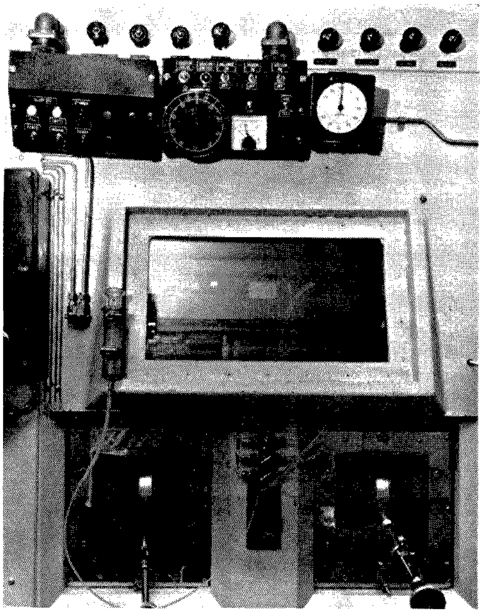

FIG. 10.—Falling drop specific gravity apparatus.

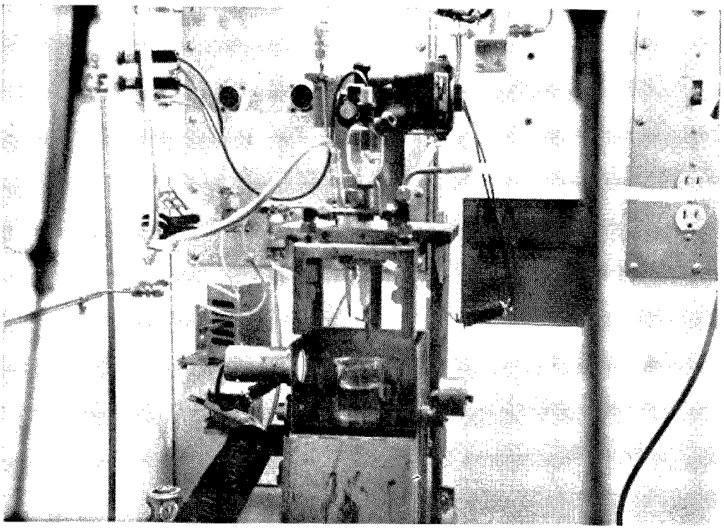

FIG. 11.—Remote sulfate titrator box installation.

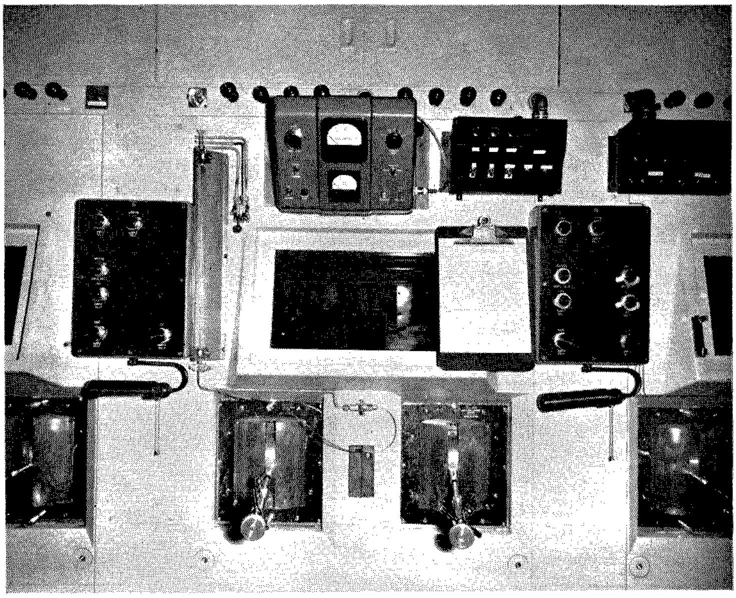

FIG. 12.—Remote sulfate titrator.

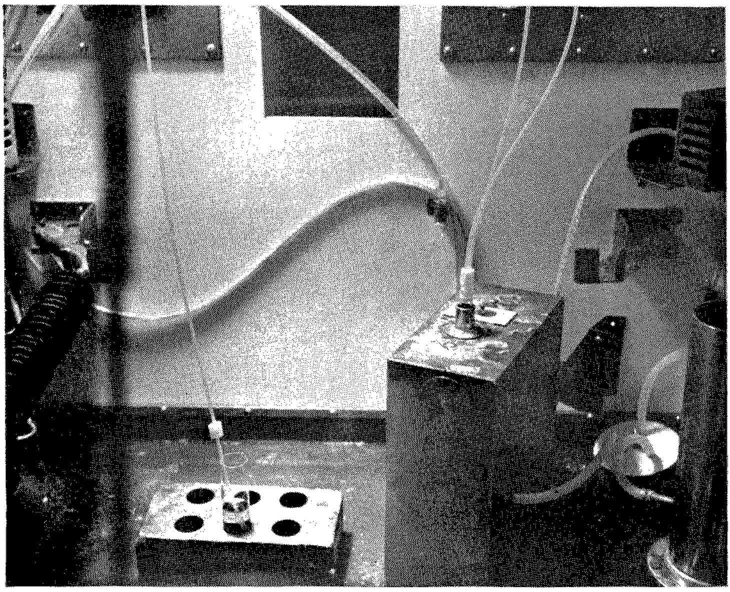

FIG. 13.—Remote colorimetric nitrate box installation.

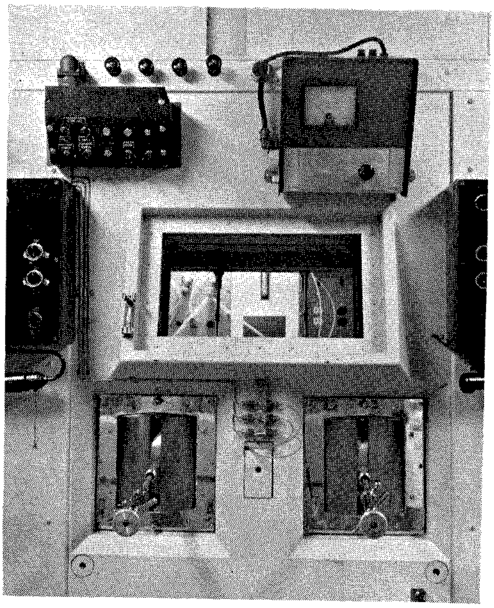

FIG. 14.—Remote colorimetric nitrate apparatus.

of sample is dropped through an immiscible organic liquid (a mixture of *o*-nitrotoluene, α-chloronaphthalene and α-bromonaphthalene) and the time for the drop to travel a known distance is determined. The remote apparatus used for this measurement is shown in Figs. 9 and 10.

The procedure requires that a 0.005 ml drop be formed on the pipet tip while submerged in the liquid. The drop is released as the pipet tip breaks the surface of the liquid as it is withdrawn. The time for the drops to fall a measured distance is obtained. An average time for five drops is obtained. Specific gravity is then read from a working curve prepared from known standards.

Total β- and γ-activity in coarse feed and first cycle extraction column product

Gross β- and gross γ-activities are reported on these samples as a complete fission product analysis is costly and time consuming. Activities from one stream are compared to the other in order to determine the effectiveness of the decontamination process. Dilutions of these samples from 100 to 10,000 fold are prepared using $0.1N$ HNO_3 as a diluent. Original dilutions are prepared in the Remote Analytical Facility and transferred to the conventional laboratory for further work.

The gross beta measurement is very simple. An aliquot of the diluted sample is pipetted onto a 1-in. watch glass and evaporated to dryness under infrared lamps. The watch glass is covered with cellophane tape and mounted on a paper card. The sample is counted on a proportional counter at 10 per cent geometry and reported as counts per minute per ml.

The entire dilution is used in the gross gamma measurement. The sample is deposited into the thimble of a high-pressure ion chamber and read at 100 per cent geometry. Since the sample contains a large number of gamma energies and decay schemes are unknown, results are reported in terms of radium equivalents per ml.

Sulfate in coarse feed

Since sulfuric acid is used in the first dissolution step, sulfate data are necessary in obtaining material balance checks over the feed end. A rapid titrimetric method is used. The method involves the amperometric titration of sulfate ion with lead nitrate at −1.2 V versus the saturated calomel electrode with a dropping mercury cathode. The technique was proposed by Elving and Grodzka[11] and further developed by the Analytical Development Group at the Idaho Chemical Processing Plant. Remote apparatus for this method is shown in Figs. 11 and 12.

The procedure is as follows.

To a 150-ml beaker is added 10 ml of absolute alcohol. A volume of distilled water is added to give a total aqueous phase of 25 ± 1 ml. This final volume also includes the sample aliquot to be added. Five drops of bromothymol blue indicator and a stirring bar are added. An aliquot of sample containing from 0.25 to 0.65 millimoles of sulfate is added to the beaker. The beaker is placed on a magnetic stirrer and $0.5N$ sodium hydroxide is added to the bromothymol blue end point (yellow to blue). The sample is scrubbed with nitrogen for 5 min. After scrubbing, the sample is swept with nitrogen during titration. The sample is then titrated with standard lead nitrate solution using 0.5 ml increments. Data are plotted on coordinate graph paper—galvanometer readings versus volume of lead nitrate. The best straight line is constructed through points on either side of the break. The intercept of the two lines is the end point. Molarity of the sample is determined from the lead nitrate titer and sample volume.

Nitrate in dissolver, dissolver wash and first cycle extraction column feed

In order to dissolve stainless-steel–uranium-fuel elements with sulfuric acid, it is necessary to have the dissolver tank free of nitrate. Nitrate renders the elements passive to sulfuric acid. After the nitric acid dissolution step, the dissolver is washed with water until the nitrate concentration is $<0.01M$. In order to determine the nitrate content of the dissolver, a sample of the wash material is analyzed for total hydrogen ion. A simple, rapid, acid–base titration using phenolphthalein as an indicator is the method involved. If an answer of $<0.01M$ is obtained, the dissolver is assumed to be clean. If an answer of $>0.01M$ is obtained, it may be due to hydrogen ion indicating nitrate content or to hydrolyzable ions being titrated with base. In this case, a more accurate check of nitrate content is obtained by the colorimetric determination of nitrate. The acid–base titration is generally a sufficient check.

The colorimetric determination of nitrate is the method used to determine nitrate concentration on dissolver and first cycle extraction column feed material. This method is dependent upon the purple complex of ferrous nitrosyl sulfate. The technique is one reported by Feigl[12], English[13], Elving and Grodza[14], and further developed by the Analytical Development Group at the Idaho Chemical Processing Plant. The Remote Colorimeter is shown in Figs. 13 and 14.

The procedure is as follows.

To a 50-ml glass centrifuge tube is added 1 ml of ferrous sulfate solution. Twenty-five ml of $15M$ sulfuric acid is added to the tube. A volume of distilled water is quantitatively added to give a total aqueous phase of 29.0 ml. This final volume should include the sample aliquot to be added later. The tube is then cooled in an ice bath until its content is less than 5° C. While the tube is still in the ice bath, an aliquot of sample containing from 0.007 to 0.16 millimoles of nitrate is added. The tube is removed from the ice bath and the color is allowed to develop. The absorbance of the sample is read on a spectrophotometer at a wavelength of 530 mμ. Because of the transient nature of the color, the absorbance measurement is made between 35 and 45 min after removal of the tube from the ice bath. Millimoles of nitrate corresponding to the sample absorbance is read from a standard curve.

QUALITY CONTROL AND RELIABILITY OF THE METHODS

A quality control program similar to those described for the analytical programs on aluminum–uranium[1] and zirconium–uranium[16] fuel processing was maintained on the analytical program for stainless-steel–uranium-fuel processing. Also, all analysts were trained and tested on the methods used according to the training and testing program described by Huff and Tingey.[17]

Bench standards were used to check performance of apparatus and reagent purity from shift to shift. Control samples for each method were submitted to the laboratory and analyzed at a rate of 8 per method per month. Where practical, bench standards and controls were prepared in matrices similar to process samples.

The reliability data listed in Table II were calculated from the results of control samples.

TABLE II.—PRECISION AND ACCURACY OF METHODS UNDER ROUTINE OPERATING CONDITIONS

Analysis	Range	Precision$^{(A)}$	Bias$^{(B)}$
Uranium concentration by isotopic dilution mass spectrometry	1.8 mg/ml	0.04 mg/ml	None
Uranium isotope Distribution	50 % U-235 1–6 % U-236	0.08 %$^{(C)}$ 0.02 %$^{(C)}$	None None
Uranium, spectrophotometric	2.20–14.80 mg/ml	0.04–0.18 mg/ml	+0.03–0.04 ±0.03 mg/ml
Uranium extraction, fluorophotometric	8.0×10^{-5}–9.0×10^{-2} mg/ml	37.48 %	None
Nitrate, spectrophotometric	0.008–3.0M	0.016M	None
Specific gravity, falling drop	1.15 to 1.34	0.006	None
Acidity—pH Titration with oxalate complexing	1.44 N^{B}–4.44N^{A}	0.10N	0.05 ± 0.02N
Sulfate, amperometric	2.60–5.80M	0.21M	None

Note: (A) Precision is expressed as 95 per cent limits of uncertainty for a single determination.
(B) Precision of the bias is also expressed as 95 per cent limits of uncertainty.
(C) Expressed in absolute percentage units.

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Talanta, 1960, Vol. 6, pp. 112 to 116. Pergamon Press Ltd. Printed in Northern Ireland

A SIMPLIFIED METHOD FOR RADIOIODINE ANALYSIS*

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Summary—A radiochemical method of analysis for gross iodine activity in the primary coolant of pressurized water reactors has been developed at K.A.P.L. It is based upon the rapid isotopic exchange which occurs under suitable conditions between fission product iodine and the iodine atoms in preformed silver iodide. The principal steps in the procedure are the following: (a) about 20 ml of the slightly basic coolant is oxidized with sodium hypochlorite. Lanthanum hydroxide is formed by adding lanthanum nitrate to the solution, (b) the lanthanum hydroxide scavenger is removed by filtration, (c) the solution is acidified and treated with sodium bisulfite to reduce the iodine to an exchangeable form, (d) the solution is contacted with preformed silver iodide, (e) the silver iodide is removed by filtration, washed, mounted and counted. The procedure has been found to give excellent decontamination from fission products and activated corrosion products which occur in the primary coolant of pressurized water reactors. The recovery of iodine has been shown to be 88 ± 5 per cent. During the past year, the procedure has been used extensively at K.A.P.L. for applications where speed and simplicity are of greater importance than highest accuracy.

A RADIOCHEMICAL analysis for total iodine activity in the primary coolant of pressurized water reactors must be performed frequently. This analysis serves two purposes. First, it serves as a basis for determining whether or not the I^{131} content of the water exceeds the limit allowed for safe disposal as radioactive waste; Second, it serves as a monitor for detecting fuel element rupture in the reactor.

The choice of a procedure to be used in the iodine analysis was affected by several factors. The use of solvent extraction was severely restricted, for example, because volatile organic solvents, which might constitute a potential hazard in a closed environment, could not be used. Other items common to radiochemical practice, such as an analytical balance and a vacuum line, were not available. The equipment used in the analysis had to be durable and simple, and the procedure itself had to be relatively uncomplicated so that it could be performed by personnel with little training in analytical techniques. Finally, the radioactivity measurement was restricted to β-counting on a G-M counter.

The isotopic exchange approach to this analysis was suggested by Sunderman and Mienke.[1] They found that carrier-free silver-110 could be separated from a large number of other activities by isotopic exchange with silver chloride. It seemed reasonable to expect, therefore, that carrier-free radioiodine would exchange with silver iodide or some other insoluble iodide salt.

In order to test this hypothesis, several tracer experiments were conducted with carrier-free I^{131} from Oak Ridge.

In Table I, results are given of an experiment in which solutions of carrier-free I^{131} tracer were contacted with AgI and Cu_2I_2. The pH of the solution was adjusted with HCl and NaOH. Silver and cuprous iodide were chosen because these salts are easily prepared and they are quite insoluble. It can be seen that the maximum exchange

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* Operated for the U.S. Atomic Energy Commission by the General Electric Company under Contract No. W 31 109 Eng 52.

occurred with AgI in strongly acidic solution. Exchange with Cu_2I_2 was only 85 per cent complete at best, and it was quite sensitive to the pH of the solution.

TABLE I.—ISOTOPIC EXCHANGE WITH AgI AND Cu_2I_2

pH of solution	Exchangeable I^{131} on AgI, %	Exchangeable I^{131} on Cu_2I_2, %
1	95	16
3	85	84
5	65	36
9	62	32
11	50	19

Note: exchange time = 3 min.

Table II shows the results of another tracer experiment in which carrier-free solutions of I^{131} were contacted with AgI for varying periods of time. The solutions were $0.1M$ in HCl. Maximum exchange was attained within the first 3 min.

TABLE II.—EFFECT OF CONTACT TIME ON PER CENT EXCHANGE

Contact time, min	Exchangeable I^{131} on AgI, %
1	80
3	94
5	100
7	96
10	104

The procedure was then tested on freshly prepared solutions of fission products. It was soon evident that any procedure based upon isotopic exchange with AgI would require a step to convert all the radioiodine to a chemical form exchangeable with AgI. Furthermore, a decontamination step would be required to prevent other activities being carried on the AgI during the isotopic exchange step.

The conventional method of converting radioiodine to an exchangeable form consists of hypochlorite oxidation in alkaline solution, followed by bisulfite reduction in acidic solution. This method was found to be satisfactory for our purposes and was adopted for use in the present method.

Scavengers tested for use in the decontamination step were $Fe(OH)_3$, $La(OH)_3$, $Al(OH)_3$ and filter paper pulp. When iron hydroxide was used, the recovery factors for iodine were extremely low. This was attributed to the fact that ferric iron oxidizes iodide ion to molecular iodine. Lanthanum hydroxide appeared to be more effective than either aluminum hydroxide or filter paper pulp as a scavenger. Consequently, a $La(OH)_3$ scavenging step was combined with the oxidation–reduction cycle in the procedure.

As mentioned earlier, the principal aim of this work was to develop a simple, reliable procedure utilizing a minimum of rugged laboratory equipment. Highest accuracy and precision were not of paramount importance. The procedure which is diagrammed in Fig. 2 and outlined in detail in the Appendix was also designed to accomplish this with limited laboratory facilities.

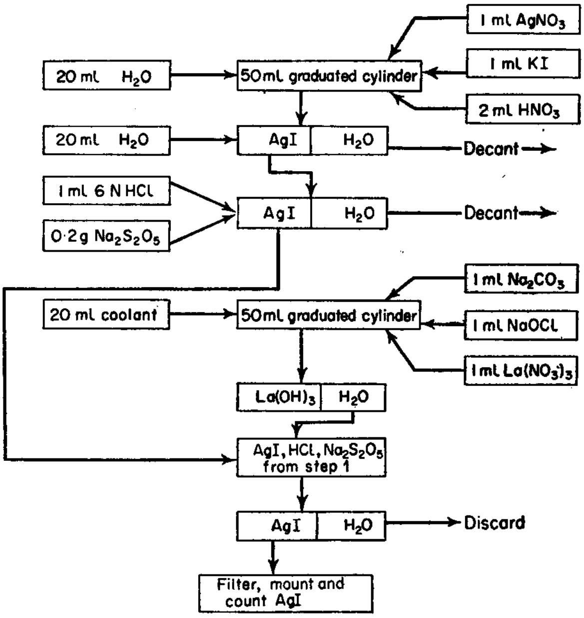

FIG. 2.—Block diagram of procedure.

The first step of the procedure consists of preparing about 50 mg of silver iodide for use in the exchange reaction. This is done by mixing the appropriate amounts of $AgNO_3$ and KI in a 50-ml graduated cylinder. A few ml of HNO_3 will hasten coagulation of the precipitate. The AgI is washed once with water by decantation. Sodium metabisulfite and HCl are added to the graduated cylinder containing the precipitate and it is set aside for later use.

The second step of the procedure is a combination of the oxidation-reduction cycle and the scavenging step. Twenty milliliters of the primary coolant is measured into a 50 ml graduated cylinder. Sodium carbonate, sodium hypochlorite and lanthanum nitrate are added in that order. Lanthanum hydroxide forms in the solution and the mixture is shaken for 1 min.

In the third step of the procedure, the $La(OH)_3$ scavenger is removed by filtering the mixture from step 2. A short-stem funnel containing a fast filter paper (Whatman No. 41-H) is placed on the graduated cylinder from step 1 which contains the AgI precipitate. The scavenged solution from step 2 is poured into the funnel. The HCl in the funnel acidifies the solution, and the sodium metabisulfite reduces the radioiodine to iodide.

In the fourth step, the isotopic exchange step, the cylinder containing the treated coolant and the AgI precipitate is shaken frequently during a 4-min interval. Finally, the AgI precipitate, which now contains the radioiodine, is collected on a 24-mm glass fiber filter disc, dried under a heat lamp and mounted on a card for counting.

The filtration apparatus used to collect the AgI precipitate is shown in Fig. 1.

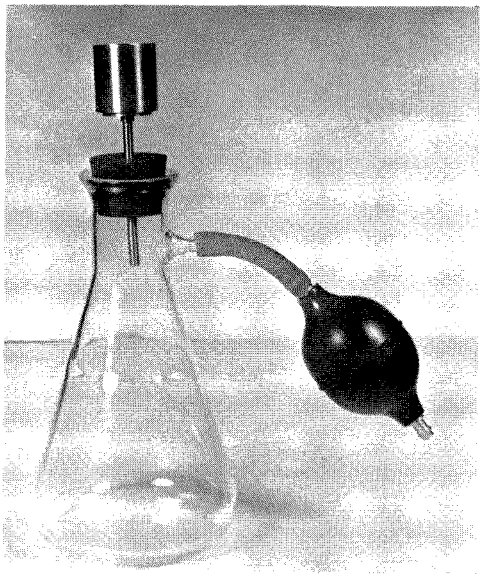

FIG. 1.—Filtration apparatus.

It consists of a stainless-steel filter chimney available from Tracerlab and a suction flask which can be partially evacuated by means of the rubber exhaust bulb.

This procedure has been tested by representatives from K.A.P.L. and the Westinghouse Bettis plant with coolant from a prototype reactor operated by K.A.P.L. Each of 22 coolant samples was analyzed two or more times by the isotopic exchange method and once by a conventional CCL_4 extraction procedure[2] for which the carrier recovery was measured. Five different analysts were used to perform the isotopic exchange analyses. The efficiency of the isotopic exchange procedure for each analysis was calculated on the basis of the β-count rate of the AgI precipitate obtained by CCl_4 extraction after correction for carrier recovery. The efficiency values ranged from 77–97 per cent in this test. The average value was 88 per cent; the standard deviation was 5 per cent.

It can be said in summary that the method described here is satisfactory for determining gross iodine activity in the primary coolant of a pressurized water reactor. It can be used for radioiodine analyses where simplicity and speed are of greater importance than highest accuracy and precision.

APPENDIX

Stepwise procedure

(1) Prepare a precipitate of AgI by pipetting into a 50-ml graduated cylinder (with ground glass stopper) 1 ml each of $0.3M$ $AgNO_3$ and $0.25M$ KI solutions. Add 20 ml of deionized water and 2 ml of $6M$ HNO_3. Shake for 10 sec and allow to stand until AgI settles. Pour off the solution and add 20 ml of water to the graduated cylinder containing the AgI. Shake again for 10 sec and allow the AgI to settle. Discard all but about 2 ml of the water. A loss of 10–20 per cent of the AgI during this step of the procedure is allowable.

(2) Add 1 ml of $6N$ HCl and 0.2 g of $Na_2S_2O_5$ to the graduated cylinder containing the AgI and set aside for later use.

(3) Measure 20 ml of coolant into a clean 50-ml graduated cylinder and add the following reagents:

1 ml of $2M$ Na_2CO_3 solution
1 ml of NaOCl solution (5 per cent available Cl)
1 ml of $0{\cdot}1M$ $La(NO_3)_3$ solution

Shake for 15 secs.

(4) Place a 90-mm filter paper (Whatman No. 41-H) in a short-stemmed funnel and rinse down the sides of the paper once with water. After the water has drained out, place the stem of the funnel in the top of the cylinder containing the AgI so that the mouth of the cylinder supports the funnel.

(5) Carefully pour the treated coolant into the filter paper, allowing the filtrate to drain into the cylinder containing AgI. After all of the solution has been filtered, rinse down the sides of the filter with water. When the filter has drained, remove the filter paper and allow any solution in the stem of the funnel to run into the cylinder.

(6) Place the stopper on the graduated cylinder and shake intermittently for 4 min to assure a good dispersion of the AgI in the solution.

(7) Place a 24-mm fiber glass filter in the stainless-steel filtration apparatus and fill the chimney with the freshly shaken mixture of coolant and AgI. Apply suction by rapidly squeezing and releasing the rubber bulb of the filtration apparatus. Continue

refilling the chimney and filtering until all of the AgI has been collected on the filter. A few ml of water can be used to transfer the last traces of AgI from the cylinder into the chimney. The walls of the chimney should be washed down with a few ml of water from the wash bottle. Excessive washing of the precipitate should be avoided.

(8) Maintain suction on the filter for 30 sec after all visible water has run out of the chimney and then remove the chimney with a twisting motion. Remove the filter carefully with the flat tipped tweezers and dry it under the heat lamp for 4 min. Place the filter in a nickel counting planchet, and β-count under the G-M counter.

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Talanta, 1960, Vol. 6, pp. 117 to 132. Pergamon Press Ltd. Printed in Northern Ireland

RADIOCHEMICAL ANALYSIS OF REACTOR EFFLUENT WASTE MATERIALS AT HANFORD*

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Summary—Analytical procedures are described which were found to be suitable for the measurement of radioisotopes in effluent water and in erosion products deposited from effluent water. The procedures have been applied in studying the changes in concentration of radioisotopes in effluent water following reactor start-up and in identifying and measuring the radioisotopes deposited on metal surfaces during operation.

The increase in concentration of nine radioisotopes in the effluent water from a chemically cleaned (purged with Turco 4306B) process tube has been measured. The concentrations of all radioisotopes studied in the effluent from the purged tube were, with the exception of Na^{24}, less than those removed from the control tube during the first two days of operation by factors of 5 to 100; several of the radioisotopes, including P^{32} and As^{76}, were less than 25 per cent of their normal value 2 weeks after the purge. It was demonstrated by means of this study that radioisotope concentrations increased rather slowly in the effluent water during the 1½ month period of the test.

The relative amounts of the sixteen radioisotopes in the effluent water, absorbed during a 35 day exposure on Al, stainless steel and carbon steel surfaces, downstream from both a normal tube and a chemically cleaned tube were measured. The amounts of the majority of the radioisotopes on the Al and stainless-steel surfaces downstream from the purged tube were lower by factors of 2 to 7 than the amounts from the control tube. A smaller difference was observed for the carbon steel samples. The relative affinity of the metal surfaces for the radioisotopes studied was found to vary by a factor of about 3×10^3; the most readily adsorbed radioisotopes being the lanthanides and the least readily adsorbed being Np^{239}. Calculations based on the relative amounts of these sixteen radioisotopes indicate that, for a short exposure (35 days), La^{140}, As^{76} and Cu^{64} are the major short-lived radioisotopes contributing to the γ-ray emission at the rear face of the reactor, while Zn^{65} and Sc^{46} are the major long-lived radioisotopes. For purpose of comparison, measurements were made of radioisotopes adsorbed on original reactor piping after 15 years of exposure. From these measurements, it was shown that La^{140}, As^{76} and Cu^{64} were still the major short-lived contributors; however, Eu^{152}, Co^{60}, Tb^{160} and Fe^{59}, in addition to Zn^{65} and Sc^{46}, were important long-lived contributors.

INTRODUCTION

In studying the origin of radioisotopes in effluent water from a reactor, it is of interest to know the effect of the film, which normally forms on fuel element jackets and process tubing, on the observed radioisotopic content of the effluent. It is also important to know the chemical and physical condition of the radioisotopes leaving the film in order to understand and predict their downstream behavior in the process tubing as well as their ultimate behavior in the Columbia River.

Production tests have recently been performed by the Irradiation Processing Department,[1] using the chemical cleaner Turco 4306B on process tubing, with the object of reducing rear face dose rates. These tests have provided an opportunity to study the build-up of radioisotopes in the effluent water after the process tubing and associated fuel element jackets have been cleaned chemically. They have also provided an opportunity to measure the uptake of radioisotopes in effluent water on aluminum, stainless steel and carbon steel surfaces downstream from the reactor.

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*Work performed under contract with the U.S. Atomic Energy Commission.

The relative radioisotope concentrations observed on these metal surfaces have been compared with those present on downstream surfaces after 15 years of operation to permit interpolations to other times of interest. This information is useful in understanding the chemical and physical form of the radioisotopes, for designing future studies of in-pile water treatment, and for calculating the contribution of the various radioisotopes to the γ-ray dose on the rear face of the reactor.

An outline of the analytical procedures which were developed or adapted for use in the measurement of the sixteen radioisotopes included in this study is presented.

EXPERIMENTAL

All of the reactor effluent water and metal samples which were analyzed in this study were obtained from reactors during their normal course of operation. The specifications of the reactor process water are given elsewhere.[2]

Radioisotope build-up in the effluent from a chemically cleaned process tube

This experiment followed the build-up of radioisotopes in the effluent water from a chemically cleaned tube. It was expected that the concentrations of radioisotopes in the effluent water observed would be similar to those from a new reactor. The tube was chemically cleaned while the reactor was down, and the radioisotope concentrations in the effluent water were measured periodically during the following 1½ months. Four sets of samples were collected during this time from the above tube, from a control tube of similar history (that was not purged with Turco), and from the whole reactor effluent. The exposure of metal in the purged and control tube was almost the same.

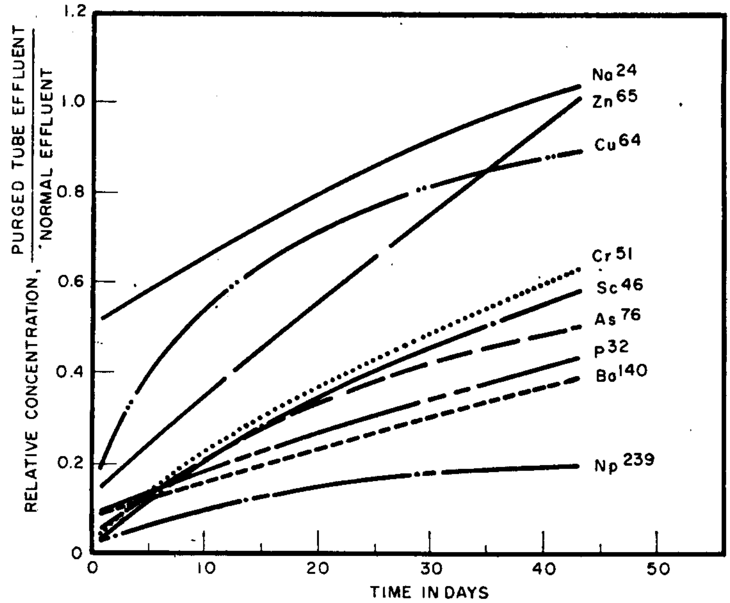

FIG. 1.—Build-up of radioisotope concentrations in effluent water from a Turco purged tube.

The first effluent water samples were collected after 26 hr of reactor operation. A continuously running sample line, which permitted sampling without turning on a valve, was used for all sampling. Because of sampling difficulties, only two samples were taken from the control tube. However, it was found that the control tube had essentially the same concentrations of radioisotopes as the total effluent, so the total effluent was used as a control in following the concentrations of radioisotopes in the purged tube.

The ratios of the effluent radioisotope concentrations in the purged tube to the total effluent are given in Table I and are presented graphically in Fig. 1. From the curves in Fig. 1, it is evident that chemical cleaning reduces the concentrations of most of the radioisotopes in the effluent water by a considerable amount, and that their concentrations increase slowly toward normal operating values over a period of weeks to months. With the exception of Na^{24}, all of the isotope concentrations were lower by at least a factor of five than the total effluent during the first 2 days of operation. The effluent concentrations of P^{32}, Sc^{46}, Cr^{51}, As^{76}, Ba^{140} and Np^{239} were reduced by a factor of 10 to 100 during this period. Also, the concentrations of these isotopes were less than 25 per cent of normal for 2 weeks after the purge and less than 65 per cent 6 weeks after the purge. These data support previous observations[3] that the process tube film is an important reservoir for radioisotopes and parents of radioisotopes.

TABLE I.—RATIO OF THE RADIOISOTOPE CONCENTRATIONS IN THE CHEMICALLY CLEANED TUBE TO THAT OF THE TOTAL EFFLUENT

Date	Na^{24}	P^{32}	Sc^{46}	Cr^{51}	Cu^{64}	Zn^{65}	As^{76}	Ba^{140}*	Np^{239}
29 January 1959	0.523	0.0692	0.0106	0.0346	0.222	0.133	0.0540	0.085	0.0130
30 January 1959	—	0.123	0.0624	0.0872	0.134	0.199	0.0789	0.23	0.0295
2 March 1959	0.716	0.229	0.295	0.303	0.673	0.463	0.297	0.13	0.145
12 March 1959	1.05	0.435	0.582	0.629	0.893	0.991	0.501	0.39	0.194

* The precisions of the Ba^{140} measurements were relatively poor. Standard deviations were 25–50 per cent, compared with less than 5 per cent for the other radioisotopes.

It is interesting to note that even the Na^{24} in the effluent from the purged tube is lower by a factor of two. This is probably due to the lack of good "ion-exchange surface" on the freshly purged tube to hold the parent Na^{23}.

Radioisotope deposition on metal surfaces during a short exposure

In this experiment, a description is given of the measurement of effluent water radioisotopes adsorbed on metal surfaces downstream from a normal and a chemically cleaned process tube. Dummy rings about 1·4 in. external diameter by 1 in. internal diameter by 0·5 in. long were located in the normal downstream dummy positions of two process tubes in a production reactor and allowed to remain for 35 days. One of these tubes was chemically cleaned by purging with Turco solution prior to positioning the rings. The second tube was used as a control. Dummy rings of aluminum, stainless-steel and carbon steel were studied. The relative amounts of the sixteen radioisotopes measured on these rings are listed in Table II. To better illustrate the relative uptake of these isotopes by the dummy rings in the chemically cleaned and normal tubes, the relative activities of these isotopes are shown on bar graphs as Figs. 2, 3 and 4 for aluminum, stainless steel and carbon steel, respectively. With two exceptions, namely Cu^{64} and Co^{60}, the amounts of the radioisotopes found on the aluminum and stainless steel rings were much less for the chemically cleaned tube (a factor of 2 to 7 less) than for the normal tube (Fig. 2 and 3). These differences were smaller for the carbon steel rings (Fig. 4). In this case, the normal tube ring had about

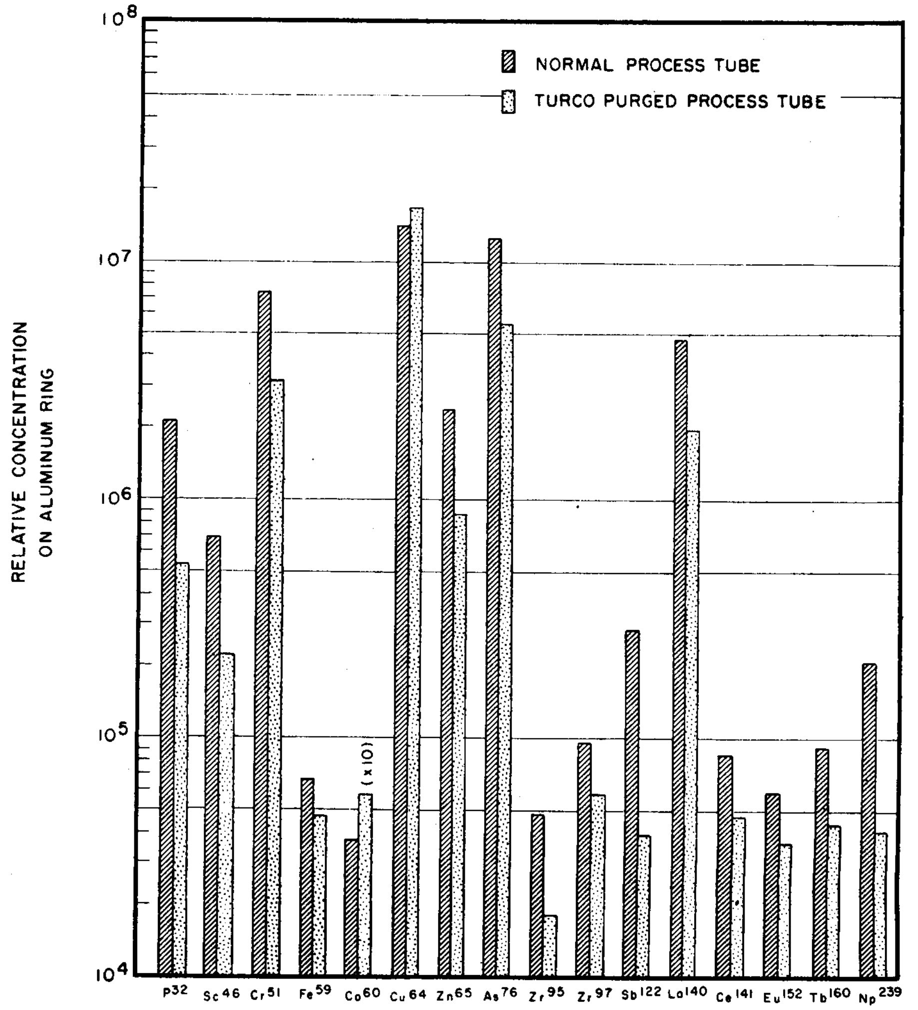

FIG. 2.—Radioisotopes deposited on downstream aluminum from a normal and a purged process tube.

the same or slightly less Co^{60}, Cu^{64}, Zn^{65}, Sb^{122}, La^{140}, Ce^{141} and Eu^{152} (13 years) than the purged tube.

Aluminum, stainless steel and perhaps some carbon steel are the major materials with which effluent water is in contact on the rear face of the reactor. It is, therefore, important to know the relative contribution of each radioisotope to total γ-ray dose from the radioisotope mixtures observed on these surfaces. The relative dose rates for the observed mixtures in Table II have been calculated for a distance of 1 ft from a flat surface. These values were calculated for the control tube only and are normalized to La^{140} as 100 (Table III, Fig. 5). It is apparent that La^{140}, As^{76} and Cu^{64} are the major short-lived contributors to the γ-ray dose, while Zn^{65} and Sc^{46} are the major long-lived contributors.

To illustrate the relation between the radioisotopic content of the effluent water and that on the metal rings, the ratios of the radioisotopes on the rings to the radioisotopes

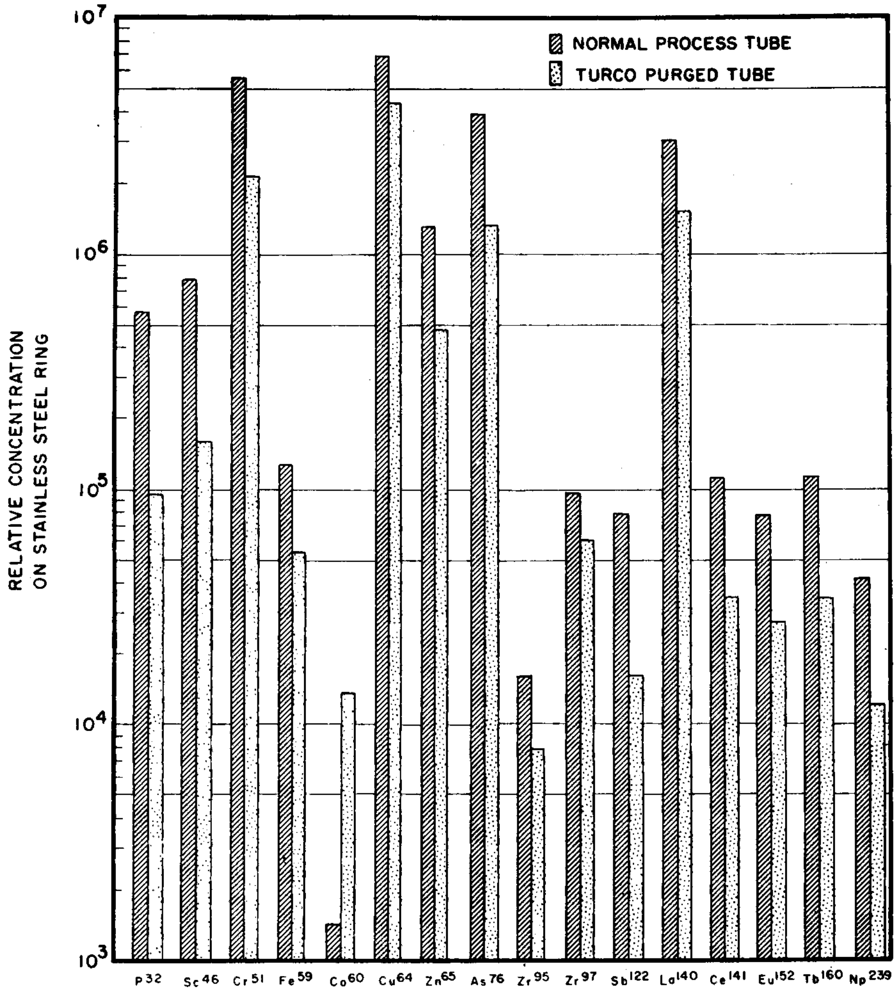

FIG. 3.—Radioisotopes deposited on downstream stainless steel from a normal and a purged process tube.

per ml of effluent are shown as a bar graph in Fig. 6. This graph covers the ring samples for the normal tube only. These values give an indication of the relative affinities of the metal ring surfaces for the various radioisotopes; however, these relationships do not give a complete picture since they are not corrected for radioactive decay or erosion. The relationships are very useful, however, in understanding and interpreting the behavior of these elements in film formation. It is apparent that Sc^{46} and the lanthanons (La^{140}, Eu^{152} and Tb^{160}) are most readily adsorbed, being present on the ring film at 2–3 × 10^5 times that of 1 ml of effluent water. Np^{239} is the least readily adsorbed, being present at 10^2 times that of 1 ml of effluent. Figure 6 also illustrates the relative uptake of each radioisotope by aluminum, stainless steel and carbon steel surfaces. It is apparent that the uptake of most of the isotopes is much lower on stainless-steel surfaces than on aluminum or carbon steel. Sc^{46}, Fe^{59} and the lanthanons are exceptions, being about equally well adsorbed on the three materials.

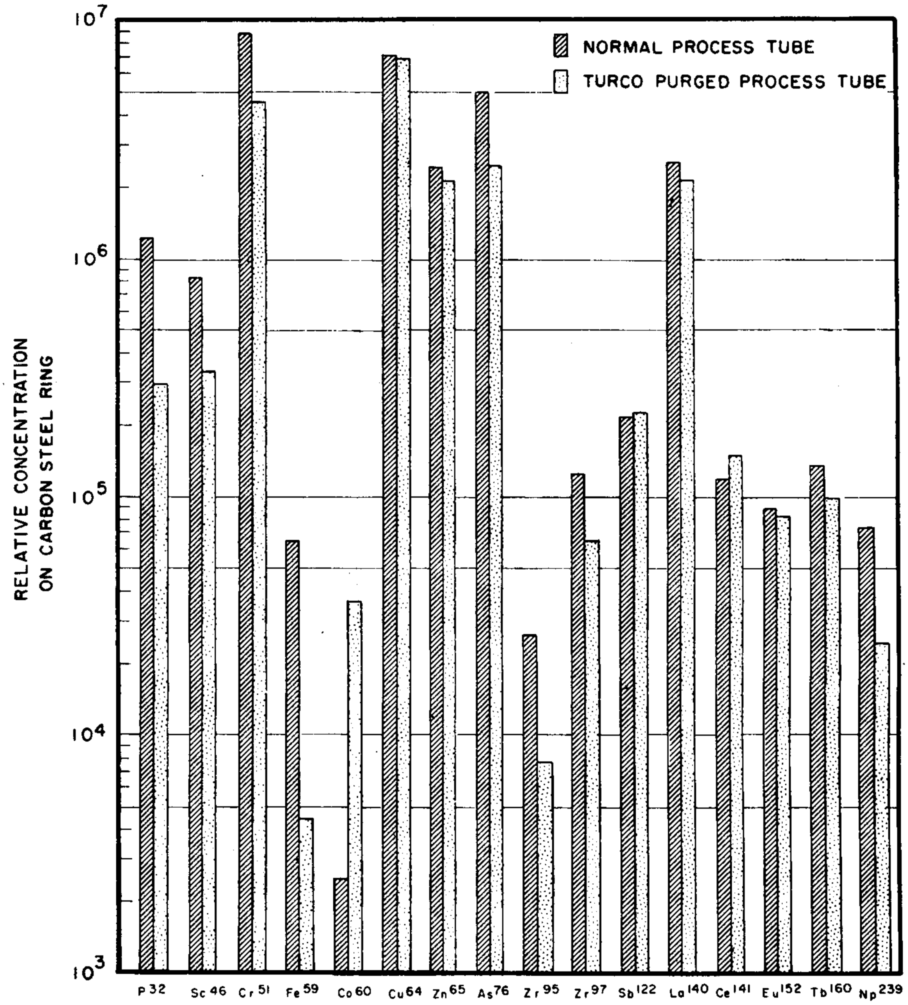

FIG. 4.—Radioisotopes deposited on downstream carbon steel from a normal and a purged process tube.

Radioisotope deposition on metal surfaces during long exposures

Since the radioisotope mixtures observed in the above work were the result of a rather short exposure (35 days), it was of interest to compare these relative concentrations with those present after prolonged exposures.

Sections of three stainless-steel pigtails on the rear face and three aluminum process tubes (from a location downstream from the neutron flux region), which had been in a reactor for 15 years, were obtained, the films removed, and their radioisotope compositions measured. Their observed relative concentrations and their corresponding relative dose rates, normalized to Eu^{152}, are presented in Tables IV and V and are shown graphically in Figs. 7 and 8. The difference in relative concentrations of isotopes from these two types of material may be partially due to their positions in the reactor. Unfortunately, the pigtails were from fringe tubes while the tubing samples were more

TABLE II.—RADIOISOTOPES DEPOSITED ON METAL RINGS DOWNSTREAM FROM A TURCO PURGED AND A NORMAL PROCESS TUBE (35 DAY EXPOSURE)

Relative D/M/Ring

Radioisotope	Aluminum		Stainless steel		Carbon steel	
	Normal	Turco cleaned	Normal	Turco cleaned	Normal	Turco cleaned
P^{32}	212	51.8	55.8	9.51	122	29.1
Sc^{46}	68.2	21.9	76.8	15.5	81.6	33.1
Cr^{51}	715	306	560	209	898	455
Fe^{59}	6.52	4.64	12.7	5.26	6.42	0.434
Co^{60}	0.365	0.558	0.140	1.35	0.252	3.65
Cu^{64}	1380	1660	665	439	718	691
Zn^{65}	237	86.0	128	47.9	244	211
As^{76}	1200	533	384	128	499	247
Zr^{95}	4.82	1.79	2.54	0.771	2.65	0.769
Zr^{97}	9.81	5.92	9.54	5.91	12.3	6.24
Sb^{122}	28.3	3.91	7.70	1.58	21.7	22.3
La^{140}	472	193	300	148	254	213
Ce^{141}	8.56	4.55	11.0	3.35	12.1	14.8
Eu^{152}	5.84	3.59	7.69	2.60	9.24	8.29
Tb^{160}	9.03	4.29	11.2	3.36	13.6	9.86
Np^{239}	20.7	4.05	4.09	1.18	7.39	2.42

TABLE III.—FILM MATERIAL FROM METAL RINGS

Relative disintegration rates of the observed radioisotope mixtures and their corresponding γ-ray dose rates[4] at 1 ft from a flat surface

Isotope	Aluminum		Stainless steel		Carbon steel		Average	
	D/M	Dose	D/M	Dose	D/M	Dose	D/M	Dose
La^{140}	100	100	100	100	100	100	100	100
As^{76}	254	89.2	128	44.9	197	69.1	193	67.7
Cu^{64}	293	27.2	221	20.5	283	26.3	266	24.7
Sc^{46}	14.5	14.0	25.6	24.7	32.2	31.0	24.1	23.2
Zn^{65}	50.2	12.5	42.6	10.6	96.1	23.8	63.0	15.6
Cr^{51}	152	1.87	187	2.30	354	4.35	231	2.84
Sb^{122}	6.00	1.48	2.56	0.540	8.55	1.80	5.70	1.27
Tb^{160}	1.91	1.05	3.73	2.81	5.36	4.03	3.67	2.63
Fe^{59}	1.38	0.780	4.23	2.39	2.53	1.43	2.71	1.53
Eu^{152}	1.24	0.747	2.56	1.55	3.64	2.20	2.48	1.50
Zr^{97}	2.08	0.745	3.18	1.14	4.85	1.74	3.37	1.21
Zr^{95}	1.02	0.349	0.846	0.289	1.04	0.356	0.969	0.331
Np^{239}	4.39	~0.2	1.36	~0.1	2.91	~0.2	2.89	~0.17
Co^{60}	0.0774	0.0929	0.0466	0.0559	0.100	0.120	0.0750	0.0896
Ce^{141}	1.82	0.0371	3.66	0.0747	4.77	0.0972	3.42	0.070

centrally located. Also, some information is lacking in comparing these tables since the tubing (Table V) was not received in time to measure the short-lived isotopes As^{76}, La^{140} and Cu^{64}.

If one compares the relative concentrations of radioisotopes in the film from the

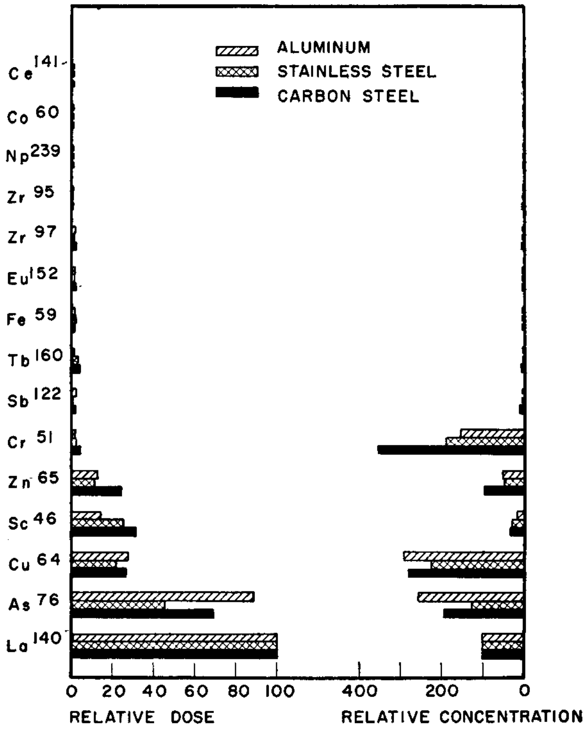

FIG. 5.—Film material from metal rings.

TABLE IV.—FILM MATERIAL FROM STAINLESS STEEL PIGTAILS

Relative disintegration rates of the observed radioisotope mixtures and their corresponding γ-ray dose rates[4] at 1 ft from a flat surface

Isotope	Pigtail 1		Pigtail 2		Pigtail 3		Av erage	
	D/M	Dose	D/M	Dose	D/M	Dose	D/M	Dose
Eu^{152}	100	100	100	100	100	100	100	100
As^{76}	351	204	168	97.7	364	211	294	171
Zn^{65}	294	121	162	66.8	216	88.9	224	92.2
La^{140}	51.2	85.0	—	—	22.2	36.8	36.7	60.9
Sc^{46}	35.8	57.2	18.4	29.3	32.1	51.4	28.8	46.0
Cu^{64}	110	16.9	45.6	7.02	121	18.6	92.2	14.2
Co^{60}	8.08	16.0	2.44	4.84	2.56	5.08	4.36	8.64
Fe^{58}	8.68	7.32	3.98	3.36	16.1	13.6	9.59	8.09
Zr^{95}	6.73	3.82	5.18	2.94	18.8	10.6	10.2	5.79
Cr^{51}	345	7.04	51.3	1.04	185	3.74	194	3.94
Np^{239}	31.5	2.63	9.81	0.818	24.8	2.06	22.0	1.84
Ce^{143}	5.37	1.56	3.82	1.11	7.19	2.10	5.46	1.59
Ce^{141}	8.10	0.274	4.06	0.137	8.50	0.287	6.89	0.233

long-exposure pigtails (Table IV) with those found on the 35 day dummy ring (Table III) samples, it is obvious that the longer-lived isotopes are relatively much more abundant on the surfaces exposed for long periods of time. This is especially apparent

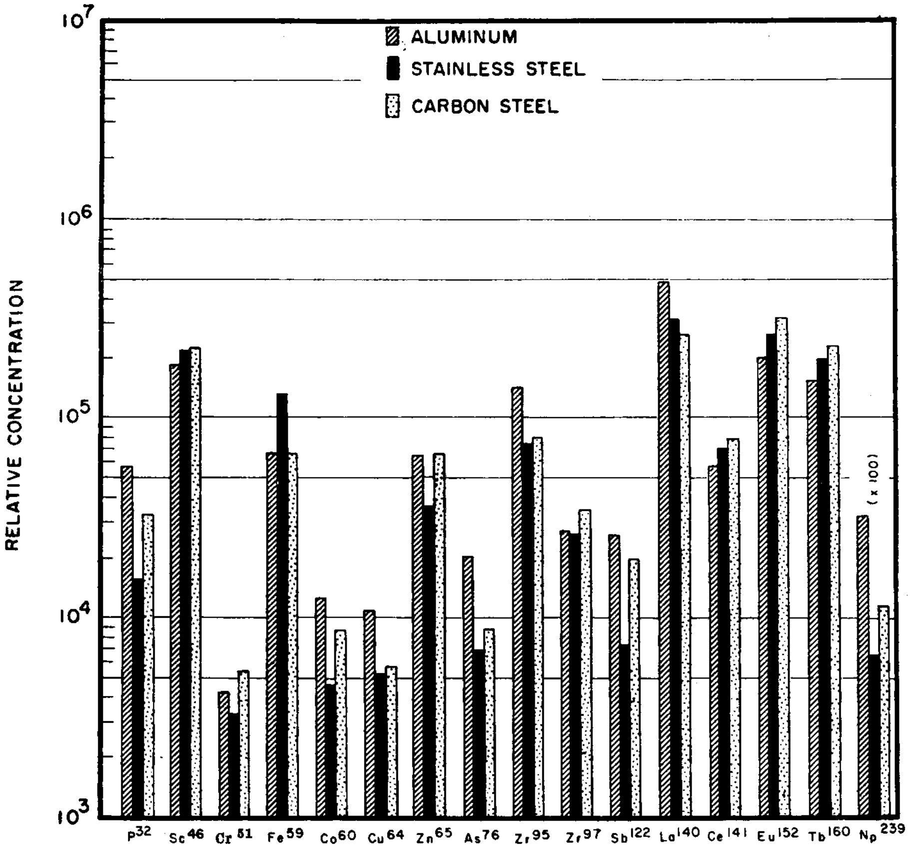

FIG. 6.—Radioisotopes deposited on metal rings relative to the radioisotope concentrations in effluent water.

TABLE V.—FILM MATERIAL FROM ALUMINUM PROCESS TUBING

Relative disintegration rates of the observed radioisotope mixtures and their corresponding γ-ray dose rates[4] at 1 ft from a flat surface

Isotope	Tube 1		Tube 2		Tube 3		Average	
	D/M	Dose	D/M	Dose	D/M	Dose	D/M	Dose
Eu^{152}	100	100	100	100	100	100	100	100
Sc^{46}	591	943	384	613	372	593	449	716
Zn^{65}	2200	905	1780	720	1530	629	1840	751
Co^{60}	101	200	126	250	84.8	168	104	206
Tb^{160}	145	133	56.6	52.2	80.8	74.4	94.1	86.5
Fe^{59}	46.0	43.4	11.9	11.3	23.5	22.2	27.1	25.6
Cr^{51}	1770	36.0	897	18.3	1080	22.0	1250	25.4
Np^{239}	378	31.5	167	13.9	190	15.9	245	20.4
Zr^{95}	28.0	15.9	28.8	16.4	22.1	12.6	26.3	15.0
Ce^{141}	52.4	1.77	38.2	1.29	38.1	1.29	42.9	1.45

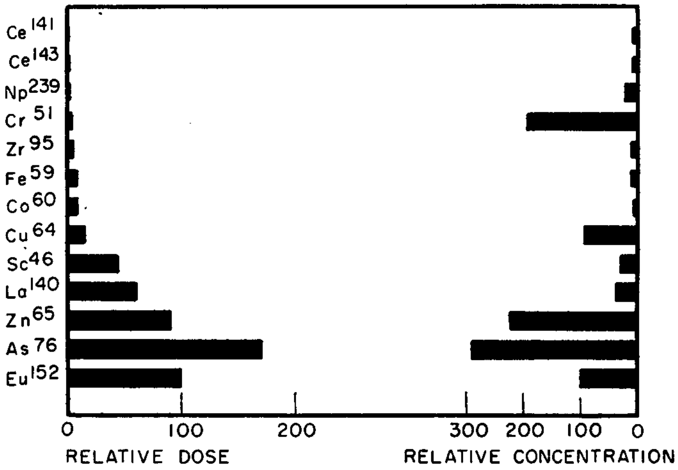

FIG. 7.—Film material from stainless-steel pigtails; average of three samples.

in the case of Co^{60} (5·2 years) and Eu^{152} (13 years). Relative to La^{140} (40 hr), these radioisotopes are about two orders of magnitude greater on the long exposure than on the short exposure surfaces.

As in the case of the short exposure study (Table III), the major short-lived radioisotopes on the stainless-steel surfaces exposed for long periods of time (Table IV) were As^{76}, La^{140} and Cu^{64}. The major long-lived radioisotopes on the long-exposure stainless steel were Eu^{152}, Zn^{65}, Sc^{46}, Co^{60} and Fe^{59}, with a considerable change in relative importance from that observed on short exposure. These radioisotopes were also major contributors on aluminum exposed for a long period of time (Table V), but they were present in different relative amounts on this material. In addition, the long-lived isotope Tb^{160} (72 days) was a major contributor on the aluminum surfaces. This isotope could not be detected on the stainless-steel pigtails from their rare-earth γ-ray spectra, and its concentration was determined to be less than five per cent of that of the Eu^{152}.

It is interesting to note that Eu^{152} (13 years), which, prior to this study, had not been measured in effluent water, is responsible for a large fraction of the rear-face

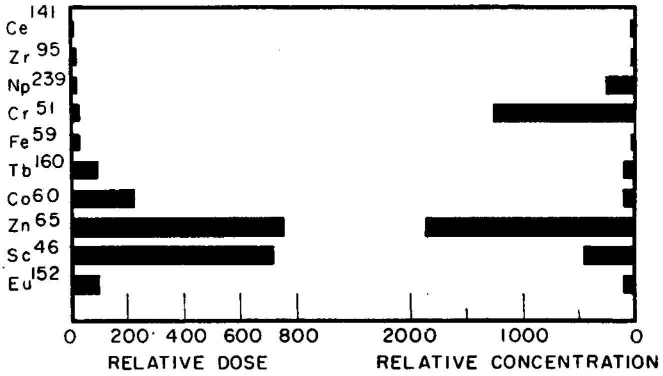

FIG. 8.—Film material from aluminum process tubing; average of three samples.

gamma-ray dose. On stainless steel exposed for a long period of time (Table IV), it is the major long-lived contributor.

DISCUSSION

These measurements have shown the marked difference that exists in the concentrations of radioisotopes in effluent water from a chemically cleaned (or new) process tube and a normal process tube. The slow build-up of the radioisotope concentrations in the effluent from a cleaned tube indicates that film formation in the tube is a slow process, and suggests that any water treatment which would prevent film formation would provide a considerable reduction in the radioisotope output in effluent water. Only nine radioisotopes were included in this phase of the work; therefore, it would be worthwhile in a future study to include several of the radiolanthanons, and also Fe^{59} and Co^{60}, since these isotopes were found to be important in accounting for the rear-face γ-ray dose.

The observed relative affinities of the radioisotopes in the effluent water for metal surfaces are of value in understanding and predicting their effect on rear-face materials of reactors and their fate in the Columbia River. The high relative adsorption for La^{140} and the rare-earth elements (Fig. 6) was in agreement with data from a previous study of effluent water, which showed about 80 per cent of the La^{140} to be associated with particulate material in the water.[5] The low adsorption of Np^{239} also agreed with observations on effluent water which showed that less than one per cent of the Np^{239} was associated with the particulate material.

It is apparent that, since La^{140}, Eu^{152} (13 years) and Tb^{160} are major contributors to the γ-ray dose on the rear-face of the reactor, other rare-earth elements will also contribute to this dose. Any subsequent study of this type should include Sm^{153}, Eu^{152} (9 hr), Ce^{143} and, perhaps, other lanthanons which are known to be present[6] in effluent water in relatively large concentrations.

Since the relative importance of most of the radioisotopes in effluent water to the γ-ray dose on the rear-face of the reactor has been determined (Tables III and IV), the problem of reducing this dose becomes a problem of removing these isotopes from the rear-face or preventing their accumulation.

ANALYTICAL PROCEDURES

Analytical procedures in which γ-ray spectrometric techniques were used to simplify or eliminate chemical separations were applied wherever possible. Also, the counting of all the γ-ray emitting radioisotopes was done on a multichannel gamma-ray spectrometer since it provided a check on the chemical separation procedures.

Phosphorus-32

The P^{32} is chemically separated by solvent extraction.[7] The molybdophosphoric acid is extracted from dilute H_2SO_4 with a 10% solution of 1-butanol in diethyl ether.

Scandium-46

The Sc^{46} is measured in the samples without chemical separation by coincidence counting of its cascade photons.[8] The 0.885 and 1.12 MeV photopeaks are viewed with 90 keV windows by the two 3 in. × 3 in. NaI(Tl) detectors of the coincidence spectrometer and the coincidence counting rate is measured. Interference from other radioisotopes is negligible. The spectrometer counting efficiency for Sc^{46} is determined by

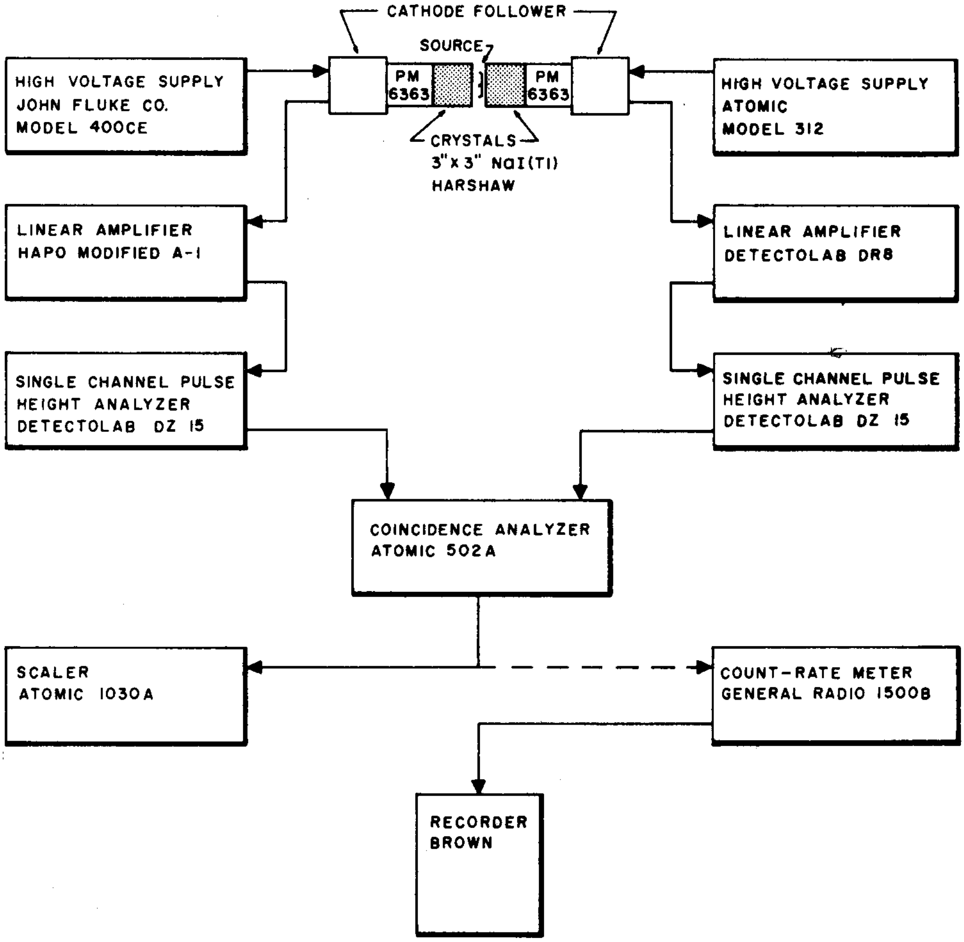

FIG. 9.—Block diagram of coincidence spectrometer system.

counting a Sc^{46} standard with each group of samples. A block diagram of the coincidence spectrometer is shown in Fig. 9.

Chromium-51

The Cr^{51} is determined from the γ-ray spectrum of the sample by measuring the counting rate of its 0.323 MeV photopeak.[8] Minor Compton corrections for interference from Sc^{46}, Zn^{65} and Ba^{140} are required. The gamma-ray spectrum of a typical effluent water sample, showing the Cr^{51} photopeak, is presented in Fig. 10.

Iron-59

The sample is boiled with concentrated HNO_3, after which the Fe^{59} is separated by a 15-min extraction with 0·45*M* TTA in benzene from a 12*N* HNO_3 solution, each washing being for a period of 5 min, after which it is evaporated on a 1 in. counting dish and plated. A 'spiked' Fe^{59} sample is carried through the procedure to determine the radiochemical yield which is about 90 per cent. The samples are counted on a multi-channel γ-ray spectrometer. If the sample contains HCl, 3 ml of $HClO_4$ are added, evaporated to 1 ml and the procedure outlined above is then followed.

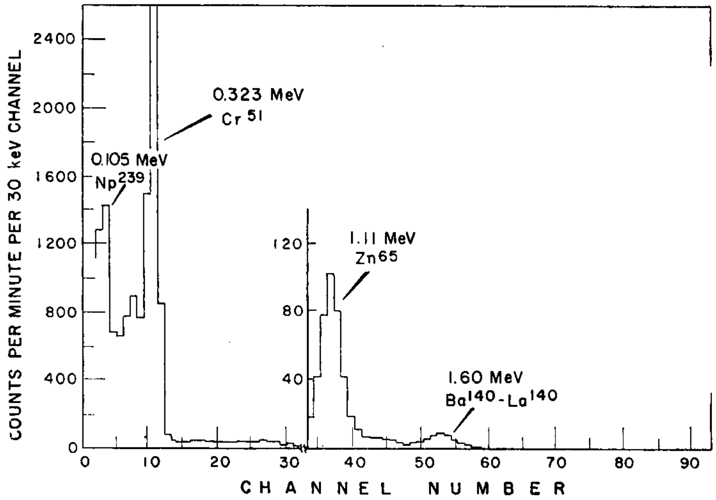

FIG. 10.—Gamma-ray spectrum of week old reactor effluent water.

Cobalt-60

The Co^{60} is uniquely measured in the samples without chemical separation by coincidence counting of its cascade photons[8] in a manner similar to that described for Sc^{46}. The 1.17 and 1.33 MeV photopeaks are viewed with 90 keV windows by the coincidence spectrometer's two 3 in. × 3 in. NaI(Tl) detectors and the coincidence counting rate is measured. The spectrometer counting efficiency for Co^{60} is determined by counting a Co^{60} standard with each group of samples.

Copper-64

In reactor effluent water, where it is a major radioisotope, Cu^{64} is measured by coincidence counting of its positron annihilation radiation.[8,9] In metal film samples, where the relative radioisotope concentrations differ considerably from that of effluent water, the Cu^{64} is first removed from the mixture by carrier electrodeposition[10], and then coincidence counted. The positron counting efficiency of the instrument is measured by using the long-lived positron emitter Na^{22} (2.6 years) as a comparator standard.

Arsenic-76

The As^{76} in effluent water is measured by a β-absorption technique[11] in which advantage is taken of the fact that the 2.97 MeV As^{76} β-particle can be counted through an absorber thick enough to shield out other β-radiations from the sample. The As^{76} in the film samples is separated by carrier precipitation from 12*N* HCl as As_2S_3 after first removing Cu^{64} by carrier electrodeposition. The As^{76} is counted on a multichannel γ-ray spectrometer. The yield for the separation is above 95 per cent.

Zirconium-95–97

Twenty ml of concentrated HNO_3 are added to the sample and the solution is then evaporated to about 5 ml. The sample is diluted to 10 ml with water and extracted with 10 ml of 0.45M TTA in benzene for 15 min. (A 60 ml separatory funnel and a mechanical shaker are used.) The organic phase is washed 5 min each with a 10 ml portion of 8 N HCl and three 10 ml portions of 6N HCl–2M $HONH_2 \cdot HCl$. The organic phase is then washed with 10 ml of 1N HNO_3 and evaporated on a 1-in. counting dish. The sample is counted on a multichannel analyzer after 24 hr, during which time the Nb^{97} grows into radioequilibrium with Zr^{97}, and again after 2 weeks when the Zr^{97}-Nb^{97} has decayed.

A Zr^{95} 'spike' is carried through the procedure to determine the yield which is about 95 per cent. Less than 1 per cent of the Nb radioisotopes are carried through the procedure.

Antimony-122

The samples are allowed to stand a week or more to permit the Cu^{64} and most of the As^{76} to decay. Twenty milligrams of As and Sb carrier are added, and also 20 ml of concentrated HCl, after which the solution is evaporated to 5–10 ml. Fifteen ml of concentrated HCl are then added and H_2S is passed through the solution to precipitate the As^{76}. The precipitate is discarded. The filtrate is diluted to 60 ml and H_2S is passed through the solution to precipitate the Sb^{122}. A Sb^{125} 'spike' is carried through the procedure to determine the yield which is about 95 per cent.

The Sb^{122} is measured from the counting rate of its 0.56 MeV photopeak and a correction is applied for the contribution of Sb^{124}. The magnitude of the correction is established from the counting rate of the 1.69 MeV photopeak of Sb^{124}.

Cerium-141

The cerium separation involves a TTA extraction similar to that described by Moore.[12]

The sample is placed in 50 ml of 4N HNO_3, 40 mg of La carrier and 0.5 g of $KBrO_3$ are added, and the solution is boiled. It is then cooled, 5 ml of concentrated HF are added and, after standing for 5 minutes, the precipitate is removed by centrifugation and the supernate is discarded. The precipitate is dissolved in 50 ml of 4N HNO_3. A second fluoride precipitation is then made as outlined above, after which $HClO_4$ is added to the precipitate and the solution is evaporated to dryness.

The residue is dissolved in 10 ml of 1N H_2SO_4–0.1M $K_2Cr_2O_7$ and extracted 15 min with 10 ml of 0.45M TTA in benzene. The organic phase is washed with two 10-ml portions of 0.1M H_2SO_4–0.1M $K_2Cr_2O_7$, and then counted on a multichannel analyzer. The Ce^{141} is determined from the counting rate of its 0.142 MeV photopeak. The yield, which is about 80 per cent, is determined by carrying a 'spiked' sample through the procedure.

Lanthanum-140, *Europium*-152 (13 *years*) *and Terbium*-160

The initial portion of this separation is the same as the Ce^{141} procedure. The first aqueous phase from the TTA extraction is diluted to 25 ml, 5 ml of concentrated HF is added and the fluoride precipitate is then separated. The precipitate is evaporated to dryness with $HClO_4$, dissolved in 5 ml of 0.5N HNO_3, transferred to a separatory funnel with 2–3 ml of water and shaken 5 min with 20 ml of TTA in benzene. The aqueous phase is adjusted to a pH of about 4 by adding 10 ml of 0.5M NaAc and the mixture is shaken for 15 min. The organic phase is then washed with two 10-ml portions of extremely dilute (about pH 4) HNO_3 and back-extracted by shaking 15 min with 10 ml of 0.1*N* HNO_3. The aqueous phase is evaporated on a counting dish and counted on a multichannel analyzer. The La^{140} is determined from the counting rate of its 1.60 MeV photopeak. The γ-ray spectrum is measured again after a month or more, to permit La^{140} and other short-lived rare-earth elements to decay, and the Eu^{152} and Tb^{160} are determined from the counting rates of their respective 1.416 and 1.18 MeV photopeaks. Since there is overlap in the two spectra at these points, simultaneous equations derived from the spectra of the pure radioisotopes are used in calculating the net counting rates of the photopeaks. The γ-ray spectrum of the elements of the rare-earth group separated from effluent water 3 months old is shown in Fig. 11 with and without the Eu^{152} component subtracted. Since the rare-earth spectrum minus the Eu^{152} matches the Tb^{160}, it is apparent that these are the only rare-earth elements which contribute significantly to the spectrum in this energy region.

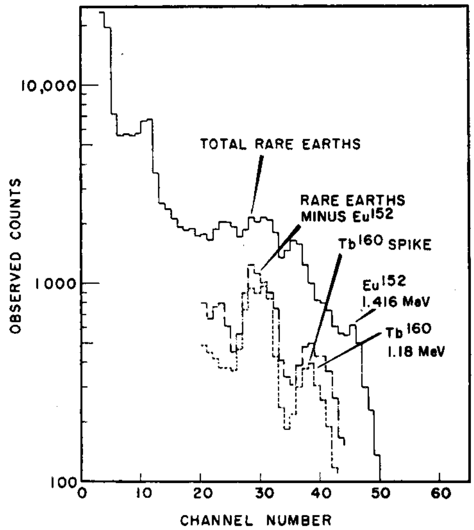

FIG. 11.—Gamma-ray spectral analysis of the rare-earth group from 3 month old reactor effluent water.

The yield of rare-earth elements is about 85 per cent and is measured by carrying a 'spike' through the procedure.

Neptunium-239

The sample is placed in 50 ml of 1*N* HCl, 20 mg of La carrier are added, and the solution is boiled gently and then cooled, after which ¼ g of ferrous ammonium sulfate is added, the solution is stirred and let stand 5 min. Five ml of concentrated HF are then added and, after 5 min, the precipitate is removed by centrifugation, dissolved in 50–75 ml of *N* HCl and the fluoride is precipitated a second time, as outlined above. Three ml of $HClO_4$ are added to the precipitate and the solution is evaporated to dryness. The residue is dissolved in 8 ml of *N* HCl and ¼ g of ferrous ammonium sulfate is added, after which the solution is transferred to a separatory funnel with the aid of 2–3 ml of *N* HCl and shaken for 5 min. Ten ml of 0.45*M* TTA in benzene are then added and the solution is extracted by shaking for 15 min. The organic phase is washed with two 10-ml portions of 1N HCl, each washing being for a period of 5 min, and then washed for 1 min with 10 ml of water. The Np^{239} is back-extracted into 10 ml of 8N HNO_3 and then counted.

The yield, as measured by β-counting, is 96.4 per cent with a standard deviation of 4 per cent.

Acknowledgements—The author wishes to express his appreciation to Mrs. B. L. Bauer for her help on the calculations, and to D. R. Edwards who performed much of the analytical work.

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RADIOCHEMICAL ANALYSIS OF CORROSION PRODUCT MIXTURES FROM HIGH TEMPERATURE PRESSURIZED WATER LOOP SYSTEMS

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Summary—This paper describes the various types of samples of activated corrosion products obtained from the high-temperature pressurized water-loop facilities in the NRX reactor and the radiochemical procedures and radioactivity assay methods which are used in analysis of these samples.

Typically, in-pile loops are simulated reactor systems, i.e. they consist of a primary flowing coolant system and auxiliary make-up, purification, sampling and cooling systems. Two of the loops in NRX, namely, the carbon steel English Electric Corporation "Leo" loop and the Bettis Atomic Power Laboratory central thimble CR-V Loop, are described with particular attention to their associated sampling facilities: autoclaves and out-pile test sections for corrosion and corrosion product deposition studies, hot and cold corrosion product filters for filtration of insoluble materials, and ion exchange columns for purification of the loop water and the study of the ion-exchange behaviour of activated water-borne corrosion and fission products.

The types of samples obtained and the method of attack used to separate and isolate specific fractions of the mixed corrosion products are described. In particular, the separation scheme devised is one which permits the isolation of elements of the first transition series and their associated activated impurities from one another. The separation is basically an anion exchange technique involving the successive elution of carrier-equilibrated species.

Resin samples from the loop purification system are attacked in the presence of carriers by either digestion with H_2SO_4–HNO_3 or by alkaline fusion.

In some cases, corrosion product deposits are assayed directly for activity distribution by means of gamma-scintillation spectrometry (differential pulse height analysis). Application of composite gamma-ray spectrum resolution to deposition coupons and pipe samples is described.

The radionuclides found in loop water and in unfilterable corrosion products are mainly radiative neutron capture products of the corroded in-pile and out-pile materials. The main nuclides analyzed for are 45.1 *d* Fe^{59}, 5.25 *y* Co^{60}, 27.8 *d* Cr^{51}, 12.8 *h* Cu^{64}, 2.58 *h* Mn^{56}, 2.56 *h* Ni^{65}, 245 *d* Zn^{65} and 65 *d* Zr^{95}. Fast neutron reactions have been also observed through the appearance of 300 *d* Mn^{54} and 72 *d* Co^{58}. Two radionuclides observed in the water and in solid corrosion products are 60 *d* Sb^{124} and 2.8 *d* Sb^{122}. The source of these radionuclides has not been positively identified. The corrosion products from the CR-V loop also contain 253 *d* Ag^{110m}, 43 *d* Cd^{115m} and 50 *d* In^{114m} arising from the corrosion of an in-pile specimen of a Ag-In-Cd alloy.

Radioactivity assay of the purified fractions from separated samples is mainly by γ-ray scintillation spectrometry. Routine activity assay utilizing comparison with standardized differential pulse height distributions for pure radionuclides has been adopted because of the versatility of its use for both separated and gross samples. Conventional end-window beta-proportional counting techniques are used for those nuclides whose decay modes and energies preclude gamma-ray intensity assay techniques.

The complexity of corrosion product mixtures from in-pile loops requires that stringent control be maintained at all phases of the program from the time of sampling to the time radioactivity assay is completed. Several problem areas are discussed. For example, large amounts of Fe^{59} contaminating Co^{60} samples and Zr^{95} contamination of Mn^{54}, are difficult to detect without considerable scrutiny of counting data. Carrier exchange is difficult to effect in some cases: e.g. Zr^{95}–Zr^{N} exchange. The gamma-counting data in particular receive careful scrutiny. The gravimetric assay of carrier yield is in some cases a doubtful and time-consuming operation; therefore, techniques eliminating gravimetric procedures should be explored.

INTRODUCTION

ONE OF the major problems confronting nuclear reactor designers is the selection of structural materials. Neutron economy considerations immediately limit the selections of the designer to those alloys having low macroscopic neutron absorption cross-sections if in-flux utilization is proposed. Metallurgical requirements must also be satisfied with respect to irradiation damage, corrosion behavior and mechanical strength. In addition to these reactor engineering requirements it is necessary that the various components of the reactor system be readily accessible in terms of personnel exposure for repair or refueling. The general requirements and techniques for irradiation testing of pressurized water reactor materials have been described by Wroughton and Cohen.[1]

Studies involving reactor spectrum radiation activation of structural and fuel cladding materials, activation of corrosion products (crud) and system contamination with released fission products and with corrosion products, are being carried out in the high-temperature pressurized water-loop facilities in the NRX reactor at Chalk River. These experimental studies are being performed by a cooperative team of Canadian (Atomic Energy of Canada Ltd.), U.S. (Bettis Atomic Power Laboratory) and United Kingdom (U.K. Atomic Energy Research Authority) scientists and engineers. The radiochemical methods described in this paper are the result of evolution and development of techniques to study the corrosion and radioactivation of materials and their subsequent transport and deposition behavior in high-temperature pressurized water systems. Radiochemical analysis of fission products in these systems is described by Lock and Bogar in a complementary paper.[2]

LOOP FACILITIES IN THE NRX REACTOR

The in-pile NRX loops are simulated pressurized water reactor systems, i.e. they consist of a core (in-pile test section), a primary flowing coolant system and auxiliary make-up, purification, sampling and cooling systems. There are presently six high-temperature pressurized water loops in the NRX reactor which may be classified into three major types. The BAPL CR-IV-X rod loops (X-1, X-2, X-3) are stainless steel throughout and have a common make-up system. The BAPL CR-VI loop and English Electric Corporation "Leo" loop like the CR-IV systems have a water capacity of $\sim$60 kg at temperature and pressure; however, they are of carbon steel out-pile with stainless steel in-pile test sections. The maximum empty-hole thermal neutron flux at the in-pile test sections of these loops is $\sim 3 \times 10^{13}$ n/cm^2/sec. The BAPL CR-V central thimble (NRX-CT) loop test section occupies a lattice position of maximum thermal neutron flux (ca. 6×10^{13} n/cm^2/sec). The CR-V loop is of larger water capacity than the other five loops ($\sim$100 kg) and has a reentrant in-pile test section; the other loops are of the straight-through type. The CR-V loop in-pile test section is zircaloy to provide maximum utilization of neutron flux. Out-pile sections are of stainless steel with the exception that out-pile runs of inconel and of monel have been used for radiochemical qualification testing of these alloys for use in primary system components.[3]

All of the loops have operating temperatures and pressures of the order of 600°F and 2000 p.s.i., respectively. Coolant pH $\simeq$10 is maintained with LiOH formed mixed-bed resin columns (Rohm and Haas type XE-154) in the purification system or in the case of "Leo" and X-2 with KOH formed resin columns (Rohm and Haas type XE-149). Total gas content is maintained at 30–50 $cm^3/kg\ H_2O$ (measured at STP) by addition of hydrogen to the systems to minimize radiation decomposition of water and to reduce O_2 concentration by radiation induced recombination.

SAMPLING SYSTEMS OF LOOP FACILITIES

Due to the structural material complexity of loop systems, samples with complicated distributions of radioactivities are obtained. Radionuclides which have been observed in NRX loops and their major target nuclide sources are shown in Table I. Close inspection of this tabulation will reveal that few activation products have unique target nuclide sources. Although the fission products and the Ag, In, Cd isotopes have unique sources, Sb^{122} and Sb^{124} are so ubiquitous that it appears conceivable that antimony impurities are in some way routinely introduced to the systems.

TABLE I.—RADIONUCLIDES OBSERVED IN LOOP SYSTEMS

Radionuclide	Target nuclide source	Probable production reaction
12.4*h* K-42	KOH	$K^{41}(n,\gamma)K^{42}$
12.4*y* H-3	LiOH	$Li^{6}(n,\alpha)H^{3}$
1.87*h* F-18	LiOH, H_2O	$Li^{6}(n,\alpha)H^{3},O^{16}(H^{3},n)$ F^{18}; $O^{18}\,(p,n)F^{18}$
5.25*y* Co-60	CS(1), S.S.(2), Inc(3), M(4)	$Co^{59}(n,\gamma)Co^{60+60m}$
72*d* Co-58	CS(1), S.S.(2), Inc(3), M(4)	$Ni^{58}(\text{fast } n,p)Co^{58+58m}$
45.1*d* Fe-59	CS(1), S.S.(2), Inc(3), M(4)	$Fe^{58}(n,\gamma)Fe^{59}$
65*d* Zr-95	Zircaloy, Uranium Contamination	F.P., $Zr^{94}(n,\gamma)Zr^{95}$
35*d* Nb-95	Zircaloy, Uranium Contamination	Daughter Zr^{95}
300*d* Mn-54	CS, SS, INC	$Fe^{54}(\text{fast } n,p)Mn^{54}$
2.58*h* Mn-56	CS, SS, INC, M	$Mn^{55}(n,\gamma)Mn^{56}$
2.56*h* Ni-56	CS, SS, INC, M	$Ni^{64}(n,\gamma)Ni^{65}$
27.8*d* Cr-51	CS, SS, INC, M	$Cr^{50}(n,\gamma)Cr^{51}$
12.8*h* Cu-64	M	$Cu^{63}(n,\gamma)Cu^{64}$
245*d* Zn-65	CS	$Zn^{64}(n,\gamma)Zn^{65}$
60*d* Sb-124	?	$Sb^{123}(n,\gamma)Sb^{124}$
2.8*d* Sb-122	?	$Sb^{121}(n,\gamma)Sb^{122}$
26.8*h* As-76	CS	$As^{75}(n,\gamma)As^{76}$
253*d* Ag-110*m*	CR-V Ag-In-Cd Specimen	$Ag^{109}(n,\gamma)Ag^{110+110m}$
43*d* Cd-115*m*	CR-V Ag-In-Cd Specimen	$Cd^{114}(n,\gamma)Cd^{115+115m}$
50*d* In-114*m*	CR-V Ag-In-Cd Specimen	$In^{113}(n,\gamma)In^{114+114m}$
Fission Products	U contamination, defected test specimen	$U^{235}(n,f)$F.P.'s

(1) Carbon Steel
(2) Stainless Steel
(3) Inconel
(4) Monel

These activities may be sampled from many points and in a variety of physical forms. The types of samples currently obtained are:

1. Water samples from various points, i.e. before and after purification columns to determine resin bed efficiency.
2. Crud (insoluble corrosion products) from hot and cold crud filters. "Hot" and "cold" here imply relative ambient temperatures.

3. Deposition coupons in autoclaves or out-of-pile test-sections.
4. Pipe sections from various parts of the loops.
5. Ion-exchange resins.

Figures 1 and 2 illustrate schematically the Leo and CR-V loops.

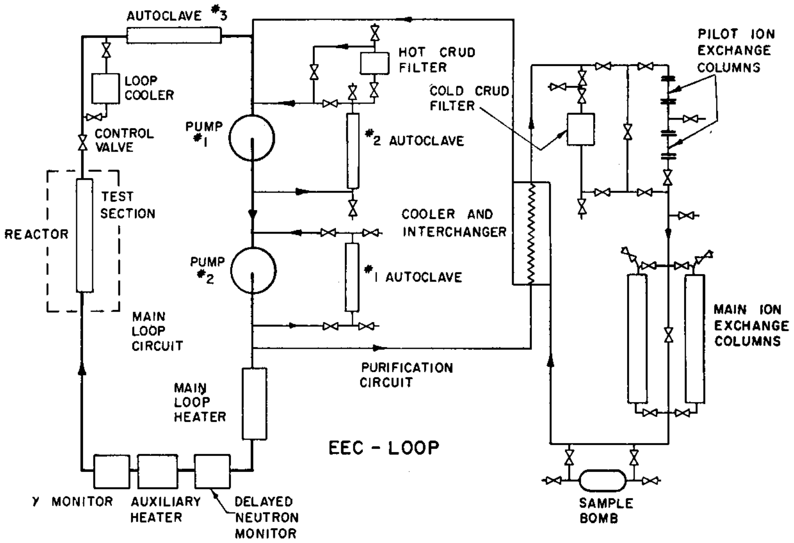

FIG. 1.—Schematic "Leo" loop

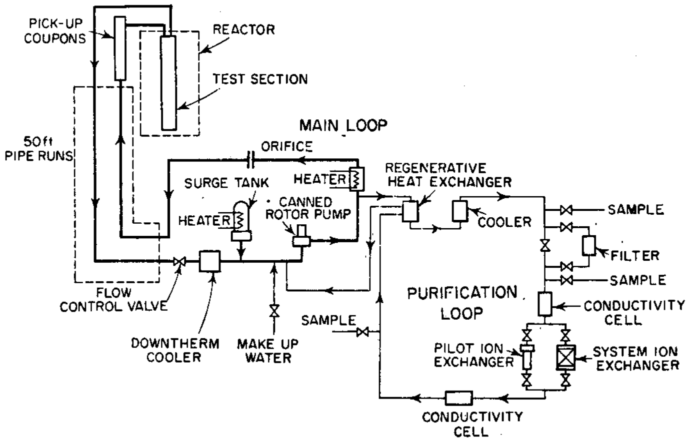

FIG. 2.—Schematic CR-V loop

The "Leo" loop has three out-of-pile autoclaves usable for corrosion product and fission product deposition studies. In both "Leo" and CR-V, the valving may be arranged so that the purification column flow passes through the crud filters. The out-of-pile test section immediately downstream of the in-pile test-section of CR-V is used for deposition and corrosion studies of various alloys suspended in the loop environment.

Because several defected fuel tests have been run in "Leo", corrosion product studies are somewhat obscured due to high levels of fission products. The CR-V loop, however, is not intended for defected fuel tests; therefore, fission product background is very low and is accounted for by superficial uranium contamination. Although the initial attack in radiochemical analysis of the samples depends primarily on the physical form of the sample, separation for and decontamination of specific radionuclides is modified, depending on the fission product level in the loop.

GENERAL ASPECTS OF CORROSION PRODUCT SAMPLING AND ATTACK

The major effort in the corrosion product work at the NRX site is directed toward the analysis of samples from the crud filters. A typical cold crud filter is illustrated in Fig. 3. Particulate matter, $>0.5\ \mu$ diameter, is filtered from the loop coolant onto 47-mm diameter type HA "Millipore" filter disks. Since this filter is accessible during reactor operation, daily crud levels may be determined. Crud is separable from the filter because of the solubility of "Millipore" filters in acetone. Refiltration of the crud through a weighed "Millipore" disk permits gravimetric assay of the collected crud. Total flow through the crud filter is recorded on a flow integrator; thus, crud concentrations in terms of p.p.m. may be determined. The hot crud filter is similar to the cold filter except that higher temperature operation precludes the use of "Millipore" filters; a sintered platinum disk is used.

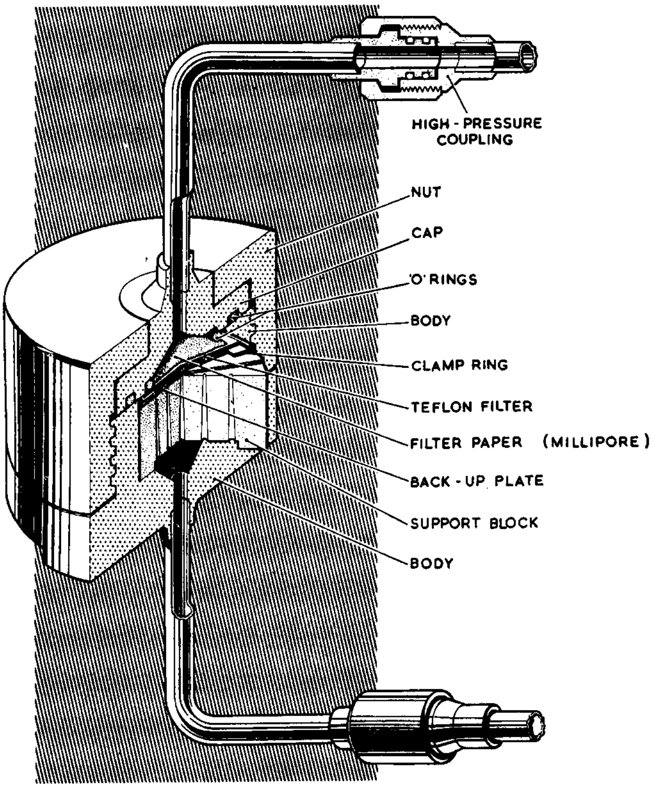

FIG. 3.—Crud filter

It has been found convenient to classify the corrosion product obtained on deposition coupons and pipe specimens into a "Brushed" fraction and an "Etched" fraction. The "Brushed" fraction is that crud which is removable by vigorous mechanical abrasion. Common nylon bristled tooth-brushes have been found to be very convenient for brushing crud. To remove the activities which have diffused into the tightly adherant oxide films of the various metallic samples, more drastic acid etchants such as $HNO_3 + HCl$ are used. This classification system has been developed to minimize dilution of the radionuclides with macro-quantities of etched metal.

Total loss of volatile chlorides such as $SbCl_5$ and loss of radionuclides by deposition on glassware surfaces is minimized by carrying out the dissolution procedures in the presence of known amounts of isotopic carriers.

Dissolution of filtered or "Brushed" crud from CR-V and "Leo" is fairly easy to accomplish by repeated digestion with aqua regia mixtures. In some cases removal of the activity in the "Etched" fraction is more difficult and in extreme cases, long periods of refluxing with strong acids are necessary. Refluxing is avoided where possible because of the large amount of inactive metal also dissolved. After dissolution of the crud has been accomplished, the solutions are reduced to dryness and converted to metal chlorides by dissolving in conc. HCl. The solutions are volumetrically diluted (usually to 25 ml) to provide a stock solution for analysis.

Ion-exchange resins after removal from the loops are dried and stored in vacuo. Alkaline attack is accomplished in the following manner:

100–200 mg of dried resin, 10–20 mg of isotopic carrier for each element to be determined, and two pellets of KOH are reduced to dryness under a heat lamp in a 20-mm diameter, 30-ml Ni crucible. About 2 g of KOH and 1 g of KNO_3 are mixed and added to the crucible and gently heated until the reaction subsides. The temperature is raised until the mass is molten and glassy. Hearing is continued for 10 minutes. The crucible is cooled and the melt is extracted with water (alkaline solution of Zn). Insoluble material is centrifuged off and extracted with conc. HCl (acid solution Fe, Co, Cr, etc.). The acid-insoluble material is centrifuged off and discarded (insoluble sulfates from resin).

Acid attack is accomplished by destruction of the resin in the presence of carriers with red fuming HNO_3–conc. H_2SO_4. The carbonaceous organic material is then destroyed with a H_2SO_4–$HClO_4$ mixture. This procedure is very time consuming (2–3 days) and its use is limited for determination of long-lived radionuclides.

Water samples ($\sim$1 L) may be obtained at various points in the purification circuit by sampling into a vessel containing a known volume (and weight) of isotopic carriers. The total volume (or weight) is then measured and the whole reduced to dryness. The residue is taken up in HCl and volumetrically diluted. Samples taken downstream from the crud filter are already filtered; therefore prior filtration is not necessary to yield a sample of the soluble species. Water samples upstream from the crud probe are filtered; the filtrate and precipitate may be combined or analyzed separately. Soluble short-lived nuclides such as Ni^{65}, Mn^{56} and Cu^{64} are analyzed from large samples of water as well as in crud samples.

THE SEPARATION SCHEMES FOR CORROSION PRODUCTS

The basic corrosion-product separation scheme is one based on anion-exchange separation of the carrier-equilibrated mixture. This scheme has been described by

Lock and Corbett previously.[4] The scheme is illustrated in Fig. 4. The Dowex-1 anion column is a bed of resin 5 mm in diameter by 15 cm long, 4–8% cross-linked, in the chloride form. Analyses are performed on duplicate aliquots of the sample stock

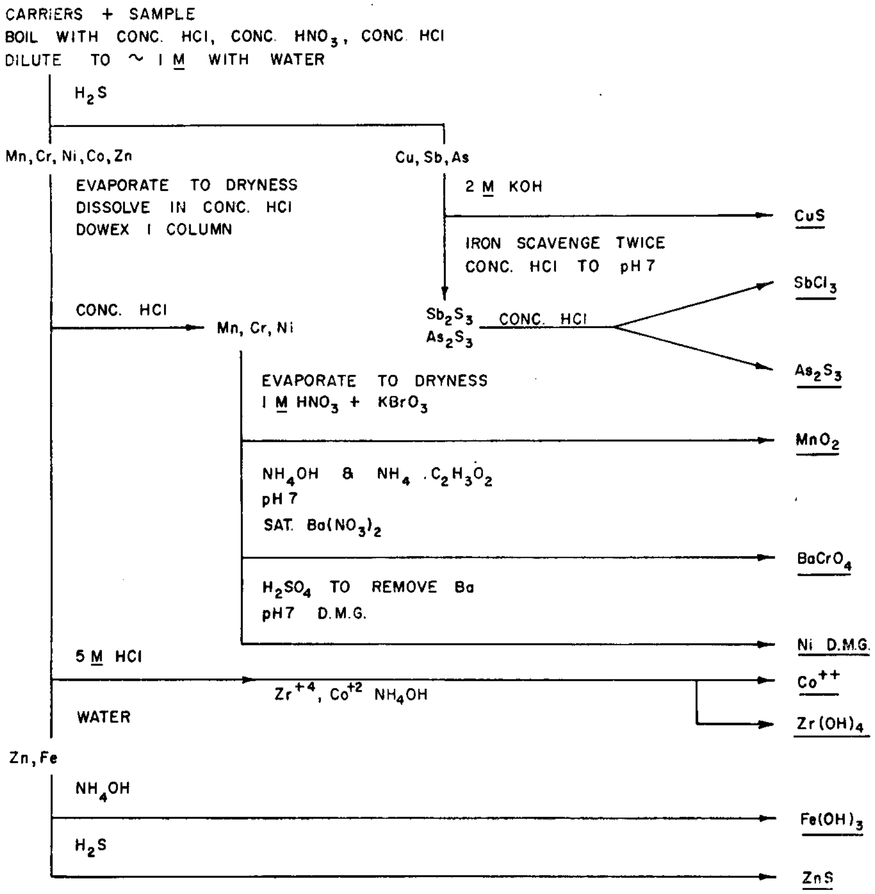

FIG. 4.—Separation scheme for Cu, Sb, As, Mn, Cr, Ni, Zn, Fe, Zr

solutions. The final precipitates, or solutions obtained from the separations, are further decontaminated using the procedures reported by Lock and Corbett[4] or by the Los Alamos Group.[5]

In CR-V crud the Ag, In, Cd radionuclides are of low specific activity; therefore several crud samples are composited when analysis for these activities is desired. The separation scheme devised (Fig. 5) is a simple and rapid scheme based on basic chemical differences of Ag^+, Im^{+3} and Cd^{+2}.

A resumé of the separated forms and final precipitates obtained is given in Table II. The precipitates are filtered onto prewashed and weighed 2.4-cm Whatman #42 filter disks; washed, dried and weighed. The filtered precipitates are positioned concentrically with a 1.500 in. o.d. × 1.020 in. i.d. × 0.024 in. thick Al ring and are sandwiched between two layers of 1.5 in. wide "Scotch" tape (type 600 M M and M). These sources are then beta-proportional and/or gamma-scintillation counted.

TABLE II.—CORROSION PRODUCT SEPARATED FORMS AND FINAL PRECIPITATES

Radionuclide	Separated as	Final precipitate
Fe^{59}	$Fe(OH)_3$	$Fe(C_9H_6ON)_3$(1)
$Co^{58,60}$	Co^{+2}	$K_3Co(NO_2)_6 \cdot H_2O$
$Mn^{54,56}$	MnO_2	MnO_2
Ni^{65}	$Ni(DMG)_2$(1)	$Ni(DMG)_2$(2)
Cu^{64}	CuS	$CuSCN$, or $Cu(C_{14}H_{11}O_2N)$(3)
Cr^{51}	$BaCrO_4$	$BaCrO_4$
Zn^{65}	ZnS	$ZnHg(SCN)_4$
$Sb^{122,124}$	$SbCl_3$	Sb_2S_3
As^{76}	As_2S_3	As_2S_3
Ag^{110m}	$AgCl$	$AgCl$ or $AgIO_3$
Cd^{115m}	CdS	$CdNH_4PO_4 \cdot H_2O$
In^{114m}	$In(OH)_3$	$In(C_9H_6ON)_3$(1)
Zr^{95}	$Zr(OH)_4$	Zr-mandelate

(1) 8-hydroxyquinolinate or "oxine"
(2) DMG = Dimethylglyoximate
(3) α-benzoin oximate ("Cupron")

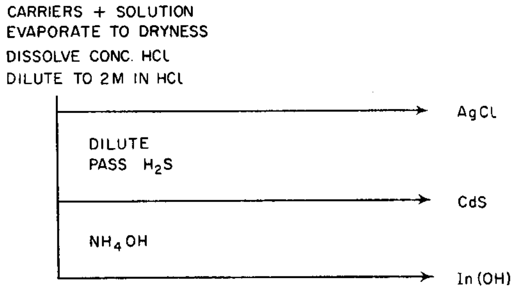

FIG. 5.—Separation scheme for Ag, In, Cd

RADIOACTIVITY ASSAY OF SEPARATED SAMPLES

Separated samples are counted on end-window methane gas flow proportional beta-counters to check chemical yields. The samples are then counted with a 1½ in. × 1 in. NaI(Tl) crystal multiplier-phototube assembly coupled to a 20-channel "Atomic Instrument Co." Model 520 differential pulse height analyzer. The gamma-scintillation counting apparatus has been described in detail by Hawkings and Edwards.[6] The NaI(Tl) crystal has been calibrated for photopeak efficiency as a function of gamma-ray energy with samples of standardized nuclides. Total efficiencies, photopeak efficiencies, peak count to total count ratios and a compilation of standard spectra obtained from samples of standardized radionuclides have been reported.[7]

Radioactivity assay for Ni^{65} and Mn^{56} is normally by end-window beta-proportional counting because low activity levels and short half-lives preclude obtaining good gamma-spectra. The samples are beta-counted at frequent intervals to provide a decay curve which is extrapolated to sampling time. Count rates are converted to disintegration rates by means of experimentally determined (4π β/end-window counter) efficiency factors. Counting data is also corrected for background, counter dead-time (~50 μ sec) and chemical yield. Cd^{115m} and In^{114m} are also beta-proportional counted because the gamma-ray abundances are difficult to establish from the decay scheme.

Efficiency factors for beta-counting have been estimated from an empirical curve of beta-efficiency vs. effective beta-energy (+) ($\overline{E}_\beta$) for several 4π β standardized radionuclide samples.

Specific activities thus may be reported as disintegrations/minute-mg crud or dpm/ml of H_2O, dpm/cm^2 pipe etc.

RADIOACTIVITY ASSAY WITHOUT SEPARATION

It is sometimes convenient to observe the distribution of radioactivities in certain samples without destroying the sample or expending an excessive amount of analyst time. Utilizing the standard spectra for samples of pure radionuclides, it is possible to resolve a gross or complex spectrum into its components by manual subtraction of spectra. The resolution of a two component system ($Co^{58,60}$) is illustrated in Fig. 6.

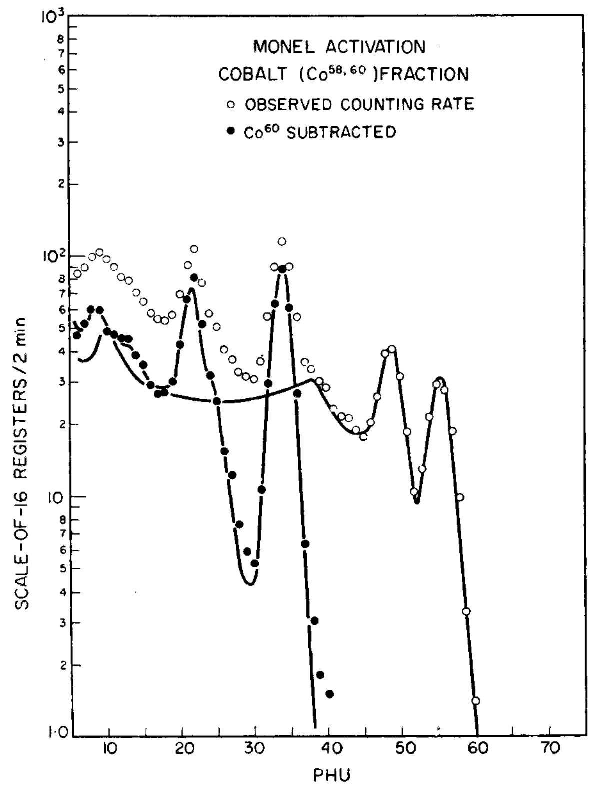

FIG. 6.—Resolution of $Co^{58,60}$ mixture

Note that the Co^{58} standard spectrum is "fitted" to the points (closed circles) resulting from the subtraction of the Co^{60} standard spectrum from the gross-spectrum (open circles).

This complex spectrum resolution technique has been extended to include the major components in CR-V crud, and is also applicable for examination of loop pipe sections. A typical case, where it was not desirable to destroy the deposition coupon for analysis but it was still possible to determine the activity distribution, is illustrated

(+) $\overline{E}_\beta = \Sigma_i E_\beta{}^i \alpha_i$ where E_β is the maximum beta-energy of the i^{th} group of abundance α_i

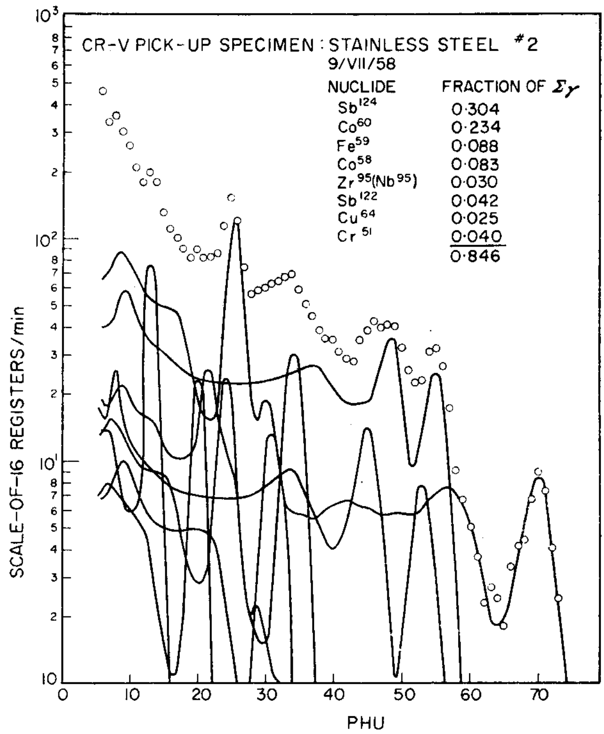

Fig. 7.—Resolution of deposition coupon gross spectrum

Nuclide	Fraction of Σ_γ
Sb^{124}	0.304
Co^{60}	0.234
Fe^{59}	0.088
Co^{58}	0.083
$Zr^{95}(Nb^{95})$	0.030
Sb^{122}	0.042
Cu^{64}	0.025
Cr^{51}	0.040
	0.846

in Fig. 7. In old CR-V samples (>30 days) ~90% of the total gamma activity may be accounted for by complex spectrum resolution. Absolute activities may also be determined because values for "photopeak count-to-total count ratios" and "total disintegrations per total count factors have been determined for the pure nuclide spectra. Accuracy of complex spectrum resolution compared to radiochemical analysis has proven to be 20–25%. Although this level of accuracy may suffice for some purposes, the resolution technique is tedious, requires absolute reproducicility from the counting apparatus, and presumes that the character of the corrosion-product activity distribution is well established.

CONCLUSION

The methods described here have been developed to provide for easy and rapid analysis of activated corrosion product mixtures. These methods have been successfully used for the past two years in loop experiments at Chalk River.

Some difficulties and pit-falls have been encountered, e.g. Zr^{95}–Zr^{N} exchange in some CR-V water samples has been incomplete. In this case prolonged agitation in the presence of HF solved the problem. In other cases Zr^{95} contamination appeared in the Mn fractions in spite of repeated decontamination. Here again, prolonged equilibration of carrier with active material and specific decontamination steps for Zr were required

Scintillation spectrometry data is subjected to careful scrutiny. For example, it is difficult to see fairly large amounts of Fe^{59} contamination in Co^{60} samples. Careful comparison of observed photopeak resolution of a suspected sample with the Co-60 standard spectrum will reveal such contamination.

One of the problem areas requiring further development is the chemical yield determination of separated samples. Precipitates such as the Cu α-benzoin oxime are voluminous, filter with difficulty and are difficult to dry to constant weight. Spectrophotometric techniques for chemical yield assay coupled with well-type scintillation counting would materially decrease analysis time.

Acknowledgements—It is a pleasure to acknowledge the help and discussion of J. A. Corbett in developing many of the methods described here. The assistance of D. McLaughlin (AECL), J. Rees (AECL), D. L. Spate (BAPL) and C. A. Rein (BAPL) in carrying out the bulk of the analyses is also acknowledged. R. F. S. Robertson (AECL), G. M. Allison (AECL) and H. A. Clawson (BAPL) directed various phases of the corrosion product program. We are also indebted to R. C. Hawkings (AECL) and W. J. Edwards (AECL) for their continued assistance in the counter standardization program.

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Talanta, 1960, Vol. 6, p. 144. Pergamon Press Ltd. Printed in Northern Ireland

REACTOR FUEL ELEMENT TYPES*

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Note—This paper is not included in the *Proceedings* because, in essence, the information contained therein can be found in a report by the Civilian Reactor Fuel Element Group, *Report on Civilian Reactor Fuel Elements*, TID-8505.

Summary—The function of a research reactor fuel element is to generate a flux of neutrons, beta rays, and gamma rays for absorption in experiments. The fuel element is usually cooled by water below the boiling point. In reactors of very low power, cooling by natural convection to the air is adequate.

The main function of a power reactor fuel element is to transfer heat to a coolant at a sufficiently high temperature for use in the production of electricity. Power reactor elements are, therefore, cooled by pressurized water, liquid metals, high-boiling organic compounds, and gases. The elevated temperatures introduce problems of corrosion and mechanical failure.

All fuel elements must contain fertile or fissile isotopes, and most elements contain both. In the interest of neutron economy, the quantities of absorbing isotopes are controlled. Analyses in the range of 0.02 to 100 p.p.m. are required for many elements, depending on their nuclear or chemical properties.

Because of the potential hazard and high cost of shutdown from fuel element failures, rigid analytical control is exercised to assure the quality of all materials and components. The concentration of impurities in each part of a fuel element must be controlled. The principal parts of a fuel element are; the fuel material, whose fissile content must fall within predetermined limits; possibly, for added stability, fuel diluent; the gap or bond between the fuel and its cladding, which may be a gas, plated metal, liquid metal, or an intermetallic compound formed by reaction of the fuel with the cladding material; the clad which separates the fuel from the coolant; possibly a moderator or a burnable poison to ease reactor control; miscellaneous hardware, such as a handle, springs, ferrules, insulators and, frequently, braze or weld material.

The two chief types of fuel elements for research reactors are cylindrical rods of natural U clad in Al, and plates of enriched U-Al alloys or tubes clad in Al and assembled into structures containing from 6 to 19 parallel plates or several concentric tubes. In both types the fuel is metallurgically bonded to the cladding.

The most common fuel element in United States power reactors consists of a bundle or cluster of rods containing ceramic fuel pellets in Zircaloy-2 or stainless steel tubes. Most reactors use pellets of slightly enriched UO_2. A few reactors use ThO_2–UO_2 pellets, and in a few reactors, the tube material is an Al-Ni alloy. Helium is used in the space between the ceramic fuel and the tube. The elements usually contain between 7 and 306 rods.

Under development are alternative ceramic fuels such as UC and dispersions of carbides of Th and U in graphite. Other cladding materials such as Be, Nb, graphite, and graphite coated with SiC, are being investigated.

Metallic fuel is also used in power reactors. The British use natural U rods clad in a finned tube composed of a Mg alloy. Rods of U-Mo alloy which are Na-bonded in stainless steel tubes and pins of the same alloy metallurgically bonded to Zr will be used.

Plate elements of highly enriched U-Zr alloy and slightly enriched U-Zr-Nb alloy, both metallurgically bonded to Zircaloy cladding, are in use. Plate elements of highly enriched UO_2 dispersed in stainless steel and clad in stainless steel are also being applied.

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* Work performed under contract with the U.S. Atomic Energy Commission.

Talanta, 1960, Vol. 6, p. 145. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF U AND Pu IN U-Pu ALLOYS OF THE FISSION ELEMENTS*

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Note—This paper is not included in the *Proceedings* because it has been submitted for publication in *Analytical Chemistry.*

Summary—A melt-refining process has been developed for reprocessing the enriched U loading(s) of the EBR-II. After a number of cycles, an equilibrium alloy will be formed which contains small percentages of the fission elements Zr, Mo, Ru, Rh and Pd. The rare-earth elements, Sr. Ba, and several per cent of the U will react with the ZrO_2 crucible and be separated as an oxide dross.

Since, in the projected operation of the reactor, Pu bred in the reactor blanket is to replace U^{235} as the fissile material in the core, it was necessary to ascertain whether or not the melt-refining process was also applicable to alloys of U, Pu, and fission elements. Therefore Pu and U analyses on both the ingot and dross material were required.

Plutonium is determined spectrophotometrically as the nitrate after it is separated from interferences; U is determined by an X-ray spectrometric method after it is separated from the Pu alpha contamination. To remove the interference of the highly colored ions of group VIII metals, the sample solution is converted to a chloride medium and treated with excess Mg. The group VIII metals are precipitated; the Pu and U are reduced to the tri- and tetravalent states, respectively. Uranium(IV) which serves as a reductant to hold the Pu in the trivalent state, is extracted from strong HCl into a CCl_4 solution of tributylphosphate. The Pu is then extracted from the same medium after it is oxidized to the tetravalent state with nitrite. The U and Pu are easily extracted from the organic phase with water or dilute HCl. These solutions are then prepared for X-ray and spectrophotometric assay by converting them to HNO_3 solutions of the proper concentrations.

In an alternate procedure, Pu is separated by coprecipitation with LaF_3. By dissolution of the precipitate in a $Zr(NO_3)_4$-HNO_3 mixture, the interference of F^- is removed and the Pu is oxidized to the tetravalent state.

The coefficients of variation for the U and Pu analyses are 0.9 and 1.2 per cent, respectively.

* Work performed under contract with the U.S. Atomic Energy Commission.

Talanta, 1960, Vol. 6, p. 146. Pergamon Press Ltd Printed in Northern Ireland

RADIOCHEMICAL DETERMINATIONS OF Ce AND TOTAL RARE-EARTH ELEMENTS BY LIQUID-LIQUID EXTRACTION*

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Note—This paper is not included in the *Proceedings* because it has been submitted for publication in *Analytical Chemistry.*

Summary—A considerable amount of supporting analytical service will be required in the pyrometallurgical processing of EBR-II fuel. In the melt refining of the U 'fissium' alloys used as an equilibrium-type fuel at startup, ingots will be produced containing more than 0.5 per cent each of Mo, Ru, Zr, Pd, and Rh, together with dross samples containing as much as 10 per cent of rare-earth elements. Since the removal of rare-earth elements is of prime importance in the fuel cleanup, it will be necessary to determine Ce and/or total rare-earth elements at several stages in the processing cycle.

Standard radiochemical procedures for determining Ce or total rare-earth elements involve numerous precipitation steps and are somewhat tedious and time consuming. Since a solvent extraction separation would offer several advantages over precipitation methods, several solvent extraction systems for separating Ce and total rare-earth elements were investigated. Data published by Peppard and his co-workers on the use of dioctylphosphoric acid (HDEHP) for extracting carrier-free rare-earth isotopes indicated that such an extraction could be used as the basis for a quantitative radiochemical method.

Using di(2-ethylhexyl) orthophosphoric acid as extractant, rapid and quantitative radiochemical methods were developed for Ce and for total rare-earth elements. Cerium(IV) is extracted from a $10M$ HNO_3–$1M$ $KBrO_3$ solution with $0.75M$ (HDEHP) in n-heptane. After scrubbing the organic phase with a fresh HNO_3–$KBrO_3$ solution, the Ce is re-extracted into a $10M$ HNO_3–3% H_2O_2 solution. In the procedure for total rare-earth elements, these elements are extracted from a $0.01M$ HCl solution with $1.5M$ (HDEHP) in toluene. After the organic phase is scrubbed with fresh $0.01M$ HCl, the rare-earth elements are re-extracted into $8M$ HCl. Since each of the separation steps in both procedures is quantitative, it is unnecessary to determine a yield factor. The solutions derived by re-extracting the organic phase are either plated for β^- counting or are gamma-counted with a well-type scintillation counter.

The methods were tested on slices of U fuel element and irradiated U 'fissium' alloys. Several samples were also analyzed by standard precipitation procedures. The results compare favorably.

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* Work performed under contract with the U.S. Atomic Energy Commission.

ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

SECTION III. ANALYTICAL CHEMISTRY OF PLUTONIUM AND THE TRANSPLUTONIC ELEMENTS

Talanta, 1960, Vol. 6, pp. 149 to 153. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL LABORATORIES FOR THE HANDLING OF PLUTONIUM*

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Summary—For the safe handling of Pu in analytical chemical laboratories, equipment is required capable of handling up to 1-g quantities of the radioactive material per analytical sample and the storage of 100-g quantities in the form of unused samples and residues. Special enclosures, known as dryboxes, or glove boxes, have been designed for this purpose. The analytical chemistry laboratories at the Los Alamos Scientific Laboratory that are so equipped are described in this paper. The philosophy of handling Pu is also discussed. These boxes are so designed that all required operations in chemical analyses may be performed safely without contamination of the room and with a minimum of risk to the analyst. Included are operations such as weighing, dissolving, precipitation, filtering, evaporating, centrifuging, and igniting of precipitates and also electrometric, polarographic, spectrophotometric, and spectrochemical techniques. The designs of individual boxes are varied to permit various operations, and at the same time they may be arranged interchangeably in circumstances requiring several boxes in a row. For routine and semiroutine analyses, these boxes are arranged for an assembly-line type of operation. The sample to be analyzed is introduced at one end of the assembly, successive steps in the analysis are performed as the sample is moved progressively through the assembly, and the residue is temporarily stored at the other end of the assembly in a suitable container.

These boxes are fabricated of stainless steel, with windows of Lucite or safety glass. All metal exposed on the inside is painted with a strippable plastic-base paint. Glove ports are located at a convenient height to permit easy use of rubber gloves. Experience has shown that Pu in solution can be safely handled in these enclosures without rubber gloves being on the ports but that for Pu in solid form, rubber gloves must be attached to the glove ports. These enclosures are equipped with all the usual laboratory services. Doors between boxes are of an unusual design, vertically operated by compressed air. Provisions are included for the operation of equipment such as centrifuges and pH meters within the boxes, yet permitting their removal in an uncontaminated condition.

Ventilation is provided through filters for all gloved boxes. It is so regulated by means of dampers in the exhaust ducts that it does not interfere with operations. In case of open front boxes, the flow of air is maintained at a minimum face velocity of 100 ft/min. Stainless steel as an exhaust duct material has been found to be unsatisfactory, especially for those boxes in which acids are fumed. Polyvinyl plastic has been used for the more recently installed exhaust ducts and has been found to be quite satisfactory.

The descriptive material is adequately illustrated by 20 photographs.

THE analytical chemistry laboratories at Los Alamos were designed for the routine and daily handling of plutonium analytical samples in solid or solution form, and of multigram size, if necessary. They were also designed so that a large variety of analyses could be done on samples of many different types, including metal, alloys, compounds and solutions. It was also understood that the plutonium would be free from fission product elements.

The radioactive nature of plutonium gives rise to alpha particles of approximately 6 meV energy, and also of very weak gamma rays which are not penetrating. Due to these facts, radiation shielding is not a factor in the design of laboratories for handling plutonium unless fission product elements are also present. Hence, under these conditions, the problems in designing laboratories for plutonium analysis arise principally

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* Work performed under contract with the U.S. Atomic Energy Commission.

from its extreme biological hazard. On the basis of a permissible total body tolerance of 0.3 μg of the element, and in consideration of the ease with which plutonium-containing materials may find their way into the laboratory atmosphere, it is clear that special care must be taken if ingestion of plutonium is to be completely eliminated or, under unusual circumstances, kept to a safe level. Partly on the basis of the established permissible body tolerance, and partly on the basis of previous experience which indicated what could reasonably be accomplished, it appeared that a working philosophy in the design of analytical chemistry laboratories for handling plutonium should have the following aims: (1) to do alpha-hot operations in essentially uncontaminated rooms with a minimum of danger to personnel, (2) to keep contamination of exposed surfaces below 20 disintegrations/min per cm^2, and (3) to keep air counts below 9 disintegrations/min per m^3. It was also clear that handling of macro-amounts of the element would be required in daily operations, and facilities must be designed for the safe handling and storage of up to 100-g quantities.

To accomplish these aims, special enclosures, called dryboxes, glove boxes, or enclosed hoods, were designed. These enclosures are essentially boxes with windows for viewing. Two general types are in use, one type being provided with ports to which rubber gloves may be fastened, the other, an "open front" design. They are equipped on the interior with all the usual and necessary laboratory services, such as gas, water, electricity, compressed air, vacuum, etc. They are designed to permit all the usual operations necessary in analytical procedures, such as weighing, filtering, centrifuging, electrolysis, drying, igniting, electrometric titration, etc. They are of various sizes, and may be 32, 36 or 58 in. long, 25 in. deep and 24 to 36 in. high.

The windows are of $\frac{1}{4}$in. thick safety glass or Lucite. In the glove boxes, the windows are set in a metal frame which, in turn, is bolted to the box, with a gasket providing the seal. In the open front boxes, the windows are framed with an S-shaped neoprene gasket which, in turn, is cemented to the box. These gaskets do not provide a complete seal.

The boxes are made of No. 304 stainless steel, 16 gage, with a satin polish surface. This material, while providing a pleasing appearance, is not completely satisfactory, being easily corroded by halogen acids.

Partly to eliminate corrosion, and partly to provide better lighting, the interior sides, tops, and backs of these boxes are painted with an acid-proof, plastic-base paint, white in color. Adequate illumination is provided by fluorescent fixtures, exterior to the boxes, and resting on the top.

These boxes are supported on metal frames with adjustable legs. Once installed, however, the height of the boxes cannot be altered without corresponding changes in the duct work.

The exhaust ducts, originally of stainless steel, corroded rapidly and are being replaced with polyvinyl chloride. These ducts are equipped with water sprays which permit them to be washed continuously during heavy acid-fuming operations. The exhaust ducts pass downward through the floor into a larger duct which carries the exhaust air to a purification system consisting of a dry filtration system. From this point it is discharged into the atmosphere.

Experience has shown that, in all operations where it can be done, it is advantageous to arrange the dryboxes in such a sequence that assembly-line-type of operations may be carried out. In other words, the sample to be analyzed is introduced at one end of the drybox series, the necessary sequential operations performed as the sample is passed along, and finally, at the other end, the residues from the analysis are stored in special containers, periodically removed and sent to recovery operations.

Figure 1 is an example of this type of operation. In this case, drybox space and equipment for the potentiometric titration of plutonium is shown. At the right, the plutonium sample is introduced into the weighing box; here it is weighed and then passed to the left where it is fumed with sulfuric acid; from there it is transferred to the titrating area where a potentiometric titration is made. The residue is temporarily stored in 2-liter bottles and later removed to the packaging area. You will note these boxes are either open front or used without gloves; obviously, they are suited for solution work only. As shown in Fig. 1, personnel wear shoe covers, a laboratory coat and rubber gloves. The pH meter seen at the floor of the box is actually under a sealed Lucite cover and supported in such a manner that it can be removed from below for servicing. Extended controls are used to operate the instrument (see Fig. 2). In these boxes, the opening at the front is 7 in. in height, which has been found adequate. It has been found necessary to provide ventilation to the extent of at least 100 linear ft/min across the face of this opening.

In this particular analysis, iron must be determined on a separate portion of the sample, and a correction made in the plutonium determination. To do this, the sample is introduced at the same place as in Fig. 1, but now it is passed to the right, into the dryboxes shown in Fig. 3, where the analysis is made, and the residue stored in the end boxes on the extreme right. In all, 40 linear feet of dryboxes are included in Figs. 1 and 2, and are required for the routine assay of plutonium. Another interesting fact comes to light. Because the equipment becomes contaminated, and also because it takes up considerable space in the dryboxes, once a series of boxes is set up for a particular analysis, it has been found from experience that it is next to impossible to use that particular drybox space for other analytical determinations. This fact simply means that a large number of dryboxes is required to do a variety of analyses.

For the handling of plutonium in solid form, as either metal or compounds, experience has indicated that the boxes should be completely enclosed, and rubber gloves placed on the glove ports. Adequate ventilation is a necessity, with the inlet air being filtered as it enters the box. In the Los Alamos laboratories the exhaust air is not filtered at the outlet of the box but it is realized there are advantages in so doing.

Figure 4 shows an arrangment wherein the boxes are equipped with gloves for work with plutonium-containing solids. Figure 5 shows a combination wherein only parts of the boxes contain gloves, and the remainder are of the open front type. This is permissible in those cases where the sample is a solid and is dissolved at some point in its analysis. Figure 6 shows an arrangement of open front boxes designed for wet chemistry with plutonium solutions. This arrangement can be used to carry out various analyses.

In Figs. 1, 2, 3, 4 and 5 there are boxes of several designs. In addition to the gloved types and the open front types, it is to be noted that some have sloping fronts and others have vertical fronts. In addition, but not noticeable in the photographs, some have reagent shelves, while others do not. Some have exhaust outlets near the bottom, others near the top. At one time it was thought the various designs were necessary for convenience of the workers in performing various kinds of analytical techniques. Experience has shown, however, this is not necessarily true. With two or three exceptions, it is now thought all analytical techniques can be carried out in a box of one design.

Although boxes of several different designs are in use, these are designed with essentially complete flexibility. It is possible to put together an assembly of any possible combination of all the various types of boxes available; a situation allowed for in the initial flanged construction and endplate design.

It has been found advantageous to isolate regions in an assembly by placing partitions and doors at the required positions. Considerable saving of space was accomplished by using a specially designed, pneumatic-operated door which rises vertically, as indicated in Fig. 7. These doors are made from two ¼-in. stainless steel plates separated by a toggle arrangement which, in turn is connected to the piston. At the end of the closing stroke of the piston, the two plates are expanded laterally against neoprene gaskets, thereby producing an effective seal.

In those cases where all the boxes in an assemblage are equipped with gloves, a problem arose as to how supplies and samples could be introduced without contaminating the room. This was solved by entrance through the bottom. For small items, including samples for analysis, a metal can, Fig. 8, equipped with a bayonet-catch lid and handle for carrying, was designed in size and shape to hold a pint ice cream container. This metal can, with gasketed lid removed, is attached to the underneath side of the box with a bayonet catch as shown in Fig. 9. A circular plate, 4 in. in diameter and gasketed flush with the floor of the box, can then be removed, and the contents of the metal can transferred to the box. The metal transfer can remains fastened to the bottom of the box until it is necessary to remove or transfer additional items. The pint-size ice cream container has proved to be a convenient, inexpensive container for packaging materials for entry into and removal from a box. It helps materially in keeping the inside of the metal can relatively free from contamination. However, these metal cans do become contaminated and, when they do, they are sent to the decontamination room. For larger items, a hole 12 in. in diameter was cut in the bottom of the box. To the bottom of the box on the underneath side a cylinder 6 in. long, designed with a flanged ring at the bottom, was bolted (see Fig. 10). A portable box mounted on a cart was designed with an opening to fit against the bottom of this cylinder, as shown in Fig. 11. This portable box can be raised into position, fitting snugly against the bottom of the cylinder and thereby affording a sealed unit for transferring equipment and supplies into and out of the gloved box. A gasketed plate, flush with the bottom of the glove box, a lid on the bottom of the cylinder, and a lid on the plastic portable box normally remain in place to confine contamination.

Because of the frequent use of centrifuges, and the advisability of keeping them uncontaminated from a servicing standpoint, they were incorporated into the boxes in the following manner. A metal box of suitable dimensions, containing a removable side as indicated in Fig. 12, was bolted and gasketed on to the bottom of the drybox. A hole with the same diameter as the opening in the centrifuge bowl was cut in the bottom of the drybox. By means of levelling screws the centrifuge could then be raised against a gasket on the underneath side of the drybox, thereby effecting a seal as shown in Fig. 13. During normal use, only the inside of the centrifuge bowl becomes contaminated. In case of repair, the instrument can easily be removed by removing the Lucite window.

The question whether sinks should be included in contaminated boxes was finally

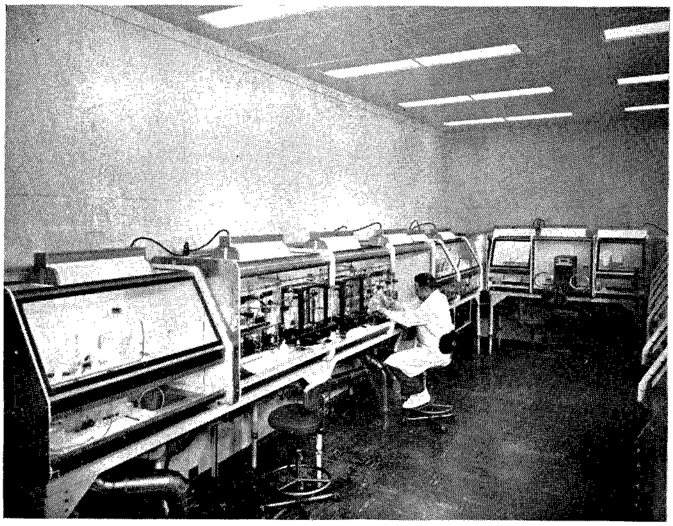

FIG. 1.—Drybox assemblage for assembly line-type of operation.

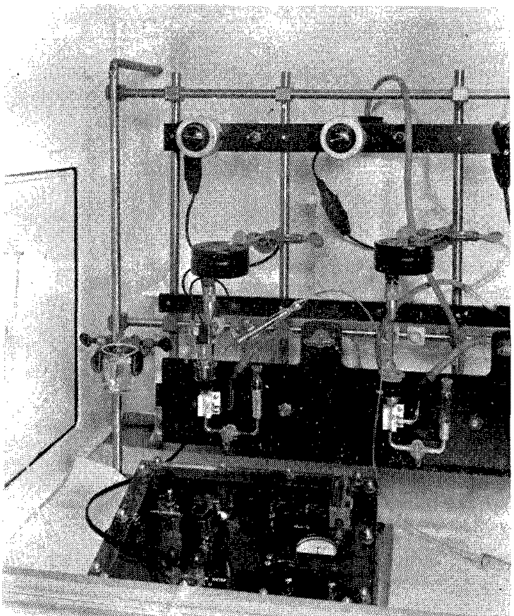

FIG. 2.—Built-in pH meter with extended controls.

FIG. 3.—Drybox assemblage for the determination of iron in plutonium.

FIG. 4.—Glove box assemblage for work with plutonium-containing solids.

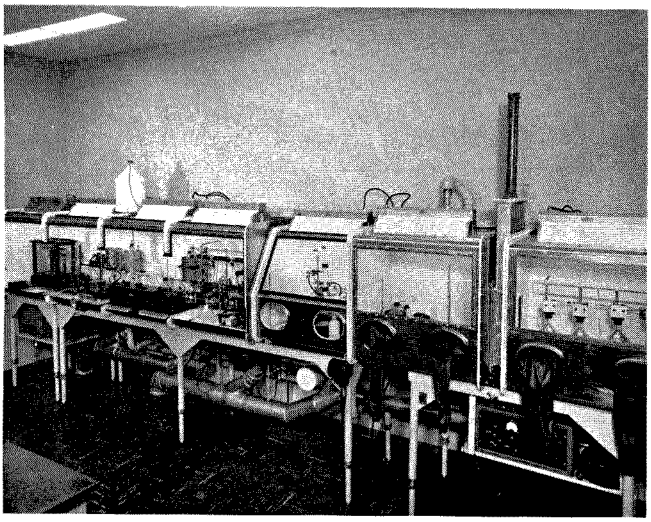

FIG. 5.—Drybox assemblage with open front and glove boxes.

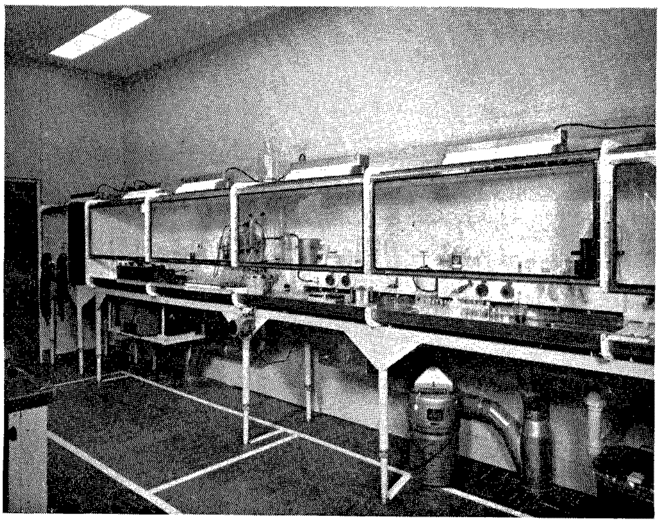

FIG. 6.—Open-front type boxes for general wet chemistry analysis of plutonium.

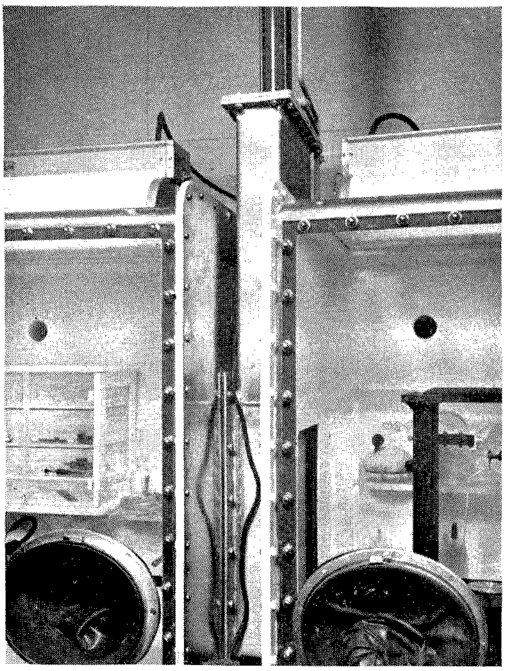

FIG. 7.—Pneumatically operated door between boxes.

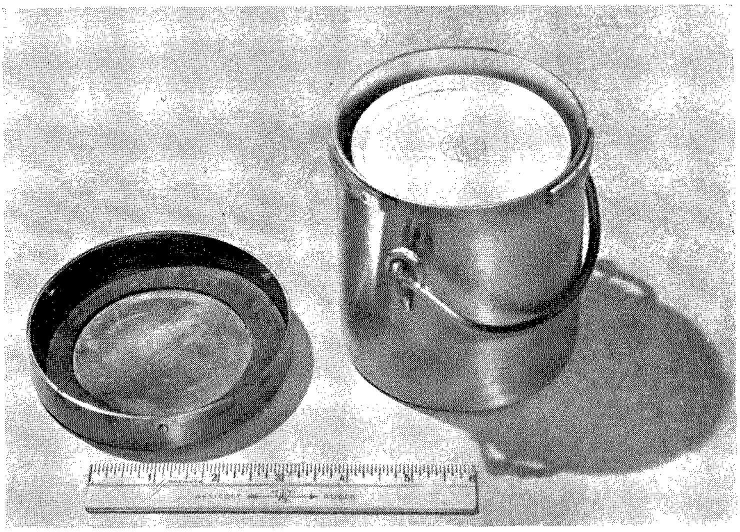

FIG. 8.—Small size transfer can.

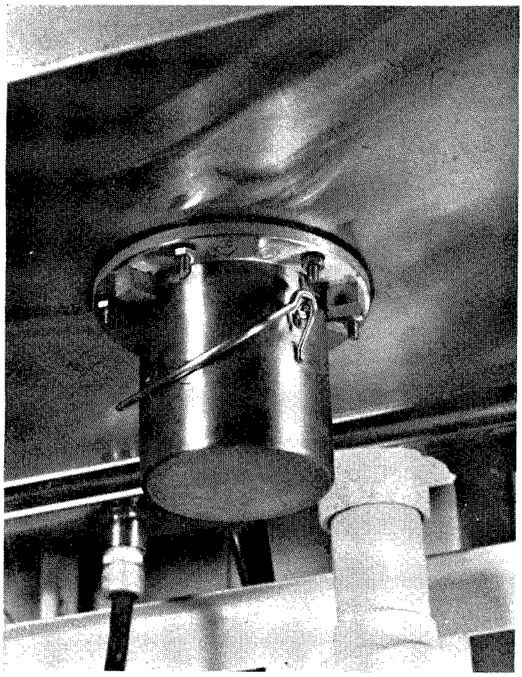

FIG. 9.—Small transfer can assembled to bottom of drybox.

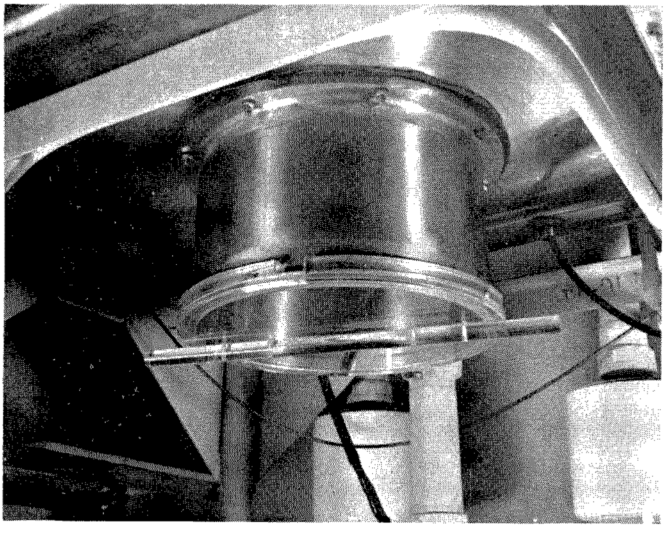

FIG. 10.—Large transfer unit connection.

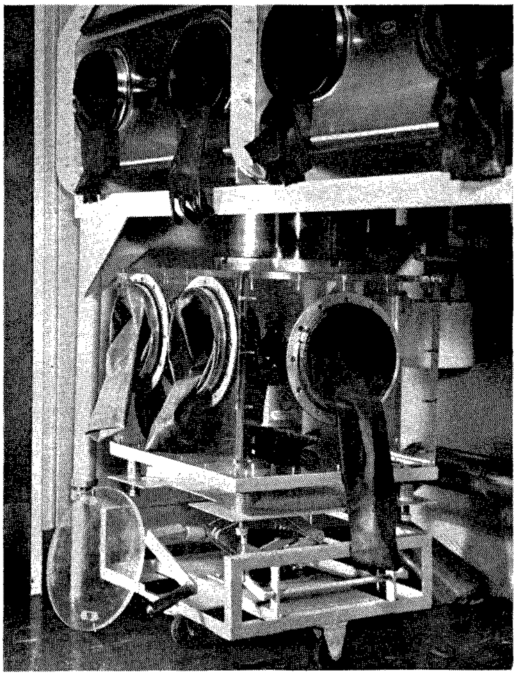

FIG. 11.—Portable transfer unit connected to drybox.

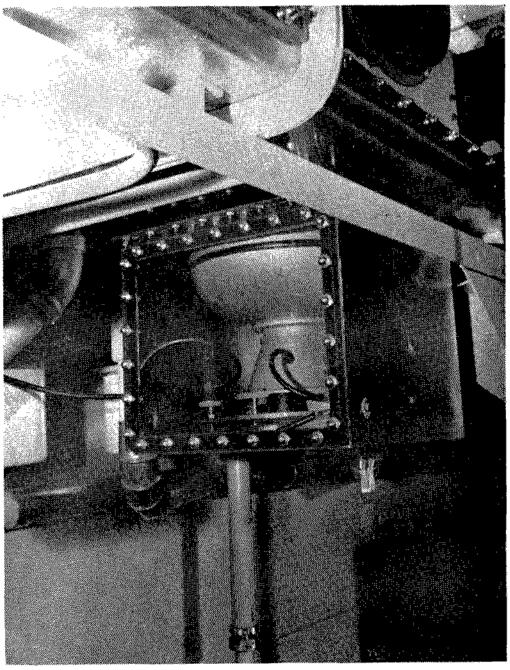

FIG. 12.—Centrifuge and housing on bottom of drybox.

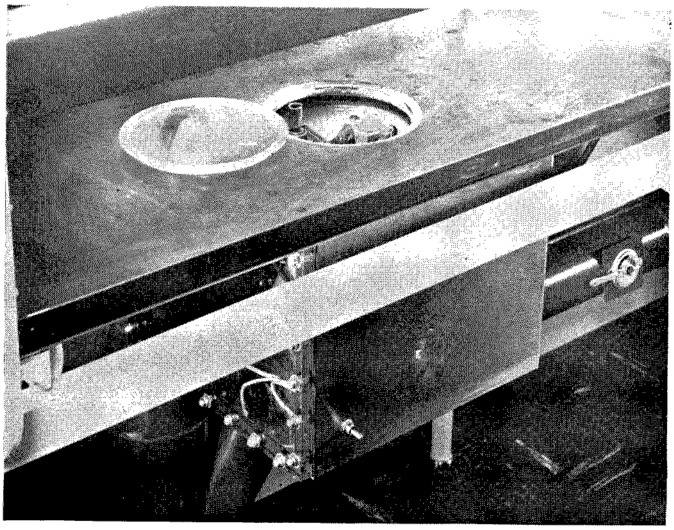

FIG. 13.—Opening in bottom of drybox for centrifuge.

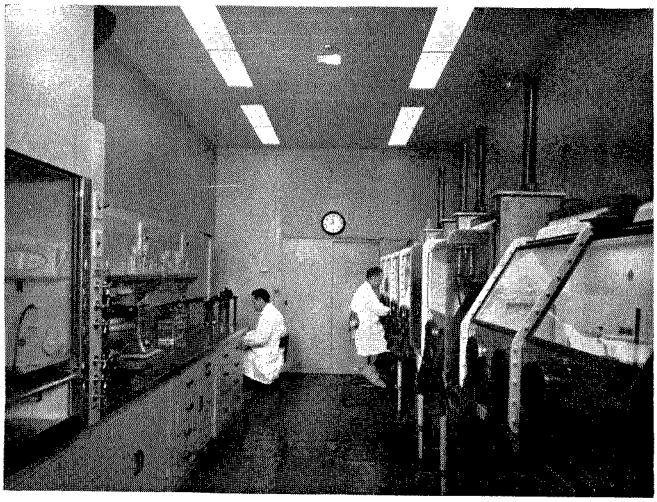

FIG. 14.—Typical plutonium analytical laboratory.

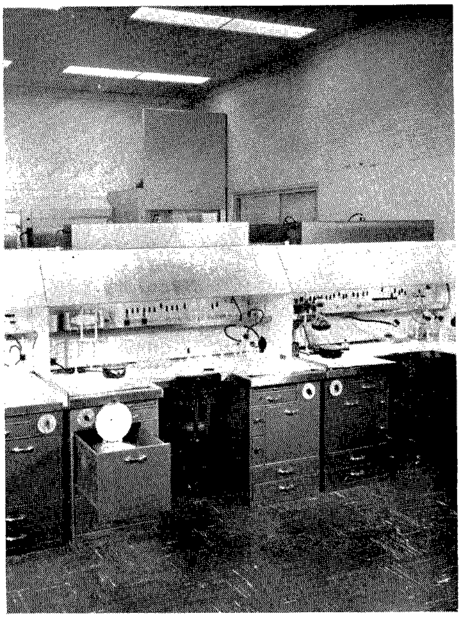

FIG. 15.—Open benches for handling micro-quantities of plutonium.

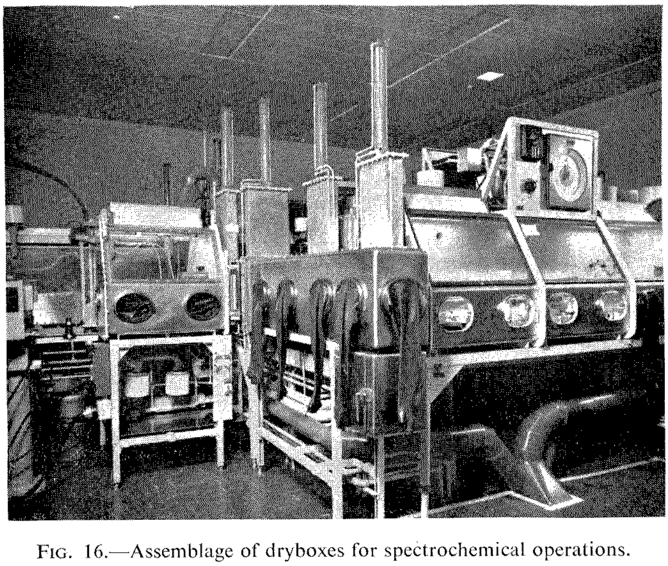

FIG. 16.—Assemblage of dryboxes for spectrochemical operations.

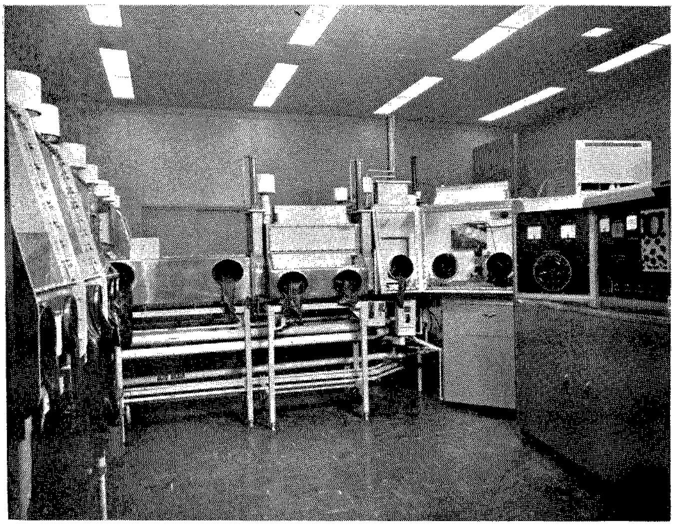

FIG. 17.—Glove box assemblage for spectrochemical operations.

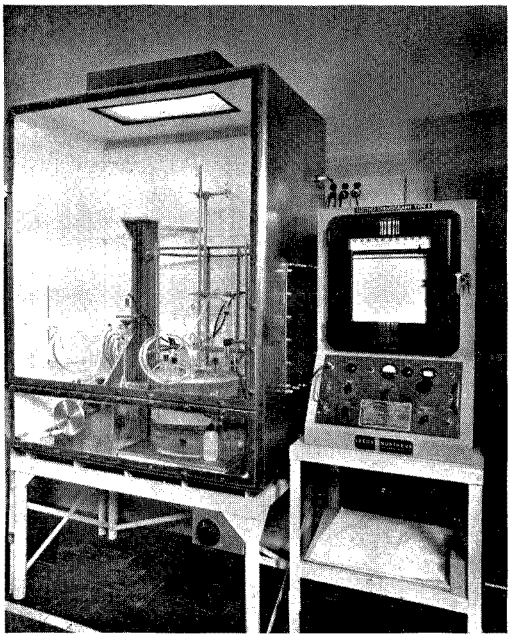

FIG. 18.—Drybox unit for polarography.

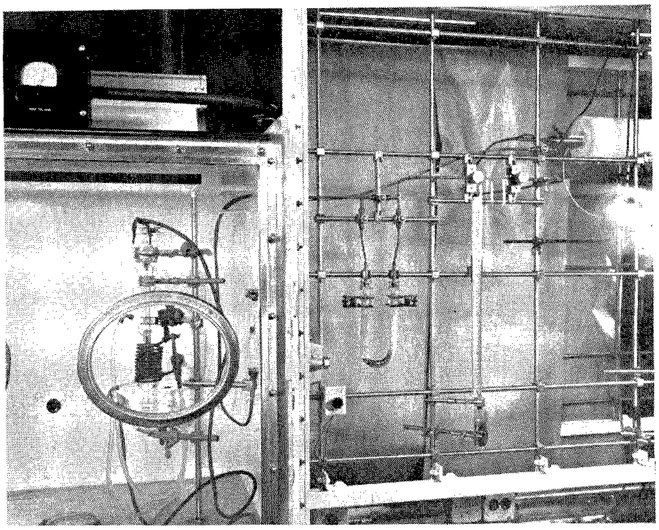

Fig. 19.—Drybox equipment for the determination of oxygen in plutonium.

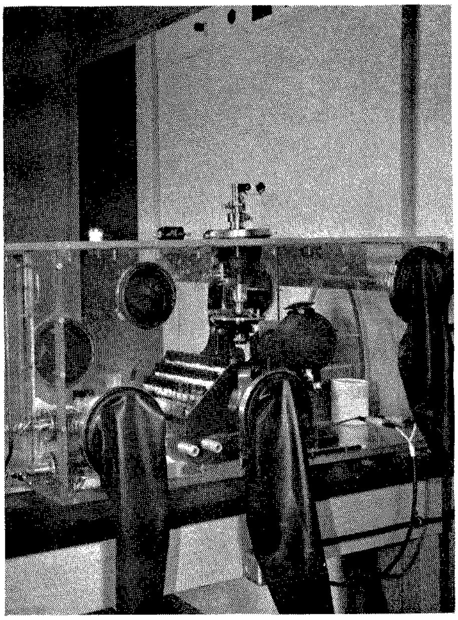

Fig. 20.—Drybox unit for chemical microscopy.

decided in their favor. However, all drains from these sinks are connected to retention tanks. The liquid in these tanks is checked for plutonium content before being released to the industrial treatment plant.

In equipping analytical laboratories with these boxes for handling plutonium, consideration must be given to the fact that a certain amount of "cold" laboratory work is necessary in order to be able to carry on the work in the boxes. For this reason, most of the laboratories for the analysis of plutonium at Los Alamos have been designed with about half the wall space equipped with dry boxes and the remainder occupied with the normal type of laboratory bench as shown in Fig. 14. This arrangement has proven very satisfactory. Experience has shown that drybox assemblages suitable for routine and semi-routine analytical chemistry work are also satisfactory for research on the analytical chemistry of plutonium, and the development of procedures for the analysis of plutonium.

It has been found possible to handle small samples of dilute solutions for radiochemical analysis in specially designed open-front hoods, as shown in Fig. 15. Ventilation is provided through a narrow opening at the bottom and also at the top of the back of the hood. This arrangement has been found to be satisfactory for such micro-operations as pipetting a few microliters of plutonium solution into volumetric flasks, diluting, pipetting a few tenths of an ml on to a glass or metal plate, evaporating the solution to dryness and flaming. These working spaces are equipped with centrifuges for separating, by precipitation, a fraction of a microgram of plutonium from other constituents of the solution. In any case, the amount of plutonium removed from the original sample bottle does not exceed 1 or 2 μg. In this work the operator always wears rubber surgical gloves.

Various combinations or arrangements of boxes suitable for special uses, are easily assembled. Figures 16 and 17 show arrangements for assembly-line type of operations in spectroscopy. Figure 18 shows a box specially designed for polarographic work wherein the constant-temperature bath and cells are placed inside the box. The mercury reservoir is also located inside the box with the adjustment extended outside the box. The polarograph itself is located outside the box and is connected to the cells with extended leads. Not shown on the left is an assemblage of boxes for sample preparation. The hinged door which opens into this assemblage may be seen on the left side of the polarographic-cell box. In Fig. 19, a set up is shown for determining oxygen in plutonium. The induction heating coil and enclosed graphite crucible are shown inside the drybox. A glove has been removed for better visibility. The rest of the apparatus is outside the drybox. This is a typical example of adapting apparatus for use inside a drybox. Figure 20 shows a specially designed box for chemical microscopy work. The eye piece of the microscope extends through the top of the box. The actual manipulation of the microscope is done inside the box. An inert, dry atmosphere may be maintained inside the box when necessary.

Nearly 5 years of operations in the boxes have proven the general philosphy to be be sound and the boxes adequate for the work done in them. In retrospect, it now seems that a single design could be made that would be satisfactory for most of the analytical operations involving plutonium that are carried out at Los Alamos.

Talanta, 1960, Vol. 6, pp. 154 to 158. Pergamon Press Ltd. Printed in Northern Ireland

THE HIGH-ALPHA-RADIATION ANALYTICAL FACILITY OF THE OAK RIDGE NATIONAL LABORATORY*

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Summary—The High-Alpha-Radiation Analytical Laboratory has been in operation since 1952. Originally concentrated Pu and U^{233} solutions were assayed in this laboratory and the control analyses associated with the ion-exchange isolation of these solutions were also carried out in this facility. However, during the past few years, the high-alpha-laboratory has been used to provide analytical services for all development programs concerned with the processing of alpha-emitting materials, such as Np^{237} and Am^{241}.

A brief description of the methods of analysis and techniques is presented. Mention is made of some of the special problems that have arisen concerning the handling of alpha-emitting materials. Future plans for a transplutonic analytical facility are also discussed.

EARLY in 1952 at the Oak Ridge National Laboratory, a special operation was initiated for the purpose of isolating the pure plutonium and uranium-233 product solutions from the metal recovery processes. The operation of collecting product solutions on ion-exchange resins had just been adopted at the recovery process pilot plant. It was the duty of the newly formed Isolation Group to elute these products from the resin and further purify, decontaminate, and concentrate them. Figure 1 shows a diagram of the isolation laboratory. Briefly, the process involved transporting the loaded ion-exchange columns to the isolation laboratory, eluting the plutonium or uranium, and purifying and concentrating the material by precipitation, filtration, and redissolution.

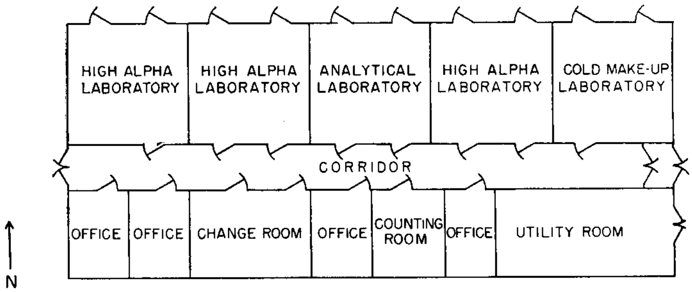

FIG. 1.—Plan of isolation building.

As improvements were made in the pilot plant processes, elution of the essentially pure product material was carried out in the recovery plant itself and the isolation laboratory was no longer needed for its original purpose. Since the initial operation of this laboratory involved the handling of high-alpha radioactive material, all research, development, and small-scale production operations involving this type of material were transferred to this laboratory.

It is the purpose of this paper to present some of the operational techniques of the high-alpha analytical laboratory. The primary duty of this laboratory is to assay the

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* Work performed under contract with the U.S. Atomic Energy Commission.

final solutions of the power reactor fuel reprocessing pilot plant. The sampling of these solutions initially was the responsibility of the Analytical Chemistry Group. The original storage and shipping containers were polyethylene bottles of 4-liter capacity from which a sample was withdrawn with a pipet. A later type of container was a stainless steel can, 6 in. in diameter and 6 ft in height. Samples were removed from these containers through Tygon tubing with a siphoning action initiated by suction applied with a 30 cm^3 hypodermic syringe. Figure 2 shows a schematic diagram of the apparatus used in sampling. Following is a stepwise description of the sampling procedure:

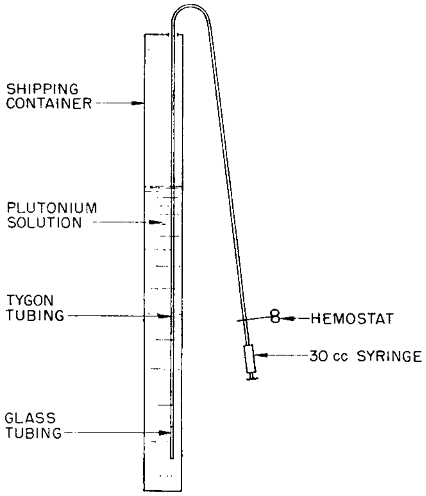

FIG. 2.—Plutonium sampling apparatus.

(1) A glass tube, 8 to 10 in. in length, is fitted into a 3/16-in. i.d. Tygon tube, 10 ft. in length.

(2) The tube, with the glass tube attached, is lowered into the solution container through a 1-in. hole in the top.

(3) The tip of a 30-cm^3 syringe is inserted into the end of the Tygon tube.

(4) Gentle suction is applied, allowing the solution to rise in the tube.

(5) When the solution approaches the end of the tube, a hemostat is clamped on the tube and the syringe is removed.

(6) The open end of the tube is placed in a sample bottle and the hemostat is slowly released, allowing the solution to flow into the bottle.

(7) The flow is again stopped with the hemostat and the bottle capped.

(8) The tube, filled with solution, is raised and the hemostat released, allowing the solution to drain back into the product container.

(9) The tube is slowly withdrawn from the container through a compress of absorbent tissue and discarded.

At the present time, samples are taken in the processing plant by recirculating type samplers in glove boxes and sent to the laboratory for assay. Table I lists the determinations made on the plutonium solutions.

Aliquots for plutonium determinations are fumed to near dryness in mineral acids

TABLE I.—ASSAY OF PLUTONIUM PRODUCT SOLUTIONS

Determination	Method[1]
Plutonium	Potentiometric ceric sulfate titration (tentatively, controlled potential coulometric titration)
Density	Direct weighing
Iron	Spectrophotometric o-phenanthroline
Uranium	Fluorophotometric
Acid	NaOH titration, phenolphthalein
Gross alpha	Methane proportional counter
Gross gamma	Scintillation counter
Gamma spectrum	Single channel recording gamma spectrometer
Plutonium isotopes	Mass spectrometer
Trace impurities	Emission spectrograph

in the high velocity hoods and diluted to volume from which aliquots are taken for analysis. Plutonium interference in the fluorophotometric determination of uranium is eliminated by precipitating the plutonium as the fluoride and then analyzing the supernatant solution. Aliquots are prepared in this laboratory for mass analysis and emission spectrographic analysis. Samples for the mass spectrometer are evaporated directly on the spectrometer filament and sealed in a polyethylene bag for shipment to the mass spectrometer laboratory. Plutonium must be removed from the samples for the emission spectrograph. This is accomplished by adsorbing plutonium(IV) on an anion resin from a $8M$ nitric acid solution. The effluent solution from the resin is submitted to the spectrographic laboratory for determination of trace impurities.

A list of the analyses performed on the uranium-233 product solutions is shown in Table II.

TABLE II.—ASSAY OF URANIUM-233 PRODUCT SOLUTIONS

Determination	Method[1]
Uranium	Potentiometric ferric sulfate titration
Density	Direct weighing
Acid	NaOH titration—Beckman Model K titrator with ferrocyanide complex of U
Thorium	Spectrophotometric—thoron
Gross alpha	Methane proportional counter
Gross gamma	Scintillation counter
Gamma spectrum	Single channel recording gamma spectrometer
% U^{232}	Alpha energy analysis of gross alpha mount
Uranium isotopes	Mass spectrometer
Trace impurities	Emission spectrograph

Interfering uranium is separated from thorium by adsorbing the uranium from $6.5M$ hydrochloric acid on an anion resin column. The thorium in the effluent is determined spectrophotometrically with thoron. Uranium is removed from sample

FIG. 3.—Solvent extraction apparatus.

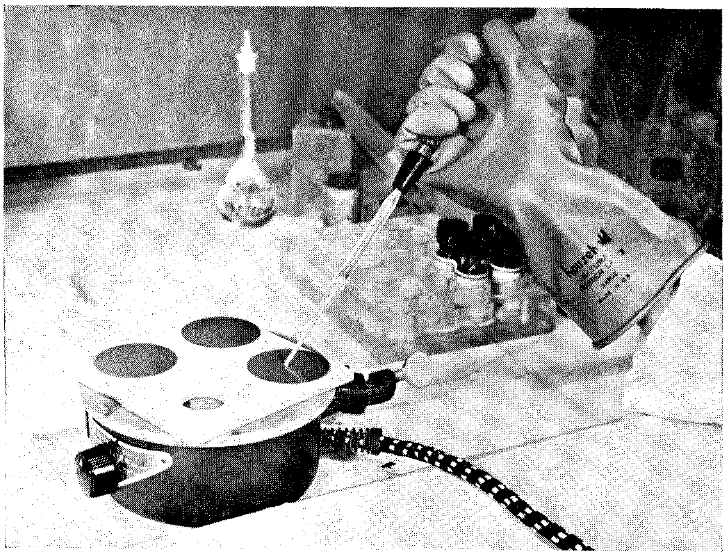

FIG. 4.—Plate drying apparatus.

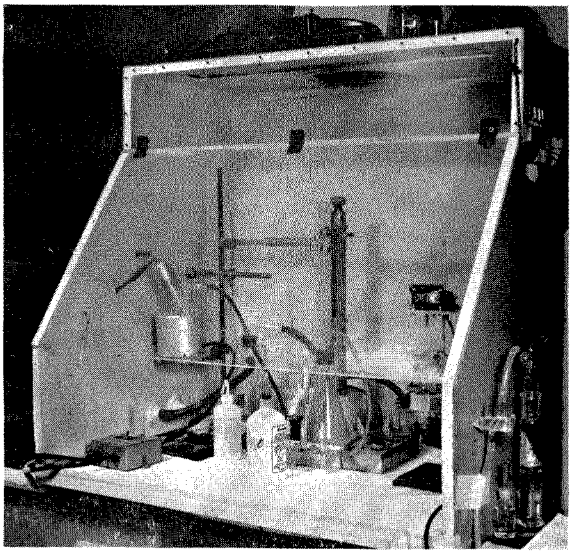

FIG. 6.—Plywood hood used for plutonium titrations.

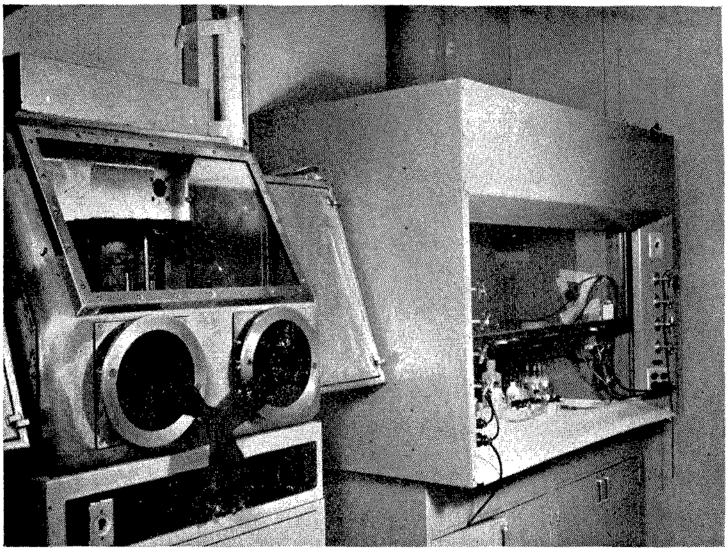

FIG. 7.—Glove box and hood in high-alpha analytical laboratory.

aliquots for the spectrographic analysis by extraction with tributyl phosphate (TBP) from 8*M* nitric acid. Mass spectrometer filaments are prepared in the same manner as for plutonium.

The research and development projects dealing with high-alpha radioactive materials require analyses in addition to the ones just mentioned. One of the most common is that of the radiochemical determination of plutonium. Solvent extraction with thenoyltrifluoroacetone (TTA) is used in an unusual apparatus (Fig. 3). The extraction vessel is a screw-cap vial, 1 in. in diameter and 2$\frac{1}{4}$ in. high. The extractors, with a plastic-coated stirring bar in each, are arranged on top of a magnetic stirring motor in a Lucite holder. The high-speed action of the stirring bars ensures adequate mixing of the two phases. After the extraction, the vials can be placed in a clinical centrifuge to aid in phase separation. Aliquots of the TTA phase can be withdrawn and mounted on stainless steel plates for alpha counting. The organic aliquots are dried on the apparatus shown in Fig. 4. It consists of a small hot plate covered with a 5-in square aluminum plate which is $\frac{3}{16}$ in. in thickness. The aluminum plate has four 1-in. holes through it over which the counting plates are placed. The plates are heated around the edge, allowing the solution to evaporate as it is pipetted into the center of the plates. The vial-type extraction vessel has advantages over the open top type in that no solution can be evaporated or spattered out during the extraction. The same apparatus is used for TTA extraction of americium and neptunium. Relatively pure americium-241 and neptunium-237 solutions, contaminated with other alpha emitters, are assayed by the alpha-energy analysis of a gross alpha mount. Gamma counting is also used for the determination of Am^{241}.

Because of their experience and equipment for handling alpha materials, the High-Alpha Analytical Group assisted the Health Physics Division in making neutron threshold detectors. The detectors are weighed portions of neptunium-237 dioxide sealed in copper capsules, $\frac{3}{4}$ in. in diameter and $\frac{1}{16}$ in. thick. The process involved calcination of neptunium nitrate solution, weighing and sealing the oxide in an inner can, and enclosing all this material in the outer capsule and soldering it closed. All of

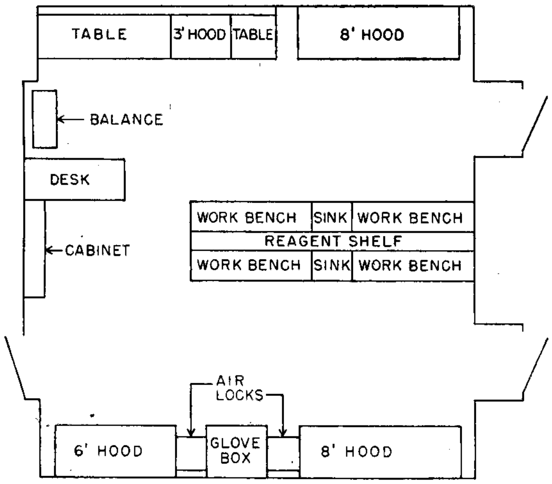

FIG. 5.—Plan of high-alpha analytical laboratory.

these operations were done in a glove box except for the final soldering which was done in a high-velocity hood.

At the present time, the facilities of the high-alpha analytical laboratory consist of hoods with a high flow of air and one glove box for handling dry alpha active materials A schematic diagram of the analytical laboratory and equipment is shown in Fig. 5. Typical hoods and glove boxes are shown in Figs. 6 and 7.

Plans are now being made for expansion of the isolation building to include additional laboratories and shielded cells for high alpha–gamma radiation facilities. The analytical group will have access to three 24- by 24-ft laboratories, a counting room, office, and one shielded cell. The new laboratories will be equipped with glove boxes for routine "line type" analytical operations and for research and development on analytical methods pertaining to high-alpha radiation materials.

REFERENCE

[1] ORNL Master Analytical Manual, U.S. Atomic Energy Commission, TID 7015. Available in reprinted form from the Office of Technical Services, Department of Commerce, Washington, D.C.

Talanta, 1960, Vol. 6, pp. 159 to 166. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF PLUTONIUM BASED ON NATIONAL BUREAU OF STANDARDS POTASSIUM DICHROMATE

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Summary—A description of the design and operation of the New Brunswick Laboratory's plutonium analytical facility is presented. The potentiometric titration of high-purity Pu is discussed.

A new laboratory, using gloved boxes of improved design, has been built to study the chemistry of Pu, develop methods of analysis, and prepare Pu compounds suitable for standards. The laboratory is equipped for spectrographic, wet-chemical, instrumental, and low-level radiochemical analyses.

High-purity Pu (99.96%) is determined by a potentiometric titration with National Bureau of Standards primary standard $K_2Cr_2O_7$. Plutonium metal dissolved in 4*N* H_2SO_4 is reduced to Pu(III) in a Jones reductor and titrated to Pu(IV) with standard $K_2Cr_2O_7$. Polarized gold electrodes are used to indicate the end-point. A relative standard deviation of 0.04 per cent has been obtained for 70- to 141-mg samples. The average results are within 0.01 per cent of the purity of the Pu metal as determined by spectrographic analysis at Hanford. The advantages of primary standard $K_2Cr_2O_7$ vs. $Ce(SO_4)_2$ as used in other methods are discussed as well as the detection of the end-point by polarized electrodes vs. the reference-indicator electrode system.

A NEW, versatile laboratory, the Plutonium Analytical Facility, has been constructed at the site of the New Brunswick Laboratory and is now in operation. In this facility, gloved boxes of an improved design are used for work involving the preparation of compounds suitable for use as analytical standards, the development of methods of analyses for plutonium and for impurities in plutonium, and, in general, the study of the chemistry of plutonium. Figure 1 shows a layout of the facility. The entrance to the building opens into the office and then into a change room before reaching the main laboratory. In addition to its usual function, the change room contains facilities for decontamination of personnel and laundry. A counting room is available for low-level radiochemical analysis. It is equipped to do counting of environmental air samples

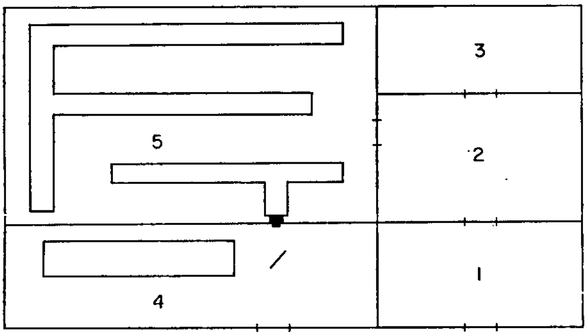

FIG. 1.—Plutonium analytical facility. 1. Office, 2. Change room, 3. Counting room, 4. Spectrograph room, 5. Main laboratory.

and liquid waste effluents in addition to making radiochemical separations. A spectrograph room, separated from the main laboratory to avoid possible contamination, houses a Baird 3-meter spectrograph. The actual arc-spark stand is located in the main laboratory in a gloved box. A series of quartz windows in the wall and in the gloved box, and an auxiliary optical system provide for transmission of the emitted light through a 90° bend in the optical path.

The main laboratory consists of 22 gloved boxes separated into two main sections, one for spectrographic work and the other for general chemical work shown in part in Fig. 2. The sloping safety plate glass windows afford a full view of the gloved box interior. The stainless steel gloved boxes can be used as either open front boxes or closed boxes by removing or adding the gloved port flanges and neoprene gauntlets as desired. Many of the boxes are equipped with space-saving, pneumatically-operated sliding doors for isolation purposes. For versatility, two gloved boxes are equipped with built-in pH meters. Additional equipment is available for carrying out spectrophotometric analyses as well as the basic laboratory manipulations of weighing, fuming, igniting and centrifuging.

One of the first projects undertaken by this laboratory was to develop an additional procedure for the oxidimetric determination of plutonium. As shown in Fig. 3, the older and most common methods for the oxidimetric determination of plutonium are based upon the reduction to Pu(III) and subsequent titration with a standardized oxidizing agent to Pu(IV).[1] Liquid or solid zinc amalgam, stannous or titanous ion may be used as reducing agents. Ceric sulfate[2] has been used extensively as an oxidant but other reagents such as bromate and permanganate are also suitable.

$$1.\ \mathrm{Pu}^{+4} \xrightarrow{\text{red.}} \mathrm{Pu}^{+3}$$

$$\mathrm{Pu}^{+3} \xrightarrow{\mathrm{Ce}^{+4}} \mathrm{Pu}^{+4}$$

$$2.\ \mathrm{Pu}^{+4} \xrightarrow{\mathrm{HClO_4}} \mathrm{Pu}^{+6}$$

$$\mathrm{Pu}^{+6} \xrightarrow{\mathrm{xsFe}^{+2}} \mathrm{Pu}^{+4}$$

$$\mathrm{Fe}^{+2} \xrightarrow{\mathrm{Ce}^{+4}} \mathrm{Fe}^{+3}$$

$$3.\ \mathrm{Pu}^{+4} \xrightarrow{\text{Zn Amal.}} \mathrm{Pu}^{+3}$$

$$\mathrm{Pu}^{+3} \xrightarrow{\mathrm{K_2Cr_2O_7}} \mathrm{Pu}^{+4}$$

FIG. 3.—Oxidimetric methods for plutonium.

In a procedure[3] recently developed at Los Alamos, hot perchloric acid is used for the oxidation of plutonium to Pu(VI), followed by reduction to Pu(IV) with a slight excess of standardized ferrous ion. The excess ferrous ion is back-titrated with a standardized solution of ceric ammonium sulfate.

These two general methods call for the use of standardized solutions of ceric or ferrous ammonium sulfate, or both, as titrants. These titrants are somewhat unstable [3,4,5] and may require frequent standardization against a primary standard. In order to eliminate the standardization problem, it was decided to develop a method for the determination of plutonium based on a stable oxidant, the National Bureau of Standards primary standard potassium dichromate.

In the method for the determination of plutonium developed at this laboratory, plutonium metal is dissolved in 4*N* H_2SO_4 and reduced to Pu(III) with zinc amalgam

FIG. 2.—Main laboratory of plutonium analytical facility at the New Brunswick Laboratory.

in a Jones reductor. A direct potentiometric titration of the reduced plutonium is made with primary standard potassium dichromate solution in which the plutonium is oxidized to Pu(IV). For greater precision, weight burets are used for the addition of more than 99 per cent of the titrant. The end-point is reached by the addition of a small volume of a very dilute solution of the titrant from a microburet.

The sensitivity of the end-point has been increased by using a gold–gold electrode system polarized by a small constant current,[6,7] and by increasing the concentration of the acid in the solution. It was also found that the use of an inert atmosphere to prevent air oxidation of plutonium(III) to plutonium(IV)[4] during the titration was not necessary. As shown in Table I a total of five variables in the procedure was investigated.

TABLE I.—EXPERIMENTAL VARIABLES

1. Reducing agents
2. Effect of concentration of titrant
3. Detection of the end-point
4. Effect of acid concentration on the end-point
5. Effect of air oxidation

Solid and liquid amalgams have been used successfully for the reduction of plutonium to Pu(III). By the use of liquid amalgam the transfer of plutonium solutions from one vessel to another is eliminated but special apparatus and long reduction times are required.[8] With solid amalgams a simple Jones reductor is used and the reduction time is relatively shorter, but the plutonium solutions must be transferred before titration.[1]

In order to eliminate some of the disadvantages of these reductants, a study was made of the effect of a rotating amalgamated zinc wire spiral[9] on the plutonium reduction process. As shown in Table II, the reduction of plutonium was neither quantitative nor rapid under any of the test conditions, even at 100°C and with a reduction time of 6 hr. Because of these adverse results, it was decided to revert to the use of a standard Jones reductor containing a bed of amalgamated zinc granules. The Jones reductor performed satisfactorily, as expected, and no reductor blank was detected. The only disadvantage of this method is the necessity for transferring plutonium solutions.

TABLE II.—THE EFFECT OF AMALGAMATED ZINC WIRE SPIRAL ON THE REDUCTION OF PLUTONIUM

Temperature, °C	Time, hr	Pu found, %
24	1	75.10
24	2	94.12
24	40	98.16
100	4	99.65
100	6	99.74

The effect of the concentration of the titrant was next studied. Preliminary tests were made using a weight buret and titrating directly to the end-point with a concentrated potassium dichromate solution. It was found that a small error in the volume of titrant added at the end-point, such as one drop or 0.04 mg of potassium dichromate, resulted in a relatively large error of 0.2 mg in the plutonium value. This situation exists because of the unfavourable plutonium to potassium dichromate weight ratio of approximately 5 to 1 in the oxidation of an equivalent of plutonium by an equivalent of potassium dichromate.

In order to minimize this concentration effect, an amount of concentrated titrant slightly in excess of that needed to oxidize 99 per cent of the plutonium to the +4 valence state was added from a weight buret. The titration to the end-point was then continued from a microburet with a more dilute solution containing 0.25 mg of potassium dichromate per ml.

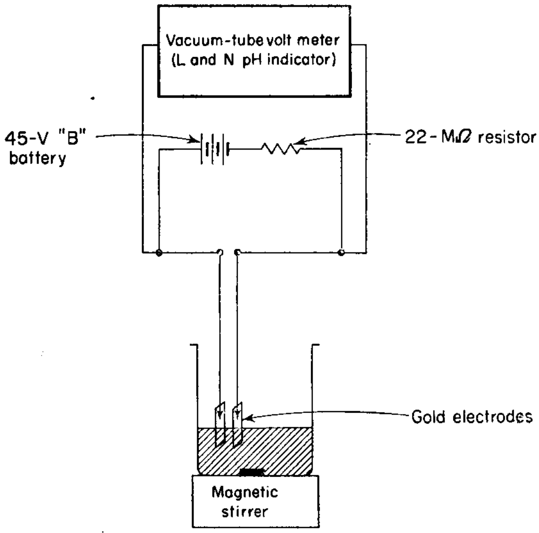

FIG. 4.—Titration apparatus.

With the advent of the use of very dilute dichromate as titrant, difficulty was encountered in detecting the end-point. In some preliminary work it was found to be advantageous to use iron as a substitute for plutonium. In titrating ferrous iron with the concentrated dichromate solution directly to the end-point, a platinum–calomel electrode system was used successfully. However, no sharp potential increase was observed when determining the end-point in plutonium solutions after changing over to the dilute dichromate solution. As shown in Fig. 4, a polarized platinum–platinum electrode system, utilizing a constant current of about 2 μA, was then substituted for the platinum–calomel system. A small 45-V "B" battery and a 20-MΩ, ¼-watt resistor were connected in series to two electrodes placed in a beaker. The electrodes were spaced about 1 cm apart. Another lead from each of the electrodes was connected to a vacuum tube voltmeter such as a Leeds and Northrup pH indicator. Agitation of the solution in the beaker was produced by a Teflon-covered stirring bar and a variable-speed magnetic stirrer. After adjustment of the acidity of the solution, as will be discussed next, the end-point was easily detected. However, platinum electrodes proved to be unreliable as they frequently became "poisoned" and unresponsive in solution. Bright gold electrodes were substituted as shown, and have exhibited little tendency towards "poisoning" at any time.

As mentioned previously, the acidity of the solution played a part in the detection of the end-point. The first few titrations, using the polarized gold electrode system in a 2*N* sulfuric acid solution, did not give a sharp end-point, as shown in Fig. 5. The potential increase at the end-point was very small and not clearly distinguishable from the potential change caused by the previous increment of titrant added. When, however, the acid concentration was increased to 4*N* sulfuric acid, a much sharper inflection and greater potential change occurred at the end-point, as shown in Fig. 6.

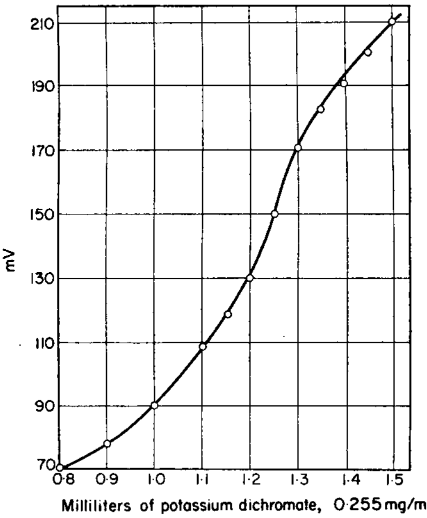

Fig. 5.—Titration curve of plutonium(III)–dichromate in 2*N* H_2SO_4.

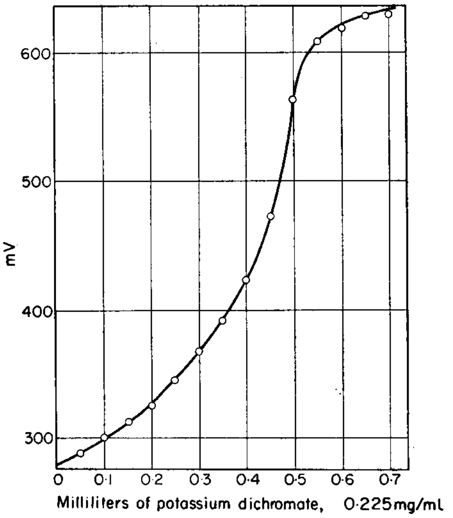

Fig. 6.—Titration curve of plutonium(III)–dichromate in 4*N* H_2SO_4.

Lastly, it has been reported that the titration of plutonium(III) to plutonium(IV) is affected by air oxidation.(4) This possibility was investigated. A reduced sample was allowed to stand exposed to air for 2 hr, without agitation. Another reduced sample was stirred vigorously in air for 2 hr. Results show that only 0.3 per cent of the plutonium was oxidized in the sample which stood in air whereas nearly 4 per cent of the plutonium was oxidized in the sample stirred in air. This effect was found to be negligible when samples were titrated immediately after reduction. However, the use of an inert atmosphere after reduction of the sample is advisable, should an immediate and rapid titration not be possible.

Finally, results for the determination of plutonium by this method, on eleven samples ranging from 70 to 141 mg, are shown in Table III. Since iron is titrated along with plutonium, all experimental and calculated values have been corrected accordingly. The standard deviation in the analysis of these samples was found to be ±0.04 per cent. The average of these experimental results is 99.97 per cent as compared to the value of 99.96 per cent calculated from the spectrographic analysis of the metal at the Hanford Works.(10) In the future, it is expected that the precision of this method will be improved greatly by selecting larger samples than those presently used, and by increasing the sensitivity of the electrodes so that less dichromate will be required for the potential change at the end-point.

APPENDIX

Reagents and apparatus

Weight buret, 30-ml capacity.

Microburet, 5-ml capacity, 0.05-ml subdivisions.

Titration apparatus. A small 45-V "B" battery and a 20-MΩ, ¼-watt resistor are connected in series to two bright gold electrodes placed in a 150-ml beaker as shown in Fig. 4. The electrodes are spaced about 1 cm apart. Another lead from each of the gold electrodes is connected to a vacuum tube voltmeter such as a Leeds and Northrup Model 7664 pH indicator. Agitation of the solution in the titration beaker is produced by a Teflon-covered stirring bar and a variable speed magnetic stirrer.

TABLE III.—DETERMINATION OF HIGH-PURITY PLUTONIUM METAL (99.96%)

Sample taken, mg	Pu found, %
78.04	99.94
78.43	100.00
83.58	99.99
72.80	99.93
70.04	99.99
103.92	99.87
89.32	100.01
83.56	99.95
78.52	100.03
140.95	99.99
82.65	99.96
	Average 99.97

Jones reductor. A Jones reductor tube is filled with a column (1 in. in diameter and 5 in. long) of granulated zinc amalgam.

Sulfuric acid, reagent-grade, 4*N*.

Potassium dichromate solutions. National Bureau of Standards primary standard potassium dichromate, sample No. 136A, is dried for 2 hr at 110°C and placed in a desiccator to cool.

Solution A, 0.7 mg $K_2Cr_2O_7$/g of solution. Weigh a 1000-ml volumetric flask to the nearest 10 mg. Weigh 0.7 g of dried potassium dichromate to the nearest 0.05 mg, add to the weighed flask, dissolve in 4*N* H_2SO_4, and dilute to 1 liter with 4*N* H_2SO_4. Reweigh the flask and contents. Calculate the concentration of potassium dichromate as mg of potassium dichromate per gram of solution.

Solution B, 0.25 mg $K_2Cr_2O_7$/ml. Weigh 250 mg of dried potassium dichromate to the nearest 0.05 mg, dissolve in 4*N* H_2SO_4, and dilute to 1 liter with 4*N* H_2SO_4 in a volumetric flask.

Plutonium metal. A supply of high-purity, alpha-phase plutonium metal was obtained through the Hanford Atomic Products Operation. The spectrographic analysis of this material, as determined at the Hanford Works, is presented in Table IV. Based upon pile exposure data, the chemical atomic weight of the plutonium is estimated by Hanford to be 239.115 ± 0.005.

Procedure

Weigh by difference 100 mg of bright, high-purity plutonium metal to ±0.02 mg and place in a 150-ml beaker. If the plutonium has a slightly oxidized surface, the oxide may be removed by gentle scraping with a spatula. If the oxide coating is heavy, it may be necessary to electropolish the metal,(3) or remove it with a file under water.

Add 10 ml of 4*N* H_2SO_4 to the beaker and cover it with a watch glass. The dissolution is complete in 15 to 20 min. The metal should be covered with sufficient acid to minimize spattering. When dissolution is complete, wash the watch glass and the sides of the beaker with a minimum amount of 4*N* H_2SO_4.

TABLE IV.—SPECTROGRAPHIC ANALYSIS OF HANFORD PLUTONIUM METAL
(Values in p.p.m.)

Element	Value	Element	Value
Carbon	200	Sodium	N.D.
Silicon	100	Lithium	N.D.
Manganese	20	Potassium	N.D.
Lead	5	Zinc	N.D.
Tin	2	Phosphorus	N.D.
Magnesium	<10	Molybdenum	N.D.
Copper	1	Vanadium	N.D.
Cadmium	N.D.	Thallium	N.D.
Silver	N.D.	Calcium	N.D.
Nickel	2	Aluminum	N.D.
Chromium	<1	Lanthanum	N.D.
Boron	20	Arsenic	N.D.
Iron	25	Beryllium	N.D.

N.D. = Not detectable.

While the sample is dissolving, pour 30 to 32 ml of potassium dichromate, Solution A, into a clean, dry weight buret without filling the tip. Cover the buret tip and stopper the buret. Weigh the buret to the nearest mg. Fill the microburet with potassium dichromate, Solution B, invert a 10-ml beaker over the top, and then proceed with the reduction step.

Pour the dissolved plutonium sample into the Jones reductor. Cover the reductor with a watch glass. Collect reduced plutonium solution from the reductor in a second 150-ml beaker, containing a Teflon-coated stirring bar. Place this beaker under the reductor so that the effluent runs down the side of the beaker. Adjust the flow rate through the reductor to about 3 ml/min, or less. When the liquid level of the sample is 5 mm above the amalgam bed, rinse the sides of the reductor and the watch glass with 4*N* H_2SO_4. Wash the original beaker, in which the sample was dissolved, twice with 4*N* H_2SO_4. Add the washings to the reductor. Wash the reductor twice with 15-ml portions of 4*N* H_2SO_4 and once with 15 ml of water.

Set up the titration apparatus with the electrodes inserted in the reduced plutonium solution as shown in Fig. 4. Rapidly add the titrant (Solution A) from the weight buret until the blue color of the sample solution changes to pale orange. Turn on the magnetic stirrer so that it gently agitates the solution. Adjust the pH indicator to zero on the +700 scale. Quickly add the titrant in five-drop portions until the potential of the solution reverses itself. Continue the titration until a meter change of 10-mV is noted. At this point add the titrant in two-drop portions until a second 10-mV increment occurs. Now add the titrant dropwise until a third 10-mV increment, usually occurring near 200 mV, is observed. Weigh the weight buret at this point. Immediately continue the titration by adding Solution B from the microburet in increments of 0.05 ml. Record the change in potential for each increment of titrant added. The titration should be continued for at least two increments of titrant beyond the end-point which usually occurs at about 450 mV and is indicated by the largest potential increase.

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THE DETERMINATION OF AMERICIUM IN PLUTONIUM ALLOY FUELS FOR FAST REACTORS*

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Summary—For the determination of americium in fast-reactor plutonium fuels, a method is required which is quantitative and which gives a product free of either alpha or gamma contaminants, since either alpha or gamma counting may be used for the detection of Am^{241}. In the present method, americium, plutonium, and the rare-earth fission products are precipitated as hydroxides from an HCl solution of the fuel sample, after the addition of lanthanum as a carrier. Ceric sulfate is added to the acidified hydroxide precipitate to oxidize plutonium to the hexavalent state. The hexavalent plutonium remains in solution when americium and the rare-earth fluorides are precipitated. After the fluoride precipitate is dissolved in HNO_3 and H_3BO_3, a second hydroxide precipitation is performed to remove fluoride. This precipitate is dissolved in a small quantity of HNO_3 and transferred to an ion-exchange column packed with Dowex 50-X4, 200- to 400-mesh resin. Americium and the rare-earth elements are eluted with 5% NH_4NO_3 saturated with ethylenediaminetetra-acetic acid at a pH of 2.3. The americium is eluted after the yttrium and just prior to the elution of the europium fractions. In fresh samples (less than 2 days old), the americium may be contaminated with Eu^{156}, but it is free of all other rare-earth elements, permitting alpha counting in a sample with low beta activity. Recovery of americium is better than 98%, with less than 2% plutonium alpha activity and with a gamma decontamination factor of 2×10^4. If the sample has aged sufficiently to allow the short-half-lived rare-earth elements to disappear, the americium may be determined by counting the gamma activity.

INTRODUCTION

RECENTLY, a study was begun at Los Alamos on the possibility of utilizing plutonium as the primary fuel in fast reactors.[5] As part of this program, an analytical method was sought for the determination of americium in neutron-irradiated plutonium. Such a method requires either the isolation of americium from plutonium alpha activity and most of the beta-active fission products to permit alpha counting of the americium, or complete isolation from the fission products so that a gamma count can be made of the americium.

Standard precipitation procedures are available for the separation of americium from plutonium and many of the fission products. For example, in the present investigation a hydroxide precipitation followed by a ceric fluoride precipitation served to produce an americium fraction which was freed of all except the rare-earth fission products. The separation of americium from these rare-earth elements is more difficult, and ion exchange was studied as a means for accomplishing this.

Several ion-exchange techniques have been reported for the separation of mixtures containing rare-earth elements and actinides. These include the anion-exchange method of Coleman *et al.*[1], in which ammonium thiocyanate is used as the eluting agent, the cation-exchange method reported by Freiling and Bunney[2] in which lactic acid is used, and the cation-exchange method of Street and Seaborg[7] in which alcoholic hydrochloric acid is used as the eluting agent. When these procedures were applied to the separation of americium from rare-earth fission products, they met with only

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* Work performed under contract with the United States Atomic Energy Commission.

limited success. Good results were obtained with aged fission samples which contain only the lighter rare-earth elements. With recently fissioned plutonium, however, containing yttrium and heavier, short-lived rare-earth elements, considerable beta–gamma contamination of the isolated americium was experienced.

Studies were made of a cation-exchange method for the separation of the americium–rare-earth fraction, using ethylenediamenetetra-acetic acid (EDTA) as the eluting agent. Mayer and Freiling[6] and Fuger[3,4] showed that the elution behavior of rare-earth elements and actinides is strongly dependent on the pH of the EDTA solution; best results are achieved at a pH of 3.6 or below. They also indicated that close attention must be paid to pH because of the limited solubility of free EDTA. In the present work it was found that EDTA is sufficiently soluble above pH 2.1 for ion-exchange application with tracer quantities of elements, and that best separation of americium from rare-earth fission products is achieved on Dowex-50 cation exchanger at a pH of 2.3.

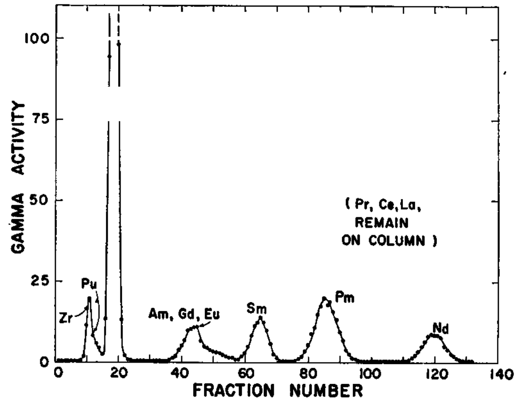

FIG. 1.—Elution of rare-earth fraction from Dowex-50 with EDTA at pH 2.30. 100 mg Pu $\sim 10^{14}$ fissions.

PROCEDURE

The samples used were plutonium buttons irradiated in the Los Alamos Water Boiler Reactor for 1 hr at a thermal neutron flux of $10^{12}/\text{cm}^2$ per sec. These buttons were dissolved in hydrochloric acid. Aliquots containing 1 mg of plutonium were treated with 1 mg of lanthanum carrier and made ammoniacal. The hydroxide precipitate which formed carried the americium, plutonium, and rare-earth fission products while other fission products remained in solution. The precipitate was dissolved in nitric acid, 4 drops of a $0.1M$ ceric solution were added and the solution was then heated for 10 min to oxidize plutonium to the hexavalent state. After cooling the solution, 3 drops of $20M$ hydrofluoric acid were added to precipitate ceric fluoride. The americium and rare earth elements were carried on the precipitate, leaving plutonium in solution. The precipitate was dissolved in nitric acid with the aid of a drop of boric acid, and an ammonium hydroxide precipitation was made to remove fluoride. The precipitate was then dissolved in the minimum quantity of nitric acid and applied to the ion-exchange column.

The ion-exchange resin was of Dowex 50-X4, 200- to 400-mesh in the hydrogen form. It was packed to a height of 19 cm in a tube, the inside diameter of which was

0.5 cm. After addition of the sample, the column was washed with 5% ammonium nitrate solution made to a pH of 2.30. This operation was carried out until the pH of the effluent reached 2.30, indicating the removal of all free acids from the resin. After this pH adjustment, the adsorbed elements were eluted with a solution containing 5% ammonium nitrate saturated with EDTA and made to a pH of 2.30.

RESULTS

A typical elution curve obtained with a freshly irradiated sample is shown in Fig. 1. The first fractions coming from the column were found to contain zirconium and plutonium. The amounts of these elements recovered represent only a small part of their original activity because, for the most part, these elements were removed during the ceric fluoride precipitation step. The next element in order of elution was yttrium and this was followed by americium. Continued elution results in the removal of samarium, promethium and neodymium. At this point praseodymium, cerium and lanthanum remain on the column. These could be removed by increasing the pH of the eluting solution to 2.60.

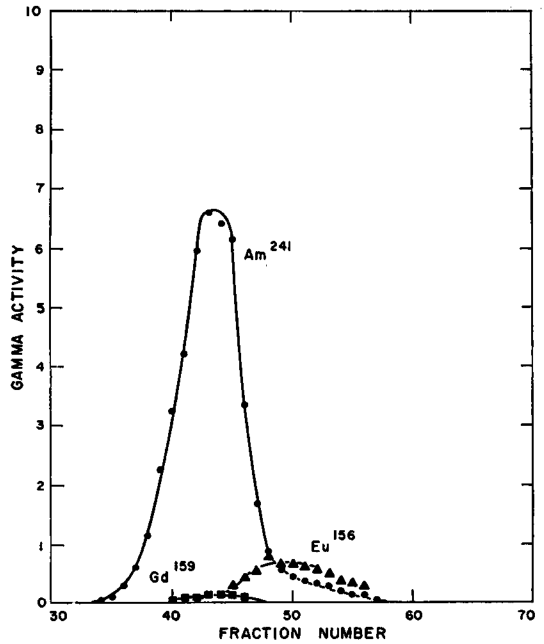

Fig. 2.—Composition of fractions containing americium.

The fractions eluted from the ion-exchange column which contained americium were found by gamma pulse analysis to be contaminated with europium-157 and to a much lesser extent with gadolinium-159. This is shown in Fig. 2.

The effect of pH on the elution behaviors of yttrium, americium and europium is shown in Fig. 3. At a pH of 2.6 and above, all three elements are eluted rapidly and no separation is achieved. With a decrease in the pH, the ease with which americium is removed from the column changes much more rapidly than does yttrium, so that a good separation of these elements can be made at the lower pH. The optimum pH was considered to be 2.3, since, under this condition, separation of americium and yttrium is complete and the removal of americium from the column occurs within a reasonably short time. As shown in Fig. 3, the separation of americium and europium cannot be made complete by varying the pH.

Thus, a good separation of americium is achieved from all the rare-earth elements except europium and gadolinium, and these elements produce only a slight beta–gamma contamination. The determination of americium involves merely combining those fractions which contain that element and evaporating a suitable aliquot for alpha counting.

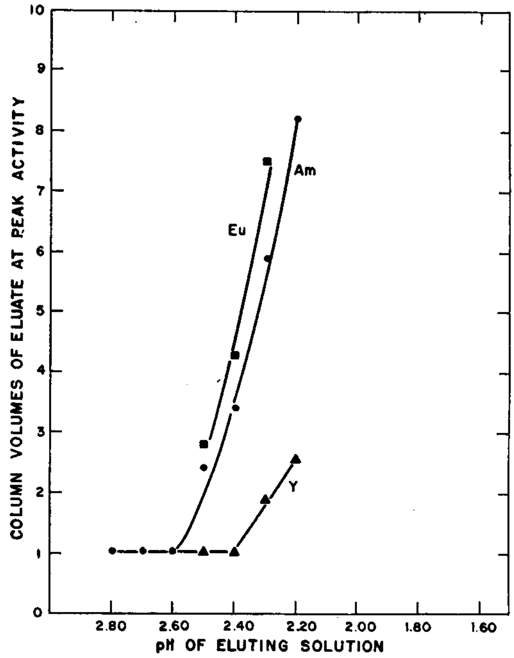

FIG. 3.—Variation of position of peak activity with pH of eluting NH_4N_3O-EDTA solution.

The results for two different irradiated plutonium samples are shown in Table I. For the first sample the average of 32 determinations was 0.230 μg of americium per mg of plutonium with a standard deviation of 2.4 per cent, while for the second sample an average of 0.245 μg of americium per mg of plutonium was obtained in eight determinations with a standard deviation of 3.8 per cent. Pulse analysis was used to demonstrate that alpha contamination by plutonium was less than 2 per cent. Since the actual americium content of these samples was not known, a check on the accuracy of the method was made by addition of known amounts of americium in several runs. By this means average recoveries of 98.6 per cent and 97.0 per cent, respectively, were found for the two samples. These data are shown in Table II.

The quantities of americium obtained from the most freshly irradiated plutonium samples (less than one day old) were contaminated to the extent of about 50 per cent by foreign gamma activity. With these samples gross gamma counting was unsuitable for measuring the americium content. This excess gamma activity decayed and after a

TABLE 1.—AMERICIUM CONTENT FOUND FOR TWO SAMPLES OF IRRADIATED PLUTONIUM BY PRECIPITATION-ION EXCHANGE

Sample No. 1

Am found, μg/mg Pu	Am α/total α %	Am found, μg/mg Pu	Am α/Total α %
0.221	990	0.225	93.4
0.220	100	0.229	97.9
0.225	100	0.221	94.8
0.224	98.8	0.233	96.8
0.226	100	0.234	99.1
0.225	100	0.233	97.5
0.226	100	0.235	100
0.222	100	0.239	100
0.233	99.2	0.231	97.8
0.230	98.4	0.237	97.6
0.232	95.6	0.236	98.7
0.226	98.6	0.237	99.0
0.235	98.1	0.230	98.6
0.233	98.1	0.227	96.7
0.226	96.0	0.230	96.9
0.237	97.2	0.231	97.4

Av. Am found, μg/mg Pu, 0.230 ± 0.005.

Sample No. 2

Am found, μg/mg Pu	Am α/Total α %
0.250	99.0
0.246	98.6
0.242	99.1
0.244	99.5
0.241	98.0
0.251	98.4
0.238	98.6
0.249	98.4

Av. Am found, μg/mg Pu, 0.245 ± 0.009.

TABLE 2.—RECOVERY OF AMERICIUM "SPIKE" FROM TWO SAMPLES OF IRRADIATED PLUTONIUM

Sample No. 1

"Spike" Recovery	"Spike" Recovery
104.5	103.8
98.7	101.1
99.4	101.9
101.9	103.2
105.1	99.4
94.2	99.4
91.0	99.4
87.8	98.7
86.5	

Av. recovery, 98.6%.

Sample No. 2

"Spike" Recovery
98.1
100
89.7
99.4
96.2
98.7

Av. recovery, 97.0%.

cooling period of 18 days amounted to about 1 per cent of the total in the americium fraction. After this time, gross gamma counting could be substituted for alpha counting in determining americium.

CONCLUSION

The present method should be applicable to the determination of americium in fissioned plutonium at the 200-p.p.m. level with an error of less than 5 per cent. It can be used successfully with samples after cooling for a period of less than 2 day.

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Talanta, 1960, Vol. 6, pp. 173 to 184. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF NITROGEN, AMERICIUM, NEPTUNIUM, AND URANIUM IN P.P.M. QUANTITIES IN PURE PLUTONIUM*

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Summary—The following methods were adapted to or developed for the determination of low-level impurities in high-purity plutonium. The lower limits of detection are nitrogen—5 to 10 p.p.m.; americium—25 p.p.m.; neptunium—1 p.p.m.; and uranium—1 p.p.m.

Nitrogen is determined by the classical method in which it in converted to NH_3 in an NaOH solution, distilled into an H_3BO_3 solution, and titrated with standardized HCl. The Kjeldahl apparatus is completely contained in a glove box, and all transfers of waste solution are made by vacuum. After dissolution of the sample, the time required per determination is about 1 hr. The precision of the method is 10 per cent of the amount present.

The americium content is calculated from the difference between the per cent of 5·5 MeV alpha activity before and after the separation of americium from plutonium. The activity of the alpha energy is determined by pulse-height analysis. The per cent of 5·5 MeV alpha activity before the separation indicates the sum of Am^{241} and Pu^{238}. The americium is separated from the plutonium in a $12N$ HCl–$0{\cdot}1N$ HNO_3 solution by means of an anion-exchange resin. The plutonium is eluted from the resin with $1N$ HCl, and a sample is dried on a platinum disk for pulse-height analysis. A better sample can be prepared for pulse-height analysis by drying some of the activity from the organic phase of a thenoyltrifluoroacetone separation of the eluted plutonium. About 1 man-hr is required per determination. The precision and the accuracy are 10 per cent.

The neptunium is extracted from $12N$ HCl containing $0{\cdot}1M$ hydroquinone and $0{\cdot}1M$ KI to keep the neptunium in the quadrivalent state and the plutonium in the trivalent state. The organic solvent is $0{\cdot}5\,F$ mono(2-ethyl-hexyl)ortho-phosphoric acid, with toluene as a diluent. The distribution coefficient for Np^{IV} is greater than 800, while that for $Pu^{III,VI}$ is about 0·1. The organic phase is washed a sufficient number of times with $12N$ HCl and $0{\cdot}1M$ hydroquinone to effect the desired decontamination from plutonium. The decontamination factor for each wash operation is about 10. The organic phase is adjusted to a volume of 2 ml, and an appropriate aliquot is dried on a platinum disk for alpha pulse analysis. The time required for the determination is 2 man-hr. The precision and accuracy are 10 per cent.

The uranium in plutonium has been determined in the range of 10 to 1000 p.p.m. A 5-mg aliquot of plutonium in $1N$ HNO_3 is reduced to Pu^{III} with $2M$ ferrous sulfamate and contacted for 10 min with 30% tri-n-butyl-phosphate in benzene. The organic phase is washed five times with a $1N$ HNO_3–ferrous sulfamate solution. The organic phase is adjusted to a volume of 1 ml and appropriate microaliquots are then added to NaF–LiF flux tablets and dried. Then flux tablets containing aliquots of the sample, standards, and standard additions of uranium are fused for reading on the fluorophotometer. The recovery is from 85 to 95 per cent with a precision of 10 per cent. The time required for analysis is about 2 man-hr.

INTRODUCTION

To carry out the basic physical metallurgical research program at Argonne National Laboratory (ANL), high-purity plutonium is required of such composition that the residual individual contaminants have no significant effect on the measured properties.[1] Consequently, methods are required for the determination of p.p.m. quantities of nitrogen, americium, neptunium and uranium. In addition to those

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* Work performed under contract with the U.S. Atomic Energy Commission.

elements, carbon, hydrogen, oxygen and silicon[2] are determined by gas analysis techniques and the remaining impurities are determined spectrographically.[3]

The plutonium purification method is essentially identical with the fused-salt electrolysis method for uranium developed by Marzano and Noland.[4] The electrolyte consists of a lithium chloride–potassium chloride eutectic to which 7 mole per cent of plutonium tetrafluoride has been added. The anode rods are made from impure biscuit plutonium and the cathodes are molybdenum strips. The temperature of the molten bath is maintained at 400–450°C.

Table I.—Typical plutonium analyses ('impure')

Mass	238	239	240	241	242
%	2 (% activity)	95	4.5	0.5	0.01

Am^{241}—250 p.p.m., Np^{327} —<5 p.p.m., N—75 p.p.m., U—100 p.p.m.,

Wet chemical methods used at Argonne for the determination of neptunium, uranium, americium and nitrogen are given in this report. The determination of neptunium is based on a recent report[5] by Peppard and co-workers at ANL. The uranium determination is a modification of the method used at ORNL.[6] The method used for the determination of Am^{241} is indirect but adequate for the range found in these samples. The nitrogen determination is the classical conversion to NH_3 with sodium hydroxide, steam distillation and titration with standardized HCl. The techniques used conform to safe practices for handling high-level plutonium.

The plutonium samples for all these determinations are dissolved in 20% HCl (redistilled), 30% H_2O_2, and a trace of 1*N* HF, when necessary. After the initial reaction with HCl has ceased, there is usually an undissolved sludge remaining. The sludge is dissolved by periodic additions of a few drops of H_2O_2 while it is warmed with a heat lamp. If a small residue still persists, it can usually be dissolved by the addition of one or two drops of 1*N* hydrofluoric acid. The hydrofluoric acid aids in the dissolution of small amounts of oxide which may be present. The nitrogen is probably present in the form of nitride which may be formed by exposure of the metal to air.

The production of Pu^{239} in a reactor from normal uranium involves the following nuclear reactions:

$${}_{92}U^{238} \xrightarrow{+n} {}_{92}U^{239} \xrightarrow{-\beta^-} {}_{93}Np^{239} \xrightarrow{-\beta^-} {}_{94}Pu^{239}.$$

In addition, other isotopes of Pu and Am^{241} are produced:

$${}_{94}Pu^{239} \xrightarrow{+n} {}_{94}Pu^{240} \xrightarrow{+n} {}_{94}Pu^{241} \xrightarrow{-\beta^-} {}_{95}Am^{241}$$

$${}_{92}U^{238} \xrightarrow[-2n]{+n} {}_{92}U^{237} \xrightarrow{-\beta^-} {}_{93}Np^{237} \xrightarrow{+n} {}_{93}Np^{238} \xrightarrow{-\beta^-} {}_{94}Pu^{239}.$$

A typical analysis of plutonium prior to purification is shown in Table I.

Uranium is found in the plutonium because of incomplete purification from the raw material. The neptunium and americium are by-products of the nuclear reactions whereby plutonium is produced. Other methods for determination of americium that have been reported include gamma counting of the Am^{241},[7] solvent extraction separation of Pu^{IV},[9] from Am^{III}, and coprecipitation of americium with ceric fluoride[9] or with lanthanum fluoride.[10] In methods recently reported for the determination of neptunium, anion exchange[16] and polarographic measurements are used.

PROCEDURE FOR THE DETERMINATION OF NITROGEN

Reagents

2% H_3BO_3 (aqueous)
Methyl red–bromcresol green indicator solution (40 mg methyl red plus 60 mg bromcresol green/100 ml of C_2H_5OH)
50% NaOH (aqueous)
0.01N HCl (standardized)
20% HCl (redistilled)
30% H_2O_2
1N HF.

Procedure

On one, or, at most, three days previous to the actual determination, samples weighing approximately 0.5 g are dissolved in a glove box. In order to prevent external contamination of the samples during this dissolving period, the glove box utilized is allowed to stand free of reagents containing nitrogen for at least a day before the dissolution is begun. When dissolution is complete, the 40-ml centrifuge tubes containing the samples (whose volumes are about 5 ml) are transferred to a glove box containing a modified Kjeldahl nitrogen distillation apparatus.*

In order to ascertain whether the distillation apparatus is clean, for two days previous to the actual sample determination the instrument is thoroughly steamed out and blanks are determined until a titration blank of approximately 0.06 ml of standardized 0.01N HCl is obtained.

The determination itself, with exceptions being made for special precautions necessarily taken with the plutonium samples, follows the classical Kjeldahl distillation procedure,[11] involving the conversion to ammonia in sodium hydroxide solution and distillation into boric acid solution for titration with standardized hydrochloric acid.

Referring to Fig. 1, stopcocks A and B are opened and stopcock C closed, and distilled water is added through the funnel tube (1) to the steam generator outer jacket (7), up to the level (16). The stopcock (A) is left open, and, utilizing a 10-ml syringe and a 4.5-in. transfer pipette arrangement (15), the approximately 5 ml of liquid sample is carefully transferred from the centrifuge tube to the sample transfer funnel (2). This funnel is then held in the upper position in order to bring about the movement, under gravity, of the sample into the inner jacket (4). After two subsequent rinsings with a total of about 7 ml of H_2O, approximately 9 ml of 50% NaOH are added to the inner jacket, followed by H_2O washings, up to the level (16), or about 25-ml total volume. A dark green, heavy precipitate is observable in flask (4) at this point. Stopcocks A and B are then closed and a 25-ml glass-stoppered Erlenmeyer flask (14) which contains 5 ml of 2% boric acid and 3 drops of the mixed indicator, is placed under the condenser (3) so that the end of the delivery tube is below the surface

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* Kirk Kjeldahl nitrogen distillation apparatus, No. 4520, Model B, available from Microchemical Specialties Co., Berkeley 3, California.

of the liquid. After this is completed, the Variac is turned to the proper setting (approximately 35 volts), and the distillation is begun. After about 10 ml of distillate have been collected (about 15 minutes are required), the collection flask is lowered, and the condenser is allowed to rinse into it for about two additional minutes. Then the flask (not externally radioactive if protected by a beaker as shown) is taken out into an adjoining open hood and titrated. A 2-ml buret is utilized for the titration, and the color change is from blue to a pink-yellow colored end point.

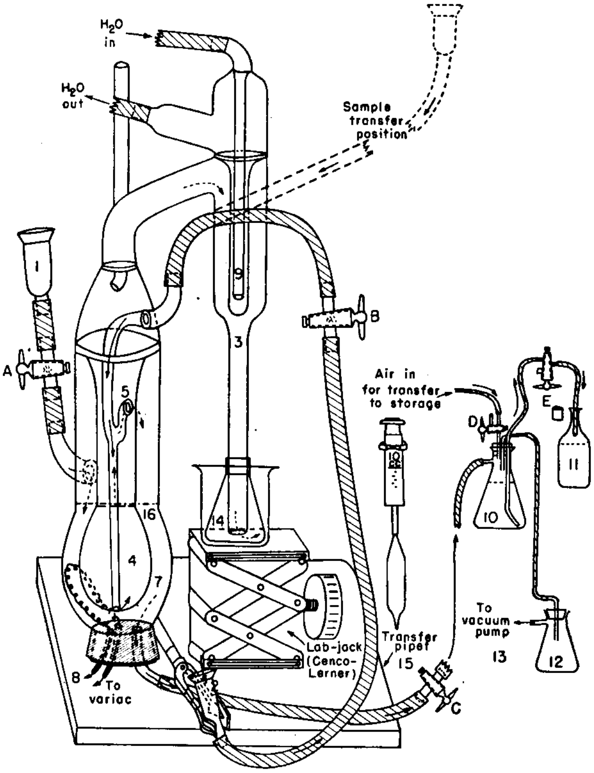

FIG. 1.—Modified Kjeldahl nitrogen distillation apparatus.
Key:
A,B,C,D,E Teflon stopcocks
(1) Funnel tube
(2) Sample-transfer funnel
(3) Condenser
(4) Inner jacket
(5) Steam inlet
(6) Heating coil
(7) Steam generator-outer jacket
(8) Variac leads
(9) Cold-finger condenser
(10) Waste container 2-l suction flask
(11) Waste storage container-1 gal P.E. bottle
(12) Trap
(13) Vacuum outlet
(14) Catch flask, 25-ml glass-stoppered Erlenmeyer flask
(15) 10-cc. syringe and 4.5-in. transfer pipette assembly
(16) Solution level before dist.

The waste solution is next transferred out of the apparatus by means of a vacuum line. Again referring to Fig. 1, stopcock *C* is opened to the vacuum line, *D* to the air, *A*, *B* and *E* are kept closed, and the vacuum pump (13) is started. By adjusting the vent at *D*, the wastes are moved out of the steam generator outer jacket (7) into the waste container (10). After rinsing the apparatus thoroughly with water, and closing *C*, the apparatus is ready for the next determination. Wastes are transferred to a storage container by means of air pressure (see Fig. 1).

It has been found necessary to determine blanks and standards in conjunction with unknown samples during each series of determinations, due to variations in the ammonia content of the reagents on a given day, and to the residual ammonia in the apparatus after each determination is completed. A typical standard would consist of 5 ml of 6*N* HCl (redistilled) containing an appropriate aliquot from a standardized NH_4Cl solution (usually equivalent to 25 to 100 p.p.m. of nitrogen).

TABLE II.—DETERMINATION OF THE ACCURACY OF THE KJELDAHL DISTILLATION METHOD

Sample No.	Sample wt, *g*	μg Added, Std. NH_4Cl	μg Recovered, total	μg N in Pu*	μg Recovered, net	μg N Error (=*p.p.m. N*)	% Error
4427	0.6415	0	9.9	9.9	0	—	—
4428	0.5745	0	10.5	10.5	0	—	—
4430	0.4031	10.1	19.3	6.8	12.5	+2.4	+24
4431	0.5476	25.1	39.1	9.2	29.8	+4.7	+19
4432	0.6674	50.3	59.1	11.2	47.9	−2.4	−5
Std.	—	50.3	49.9	0	49.9	−0.4	−1

* An average of the values for *N* in μg obtained for the two untreated samples, on the basis of an arbitrary sample weight of 0.5745 g, amounting to 9.7 μg N/0.5745 g Pu, was converted to the respective sample weights of the three treated samples, giving the corrected values listed in this column.

After the initial dissolution of the sample, the time required for one complete determination has been found to be approximately 1 man-hr.

Calculation of results

Where: T = ml of standardized HCl used in the titration,
b = number of ml for the blank
N = normality of the standardized HCl (0.01*N*)
A = atomic weight of nitrogen (14.008)
g = weight of the sample in grams.

$$\text{p.p.m. N} = \frac{(T - b)(N)(A) \times 10^3}{(g)}.$$

In order to determine whether there was any unexpected effect inherent in a determination made on an actual sample as compared with ordinary determinations on standards, a study was made in which five samples of pure plutonium metal were analyzed for nitrogen. The test results are shown in Table II.

This study, along with the results of previous determinations, indicated that the precision of the method is ±5 p.p.m. nitrogen, with the lower limit determinable for a 0.5-g sample being 5 to 10 p.p.m. nitrogen. From this it follows that, for approximately 100 p.p.m. nitrogen, the precision of this method of analysis is as good as ±5 per cent of the amount present.

PROCEDURE FOR THE DETERMINATION OF AMERICIUM-241

Reagents

$6N$ HCl
30% H_2O_2
$1N$ HF
Analytical Grade AG 1 X10 Anion-Exchange Resin (200 to 400 mesh, Chloride Form)*
$1N$ HCl
$12N$ HCl–$0.1N$ HNO_3

Procedure

Dilutions are made so that a 25-μl aliquot gives from 2 to 3 × 10^4 CPM. This aliquot is stippled onto a 0.005-in. platinum disc for alpha pulse-height analysis on a 256-channel analyzer. The per cent activity of the 5.5 MeV alpha is determined, which includes the activity for Pu^{238} and Am^{241}.

Another aliquot is taken from the stock solution and adjusted to $12N$ HCl–$0.1N$ HNO_3. It is then transferred to the anion resin (6 mm × 6 cm) which has been pre-equilibrated with $12N$ HCl–$0.1N$ HNO_3. The elution is then made by gravity at a rate of about 1 to 2 ml per minute. The column is next washed with 15 to 20 ml of the same acid mixture. Since Pu^{IV} has a very high distribution coefficient (>1000) and the Am^{III} a very low one (essentially no adsorption), the americium is easily eluted from the column. The americium-free Pu^{IV} is eluted from the column with $1N$ hydrochloric acid and the volume adjusted to contain about 2 to 3 × 10^4 c/m/25 μl. This aliquot is stippled onto a 0.005-in. platinum disc for alpha pulse-height analysis. The per cent activity in this sample from the 5.5-MeV alpha consists entirely of Pu^{238}. The difference between the per cent activity of the 5.5-MeV alpha before and after the ion-exchange treatment represents the Am^{241}. In the range ordinarily encountered in these samples (25-700 p.p.m.), an analysis accurate to about ±10 per cent can be obtained.

Calculation of results

Where: A = specific activity/g as determined from mass spectrographic and pulse height analyses
B = fraction of Am^{241} as determined by pulse-height analysis,
C = specific activity/μg Am^{241},[12]

$$\text{p.p.m. Am}^{241} = \frac{(A)(B)}{(C)}.$$

Due to factors involved in adding Am^{241} tracer to the americium-free plutonium, the determinations are biased but the average error is still only 7.5 per cent (Table III). Two plutonium samples analyzed at ANL and at Los Alamos checked within the accuracy claimed for this method (Table IV).

Since the Am^{241} content is a function of time, the values must be reported as of the date of determination. If the per cent of Pu^{241} (parent of Am^{241}) in the plutonium is

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* Supplier—Bio-Rad Laboratories, 800 Delaware, Berkeley, California.

much more than 0.1 per cent, no more than a few days should elapse between the americium separation and the pulse-height analysis.

PROCEDURE FOR THE DETERMINATION OF Np^{237}

Reagents

$6N$ HCl
30% H_2O_2
$1N$ HF
Hydroquinone
KI
$0.5F$ mono-(2-ethyl-hexyl)ortho-phosphoric acid (H_2MEHP) in toluene.

TABLE III.—DETERMINATION OF Am^{241} IN SYNTHETIC STANDARDS

Sample(a) No.	Am^{241} added, p.p.m.	Am^{241} recovered,(b) p.p.m.	% Error(c)
9915-*A*1	145	164	+13.1
9915-*A*2	145	162	+11.7
9915-*B*1	362	389	+7.5
9915-*B*2	362	391	+8.0
9915-*C*1	580	600	+3.4
9915-*C*2	580	586	+1.0
			Average = +7.5

(*a*) No. 9915 (3–433/17). 0.98 per cent activity Pu^{238}. (0.04 w/o Pu^{241}).
(*b*) 7—17 days elapsed between americium separation and pulse-height analysis.
(*c*) Factors involved in sample preparation may have produced a uniform contamination resulting in the above high percentages.

TABLE IV.—COMPARISON OF RESULTS FOR Am^{241} (ANL VS. LASL)(a)

Sample No.	Batch No.	p.p.m. (ANL)	p.p.m. (LASL)(b)
8650	3-423	360	320
9860	3-424	260	260

(*a*) Analysis corrected to same date.
(*b*) Determined by gamma counting.[7]

Procedure

The dissolved sample is diluted to a convenient volume and an aliquot containing about 250 mg of plutonium in $12N$ HCl is transferred to a separatory funnel. This aliquot is made $0.1M$ in hydroquinone and mixed gently for 30 min. The solution is then made $0.1M$ in KI, mixed and allowed to stand for 30 min. The resultant Pu^{III} and Np^{IV} are contacted for about 30 sec with an equal volume (10 ml) portion of $0.5F$ H_2MEHP in toluene. The organic phase is then washed with 25-ml portions of freshly prepared* $12M$ HCl–$0.1M$ hydroquinone. The decontamination factor for Pu from the organic phase is about 10 for each washing, with considerable tailing-off after the 6th or 7th washing. The sample should be changed to a clean separatory funnel after any two washings. The decontamination factor desired for a sensitivity of 10 p.p.m.

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* The aqueous scrub solution will remain fresh for about 2 hr.

is of the order of 10^5 to 10^6; to accomplish this, a total of 10 to 20 washings are required. A micro-aliquot from the organic phase is evaporated on a 0.005-in. platinum disk, dried, ignited and analyzed for the Np^{237} alpha activity by pulse-height analysis.

Calculation of results

Where: A = observed total c/m in the organic phase
B = fraction of Np^{237} as determined by pulse-height analysis
C = specific activity/μg Np^{237}[12]
D = sample weight (g)
E = geometry of alpha counter

$$\text{p.p.m. Np}^{237} = \frac{(A)(B)}{(C)(D)(E)}\,.$$

TABLE V.—NEPTUNIUM RECOVERIES AND DETERMINATIONS IN Pu METAL (ANALYST *A*)

Sample No.	Sample wt., *mg*	Np^{237} added, μg	No. of washings	D.F. (X10^5)	% Act. Np^{237}	Np^{237} recovered, μg	% Recovered	p.p.m.
Np^{237}	—	19.2	10	—	100	18.9	98	—
561-S	84	19.2	12	0.8	14.2	17.4	90.7	207
9870-S	158	19.2	13	6.0	39.8	17.6	91.7	111
559	159	—	16	2.3	<1	<0.7	—	<4
560	209	—	—	1.6	<2	<2.7	—	<13
561	211	—	13	8.0	2.6	0.7	—	3
2089	183	—	11	2.8	<2	<2.6	—	<14
9870	158	—	12	0.6	<1	<2.9	—	<18

TABLE VI.—NEPTUNIUM DETERMINATIONS IN Pu METAL (ANALYST *B*)

Sample No.	Sample wt., *mg*	Np^{237} added, μg	No. of washings	D.F. (X10^5)	% Act. Np^{237}	Recovered, μg	% Recovered	p.p.m.
4494-S2	249	31.5	17	1.3	20	32.9	104	132
4494-R2	186	—	17	1.1	<1	—	—	<8
4495-R3(3)	231	—	14	114	<1	—	—	<1(a)
4495-R3	231	—	14	59	<1	—	—	<1(a)
4496-R2	268	—	15	3.1	<1	—	—	<3
4496-R3	268	—	12	16	4.7	—	—	3(a)

(a) Longer reduction periods for feed before extraction.

PROCEDURE FOR THE DETERMINATION OF URANIUM

Special apparatus

Fluorescence photometer,[13, 14] designed and constructed by the Electronics Division of Argonne National Laboratory. Commercial model also available.

Fusion dishes, 1/2-in. diameter of 20-mil platinum.

Automatic 'swisher' type extractor, consisting of a pump used to draw the extraction mixture in and out of the transfer pipette for mixing (designed and made at ANL).

Solutions and reagents

1N *Nitric acid.**

2M *Ferrous sulfamate.** Heat 30 ml of water to near boiling and add 21 g of sulfamic acid. Remove from heat and add 5.5 g of iron powder. After dissolving, filter and dilute to 50 ml with water. Make fresh as this reagent is stable for the period 5–6 days only if kept in refrigeration.

30% *tri-n-butyl phosphate* (TBP).* Wash 100% TBP with saturated sodium carbonate and then wash with water. Dilute the purified TBP with benzene until the solution is 30% TBP. Just prior to use, condition this reagent by washing it with an equal volume of a 1 to 15 mixture of ferrous sulfamate and 1*N* nitric acid.

Flux for fusion of samples. This is a mixture of 98% sodium fluoride and 2% lithium fluoride, both of which are of a special grade for use in fluorophotometric applications. Commercially made pellets are also available from the J. T. Baker Chemical Company (Phillipsburgh, New Jersey).

Standard uranium solution. This contains 2 μg of uranium per ml and is prepared by dissolving U_3O_8 in dilute nitric acid.

Procedure

A 5-mg aliquot is transferred by means of a micro pipette to a clean 15-ml centrifuge cone and taken to dryness under a heat lamp. The residue is dissolved in 5 drops of 1*N* nitric acid and, when dissolution is complete, 5 drops of 2*M* ferrous sulfamate are added. A blue color usually develops immediately; however, five minutes should be allowed for complete reduction. The centrifuge cone is then mounted in the 'swisher' with a transfer pipette extending to near the bottom of the cone.

In the meanwhile, the TBP should be conditioned as described above. Condition only enough to last through the day's work as the conditioned TBP is stable for only about six hours. About 30 drops of the conditioned TBP are added to the centrifuge cone, and the 'swisher' pump is then turned on and adjusted so that the entire volume of liquid, both organic and aqueous, is drawn up into the pipette and expelled with each stroke—thus insuring thorough mixing. The extraction requires 10 minutes after which the 'swisher' is turned off and the pipette allowed to drain. The centrifuge tube is then removed and centrifuged to separate the phases. A second transfer pipette is used to remove the aqueous phase.

The organic phase is washed five times with a mixture of 8 drops of 1*N* nitric acid and 2 drops of ferrous sulfamate per wash. The ferrous sulfamate is omitted in the last wash since iron is also a fluorescence quencher. The centrifuge cone and the transfer pipette are replaced after the second wash because the high contamination of the glassware makes further washing less effective. Finally, the organic phase is concentrated to 1 ml, as measured by the calibration mark on the centrifuge tube.

Aliquots (100 μl.) of the organic phase are pipetted in triplicate onto the flux tablets in the fusion dishes and dried under a heat lamp for 20 min as are μl. aliquots of the

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* These reagents are best dispensed from dropping bottles.

standard uranium solution. One set of standards must be prepared for each batch of samples to be fused. The fusion is made over a modified gas burner which will accommodate 15 dishes, 12 sample dishes and 3 standards. Plutonium is reduced to such a low concentration (Table IX) that fluorescence quenching[15] does not occur and a 'spike' is not needed. The samples are then placed in the photometer and the measurements are made.

TABLE VII.—URANIUM RECOVERY FROM STANDARD SAMPLES

Sample	Amount present, *μg*	Amount found, *μg*	% Recovered
1	0.050	0.058	116
2	0.50	0.50	100
3	2.00	1.98	98.5
4	4.00	4.00	100

Although samples contained no plutonium, they were carried through the entire procedure.

TABLE VIII.—SAMPLE DETERMINATIONS

Sample No.	Sample wt., *mg*	U, *μg*	U, p.p.m.
2089	4.56	0.070	15
		0.068	15
1611	4.98	0.157	32
		0.143	29
1615	4.87	0.228	47
		0.219	45
560	5.23	0.549	105
		0.543	104

The dishes are cleaned by heating them in concentrated sulfuric acid, and then boiling them in water. Fusions are made (repeated if necessary) in the platinum dishes to make sure that the background reading on the fluorophotometer is equivalent to 0.001 μg of uranium or less. The dishes are then ready to be used again.

Calculation of results

Where: A = μg of uranium in standard aliquot (usually 0.2 μg)

B = average photometer reading for unknown

C = aliquot factor (usually 10)

D = average photometer reading for the standard

E = sample weight (g)

$$\text{p.p.m. U} = \frac{(A)(B)(C)}{(D)(E)}.$$

Notes

(1) If a large enough 'swisher' pump is available, (allow about 2.5 ml displacement per sample) several samples can be simultaneously extracted.

(2) It is advisable to check the manufacturer's calibration of the 1-ml mark on the centrifuge cone in which the concentration of the organic phase will be made.

(3) The lower limit of detectability of the procedure described above is 0.015 μg of uranium per 5 mg of plutonium. This limit can be lowered by using a larger sample aliquot and/or larger aliquot of the organic phase.

TABLE IX.—DECONTAMINATION OF SAMPLES

Sample No.	Sample wt., *mg*	D. F.	Residual Pu, *μg*
2089	4.56	2×10^5	0.023
		4×10^5	0.014
1611	4.98	3.5×10^4	0.17
		5×10^4	0.10
559	3.96	2×10^5	0.023
		8×10^5	0.006

Discussion

The neptunium yields are low, but the loss is probably mechanical rather than chemical. The losses could be reduced by using centrifugation when making container transfers.

The use of H_2MEHP in toluene vs. aqueous HCl for the separation of neptunium has several advantages:[5]

(1) The large distribution constant (K) for Np^{IV} makes multiple extraction unnecessary.

(2) The degree of discrimination in favor of Np^{IV} with respect to the usual M^{III} and M^{VI} contaminants is high.

(3) The reduction of Pu^{III} is rapid at room temperature.

(4) The return of Np to an aqueous phase is readily accomplished with tri-n-butyl phosphate serving as a depressing diluent to the H_2MEHP.

(5) The physical behavior of the system is completely satisfactory.

The presence of any M^{VI} during the extraction, however, does depress the K. With carefully controlled reducing conditions and with some improvement in technique, a sensitivity of the order of 1 p.p.m. could be attained when starting with about 0.25 g of plutonium.

The results obtained with the nitrogen and uranium methods are about what one would expect, based on experience with their determinations in other materials.

The limiting factor for the indirect determination of Am^{241} is the ability to differentiate between Pu^{238} and Am^{241} by alpha pulse-height analysis. The sensitivity could be greatly increased by using similar techniques on the eluant from the resin column. The main advantage of the indirect method is that the recoveries need not be quantitative. The method is adequate for the range encountered in the applications described herein.

Acknowledgements—The authors gratefully acknowledge the assistance of H. B. Evans and D. Henderson in obtaining the neptunium and pulse-height analysis data.

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Talanta, 1960, Vol. 6, pp. 185 to 188. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRONIC CONTROLLED-POTENTIAL COULOMETRIC TITRATOR FOR PLUTONIUM ANALYSIS

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Summary—An instrument that performs coulometric redox titrations at a controlled-potential is described. A stabilized printed-circuit operational difference amplifier combined with a transistor current amplifier is used to control the potential of the electrode at which the desired reaction occurs. A portion of the electrolysis current is integrated by a stabilized printed-circuit operational amplifier connected as a time integrator, and the integral is read out as a voltage. The instrument is operated completely from an a.c. line and can be operated with either manual or automatic cut-off. The calibration is absolute; results are computed from Faraday's law. Accurate coulometric titration of small amounts of substances with high equivalent weights such as plutonium is possible because of the high stability of the integrator.

THE methods used to control electrode potential and of electronic integration in this instrument are similar to those described by Booman.[1] In this instrument, however, one stabilized operational difference amplifier is used to control the electrode potential. The electrolysis current is controlled by a transistor current amplifier which is driven by the difference amplifier. The transistor current amplifier permits the use of a compact low-voltage cell power supply which can supply the high initial electrolysis current necessary for carrying out a titration in a short period of time. A small portion of the electrolysis current is integrated by a stabilized operational amplifier connected as a time integrator and the integral is read out as a voltage. This instrument contains no batteries and is completely a.c. line operated. Either oxidation or reduction reactions may be performed with good precision and the instrument may be operated manually or automatically. The titration is terminated when the electrolysis current drops to a pre-selected residual value. Stirring and electrolysis rates need not be reproducible.

This instrument differs from the ORNL model Q-2005[2] titrator in the integrator input circuitry. Figs. 1 and 2 show the sensitivity switch which has been added along with the 50-ohm power resistor and the 40K input resistor necessary for the 50 × sensitivity increase. The principles of operation of this titrator for reduction titrations are illustrated in Fig. 1. Figure 2 illustrates the operation for oxidation titrations. The input signal to the control amplifier is the algebraic sum of the control potential and the potential of the controlled electrode with respect to the solution as seen through the reference electrode. The source of the control potential is a low-voltage supply which is regulated by a Zener diode and rectified by a silicon diode. A portion of this regulated voltage is selected as the control potential.

The electrolysis current is controlled by a transistor current amplifier which in turn is driven by a chopper-stabilized difference amplifier. The difference amplifier, by negative feedback through the cell, maintains its two inputs at equal potential. The difference amplifier is a G.A.P./R. Model USA-3 printed-circuit universal stabilized amplifier[3] modified[2] so that the chopper references against input *R* which is connected directly to the controlled electrode. The transistor, a germanium PNP

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* Operated by Union Carbide Corporation for U.S. Atomic Energy Commission.

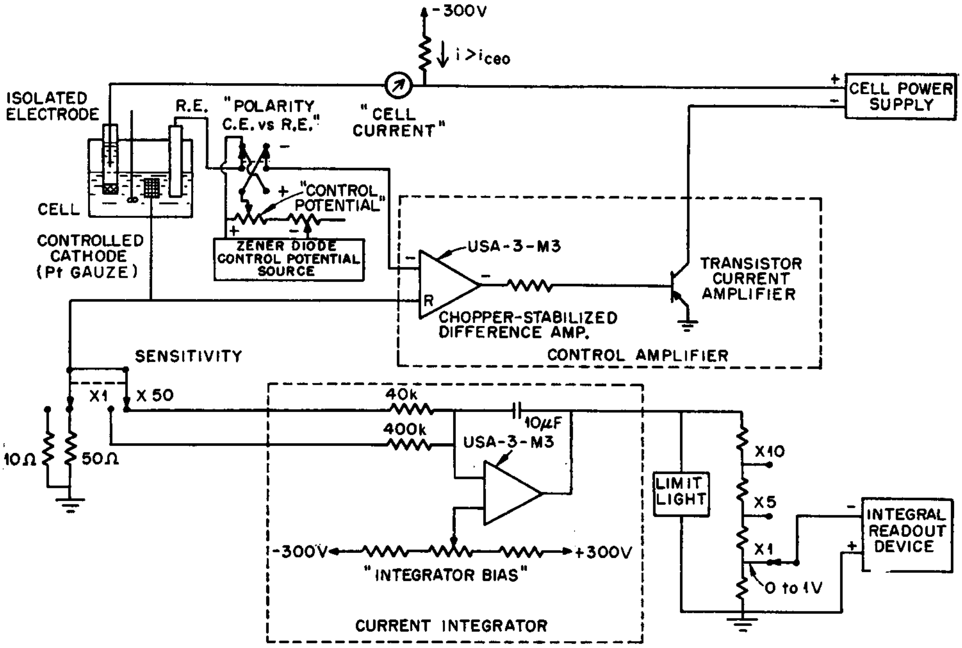

FIG. 1.—Electronic controlled-potential coulometric titrator block diagram: switched for reduction.

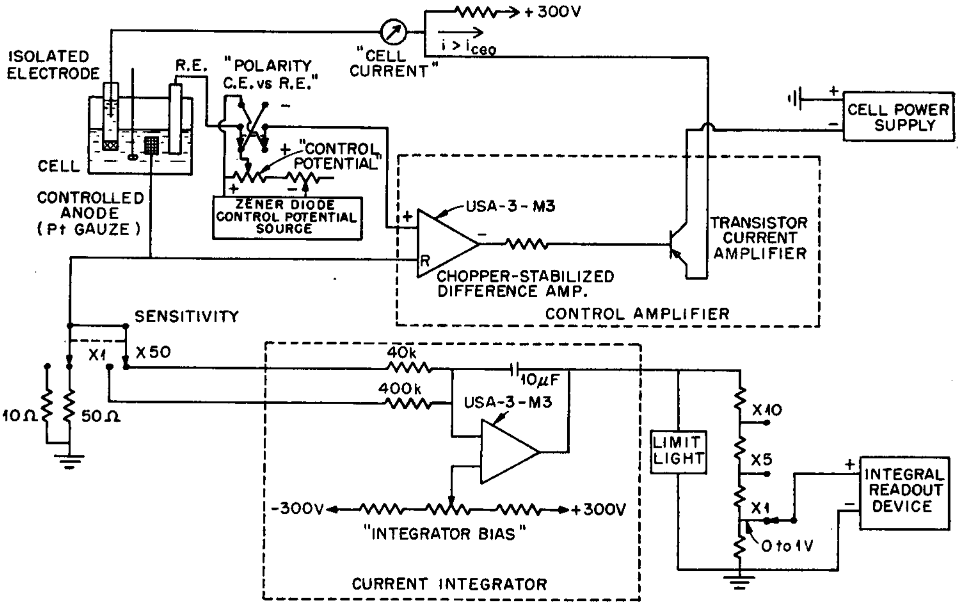

FIG. 2.—Electronic controlled-potential coulometric titrator block diagram: switched for oxidation.

high-voltage power transistor, Motorola Type 2N375, is provided with a heat sink to prevent overheating and loss of control or damage to the transistor itself. The intrinsic current, I_{ceo}, of the transistor which flows in the collector circuit with a zero base current is supplied by the G.A.P./R. Model R-100B power supply[3] through an alternative path and does not flow through the cell. In this way it is possible to attain low background currents with this instrument. Cell currents as high as 300 mA can be delivered by this instrument, but with the small cells that are used the current is limited to 25 mA by a series resistor.

TABLE I.—PROCEDURE FOR CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF PLUTONIUM

(1) Pipet the Pu sample into 8-10 ml 1*M* $HClO_4$ in cell.
(2) Position cell; start helium flow; start stirrer.
(3) Reduce automatically at +0.135 V vs. Hg—Hg_2SO_4—Li_2SO_4 to background current of 5 μA.
(4) Zero the integrator.
(5) Oxidize automatically at +0.435 V vs. Hg—Hg_2SO_4—Li_2SO_4 to background current of 5 μA.
(6) Measure readout voltage.
(7) Calculate weight of Pu oxidized.

The cell current meter has four calibrated linear current ranges and a logarithmic range. At the end of a titration, automatic cutoff is provided by the use of a meter relay with lower-limit contacts that switch power to a normally closed d.c. relay in the cell circuit. The four calibrated current ranges have overload protection furnished by a shunt diode. On the logarithmic current range the meter can be caused, by adjustment of a potentiometer in series with the meter, to read linearly on any portion or all of the lower half of the meter scale and logarithmically on the remaining upper portion of the scale. By this means it is possible to follow an entire titration on one current range while retaining the sensitivity of the lower portion of the scale for accurate manual or automatic cutoff.

The current integrator is a conventional Philbrick analog computer circuit.[3] With the sensitivity switch in the ×1 position, 1/40,000 of the cell current is integrated. The lower limit of the instrument at this sensitivity, for a relative standard deviation of 0.1 per cent, is approximately 4 C of electricity (about 5 mg U) used in the electrolysis. With the sensitivity switch in the ×50 position, 1/800 of the cell current is integrated. The lower limit, for a relative standard deviation of 0.1 per cent, at this sensitivity is approximately 0.3 C (0.6 mg Pu). The chief obstacle to extending the sensitivity limit of the instrument seems to be drift of the integrating amplifier. While the full voltage output of the integrator is being monitored, the drift rate may be adjusted to essentially zero, but it will not remain constant over a long period of time. One week after being adjusted to zero, the drift rate increases (with the readout switch in the ×1 position) to approximately 0.3 mV/5 min. This makes it necessary to check daily, and, if necessary, re-adjust the drift rate.

A new instrument is now being designed specifically for work at the 0.3 C level and lower. It is anticipated that the new instrument will have much better drift characteristics at the high sensitivities necessary for work with small amounts of substances with high equivalent weights.

A method for the determination of plutonium with this titrator has been developed by W. D. Shults. A brief outline of his procedure is shown in Table I. The precision that he obtains with various amounts of plutonium is shown in Table II.

It can be seen by a comparison of the drift rate with the readout values in Table II that the precision can be seriously affected by the drift rate at low concentrations. This makes the new instrument now being designed, with its anticipated lower drift rate, attractive for use at lower concentrations.

TABLE II.—PERFORMANCE ON × 50 SENSITIVITY
(Integrator drift $\leqslant 0.3$ mV per 5 min.)

Pu titrated, $\sim\mu g$	Readout, $\sim mV$	Rel. std. dev., (%)
1000	500	0.1
250	120	.3
50	24	1.5

Detailed procedures for the controlled-potential coulometric determination of plutonium have been published[4,5].

Acknowledgement—Tables I and II and the information on sensitivity limits and drift rates were obtained from W. D. Shults, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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Talanta, 1960, Vol. 6, pp. 189 to 195. Pergamon Press Ltd. Printed in Northern Ireland

X-RAY FLUORESCENCE ANALYSIS OF PLUTONIUM*

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Summary—An X-ray fluorescence method, using yttrium as an internal standard, has been developed for the quantitative determination of plutonium in high-level solids, in liquids, and in sludges containing plutonium in low concentrations.

Handling procedures and sample preparation techniques as well as equipment are described. An $Al(OH)_3$-MgO matrix has been used for work with solid samples. Liquid samples were analyzed by adding the internal standard to a diluted sample of the liquid and then making the fluorescence measurements. The range of the fluorescence method is from 10 p.p.m. to 100 per cent plutonium for solid samples and from 5 to 250 g/l. for liquid samples. Standard deviations between known and observed values have been established from analysis of each type of sample.

Samples that are almost impossible to analyze by any other method can be analyzed easily and rapidly by the X-ray fluorescence method, which is applicable to plutonium in almost any form and is almost completely free from cationic and anionic interference.

INTRODUCTION

IN the analysis of plutonium, difficulties are encountered which are not usually met in the analysis of other materials. Special handling procedures must be used to contain the extremely toxic material. Vacuum glove boxes are usually used for work with dry powders and the metal, with liquids generally handled in hoods. When glove boxes are used for powder work, it is difficult to prevent contamination of the sample and the sample container.

The dissolution of many plutonium compounds is very difficult and time consuming. A method was sought that would be applicable to the quantitative determination of plutonium in the ranges from 10 p.p.m. to 1 g/g. The method had to be suitable for the determination of plutonium in solid or liquid samples, rapid and independent of the isotopic concentrations of the plutonium, free from interference by other radioactive materials that could be present in the plutonium in minute amounts and cause large interferences, and, finally, the method must yield results of reasonable accuracy.

D. S. Flikkema and R. V. Schablaske[1] had reported an X-ray fluorescence method for plutonium in solution. A fluorescence method, with strontium as an internal standard[2], had been used at Rocky Flats for the determination of uranium in liquids, sludges and solids. This method appeared to be applicable to the determination of plutonium if the qualifications already stated could be met. A suitable internal standard and matrices and handling procedures had to be found before investigative work could begin. In this paper the conditions and methods established for the quantitative determination of plutonium in low-level sludges, high-level solids and solutions are described. Figures indicating the reproducibility and accuracy are presented.

EXPERIMENTAL

Instrumentation

Norelco X-ray equipment was used in these investigations and consisted of the following items: basic X-ray spectrograph with a 3-position sample holder and

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* Work performed under U.S. Atomic Energy Commission Contract AT(29-1)-1106.

spinner, scintillation detector, LiF analyzing crystal, amplifier, Model 510 Atomic Instruments single-channel pulse-height analyzer scaling panel, molybdenum tube, 1/8-inch parallel exit collimator, and a 800:1 parallel receiving collimator (see Fig. 1).

The X-ray tube was operated at 50 kV and 40 mA, the detector high voltage at 950 V and the base line and channel width on the single-channel pulse-height analyzer at 25 V and 12 V, respectively. The equipment was operated in accordance with the operating instructions supplied by the manufacturer. The pulse-height analyzer settings were determined according to Parrish and Kohler.[3]

Matrix preparation

The matrix chosen for analysis of solid samples was a wet $Al(OH)_3$-MgO mixture. An aluminum nitrate solution was precipitated with ammonium hydroxide and the $Al(OH)_3$ was allowed to settle for several days before decanting the mother liquor. The soupy aluminum hydroxide was placed in a Waring blender and dry magnesium oxide was added until a texture and consistency resembling cold cream was obtained. The sludge was stored in plastic containers.

Internal standard

Yttrium oxide was dissolved in a minimum amount of concentrated hydrochloric acid and brought to volume with water. Three concentrations were used for the analysis of plutonium. For plutonium concentrations from 0.1 to 20 per cent, 25 g of Y_2O_3/l. was used; 1·875 g of Y_2O_3/l. was used for the 0·0005 to 0·1 per cent range; and for liquids, 5 g of Y_2O_3/l. was used as the internal standard.

Sample preparation equipment and supplies

The following is a list of equipment and supplies used for sample preparation:

Analytical balance
Spex Mixer/Mill (Fig. 2)
Steel grinding vials with steel balls 1/2 in. dia. (Fig. 3)
Plastic vials with outside caps, 1 in. × 2 in. (Fig. 4)
Plastic beads 3/8 inch in diameter (Fig. 4)
Pipe caps, 3/4-in. (EP-14 Caplugs) (Figs. 4 and 5)
Plastic curtain rings, 13/16-in. inside dia. (Figs. 4 and 5)
Type C Mylar film, 1/4-mil
Masking tape, 1/2 in. and 1 in.
Tongue depressors (Fig. 4).

PREPARATION OF STANDARDS

High-level solids

Standards for preparing calibration curves were made from plutonium dioxide. Plutonium metal was heated at 850°C to produce the oxide. The resulting oxide was ground in a steel vial with three 1/2-in. steel balls for 10 min. on the mixer/mill to insure particles of uniform size.

The oxide was weighed into 1 in. × 2 in. plastic vials which contained 0.025 g of Y_2O_3 in an HCl solution. Sufficient matrix [$Al(OH)_3$-MgO] was added to give a net weight of 11 g. Eleven grams was chosen because this allowed two sample caps to be

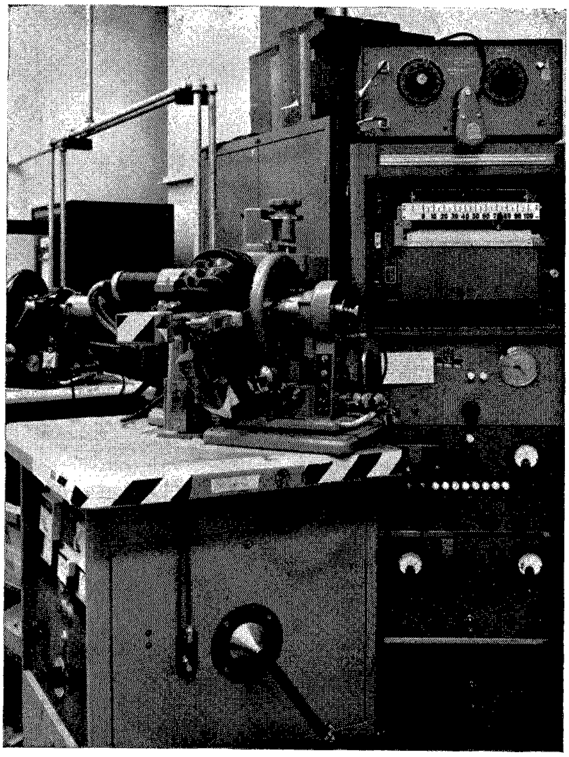

FIG. 1.—X-ray fluorescence equipment.

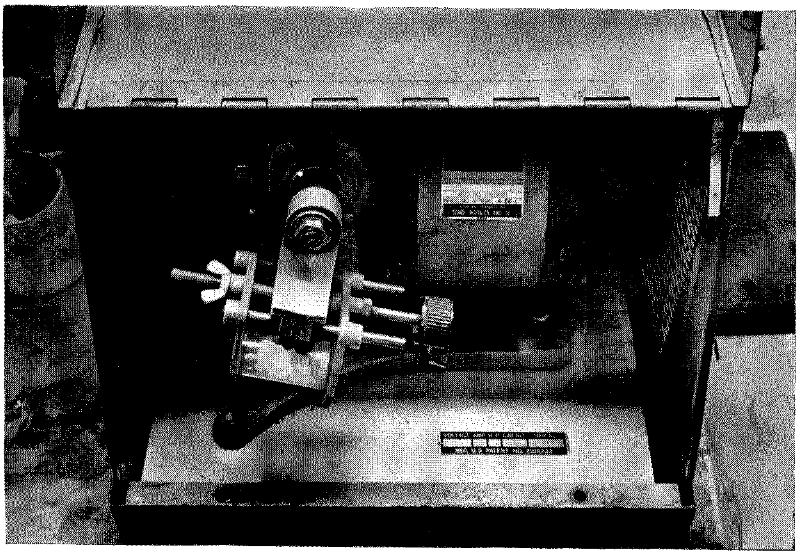

FIG. 2.—Spex Mixer/Mil.

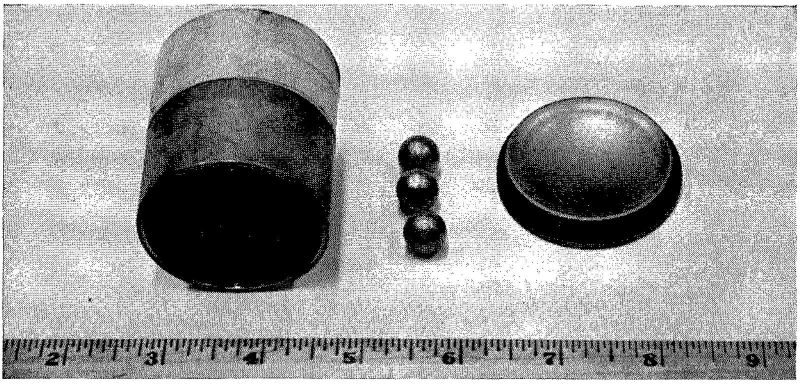

FIG. 3.—Grinding vials and balls.

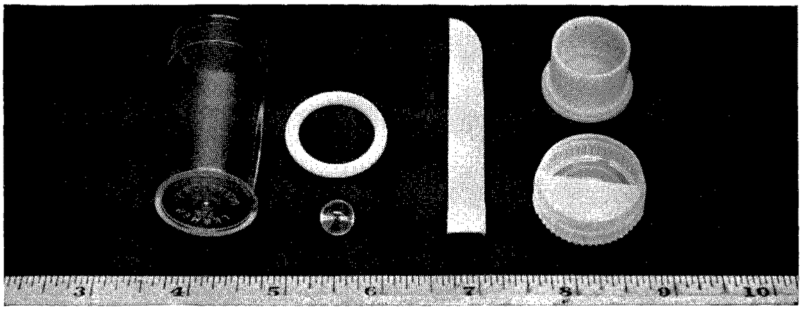

FIG. 4.—Miscellaneous sample preparation equipment.

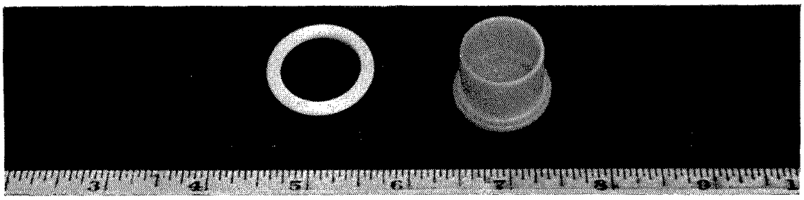

FIG. 5.—Pipe caps and rings.

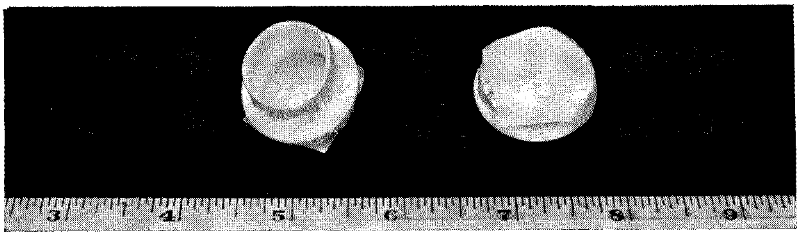

FIG. 6.—Sample loaded Caplug.

filled. A 3/8-in. plastic bead was added, the cap of the vial was taped on and the vial mixed for 10 min in the mixer/mill. All the above operations were done in a vacuum glove box. The vials were transferred to an open hood and the sample was packed into two EP-14 Caplugs with a quarter section of a tongue depressor. Two layers of ¼-mil Mylar were placed over the cap and secured with a 13/16-in. plastic curtain ring. The remaining Mylar was twisted at the back and held in place with a 1-in. square of masking tape which had the sample number on it (Fig. 6).

The cap was monitored for radioactivity and was then ready for the actual plutonium determination.

Low-level standards

A stock solution of plutonium chloride was prepared and increments of 50 λ, 100 λ, 250 λ, 500 λ, 750 λ, and 1 ml were transferred into 1 in. × 2-in. plastic vials. One ml of yttrium (0.001855 g of Y_2O_3) was added and enough matrix to give a total of 11 g. The sample was mixed and packed as described under High-Level Standards.

Liquid standards

Liquid standards were prepared by dissolving known weights of plutonium metal in a minimum amount of hydrochloric acid and bringing to volume with water. Various increments of these standards were pipetted into 10-ml volumetric flasks which contained 1 ml of Y solution (0.005 g of Y_2O_3) and brought to volume with water. A working range of concentrations was 0.1 to 40 g/l in the 10-ml flasks. The standards were poured into the Caplugs, covered with Mylar, held in place with a curtain ring, monitored and then transferred to the X-ray unit.

ACTUAL SAMPLE PREPARATION

High-level samples (0.5 % to 88 % Pu)

Generally, the samples received are wet and granular. The samples are dried and ground to a fine powder in a steel vial. Since the results must be reported on a wet basis, the moisture loss is determined. Plastic vials (1 in. × 2 in.) are prepared in a cold area as follows: the vial is tared with a 3/8-in. plastic bead, 1 ml of Y solution (0.025 g of Y_2O_3) is added and also sufficient matrix to leave room for 1 to 2 g of the sample. The vials are transferred to a glove box and enough sample is added to give a net weight of 11 g in the vial. The samples are then mixed, transferred to a hood, packed in Caplugs, and covered with Mylar as described earlier.

Low-level sludges (10 p.p.m. to 0.5 %)

Ten grams of the low-level sludge is added to 1 ml of yttrium solution (0.001875 g of Y_2O_3). The samples are mixed and packed as described above.

Liquid samples

One ml or more of the sample is pipetted into a 10-ml volumetric flask with 1 ml of yttrium solution (0.005 g of Y_2O_3) and brought to volume with water. The liquids are poured into Caplugs and covered with Mylar as described above.

Determination of plutonium

The prepared pipe caps were placed into the 3-position sample holder and the samples were rotated during the count period. A fixed count was used rather than a fixed time. The following data gives the angles used.

Yttrium $2\theta = 23.75°$ (K_α, $\lambda = 0.829$ Å)
Plutonium $2\theta = 24.90°$ (L_α, $\lambda = 0.8682$ Å)
Background $2\theta = 27.0°$

TABLE I.—PLUTONIUM OXIDE RECOVERY IN KNOWN STANDARDS

Observed (X-ray) % Pu	Calculated % Pu	Observed × Dilution Factor in % Pu
2.92	2.90	88.73
13.30	13.27	88.39
9.95	9.94	88.27
11.04	11.19	87.06
12.35	12.40	87.87
5.90	5.94	87.58
4.03	4.04	88.17
8.00	8.05	87.82
11.80	11.78	88.34
17.60	17.66	87.92
3.55	3.50	89.36
10.20	10.22	87.07
6.10	6.09	88.29
	Average =	88.14
	Theoretical value =	88.19

Standard deviation = ±0.63 per cent.

A minimum count of 12,800 was made on the yttrium and plutonium, and 1600 for background. The time for counting each element was greater than 30 sec.

The following formulas were used for calculating the final results.

(1) $\dfrac{\text{Scale factor} \times 100}{\text{Time (seconds)}} = \text{counts/sec.}$

(2) $\dfrac{\text{Cps (Pu)} - \text{Cps (Bkg)}}{\text{Cps (Y)} - \text{Cps (Bkg)}} = \text{Pu/Y ratio.}$ (Cps = counts/sec.).

(3) The Pu/Y ratio was referred to a graph for establishing the Pu concentration.

(4) Pu concentration (% or g/l.) × dilution factor = total Pu concentration in sample.

(5) Total Pu concentration (%) on dry basis × $\dfrac{\text{dry weight}}{\text{wet weight}}$ = Pu concentration on wet basis.

RESULTS AND DISCUSSION

Working curves were plotted for the high- and low-level solids and for liquids. Table I shows the results of 13 determinations of plutonium ranging from 2.90 to 13.27

per cent plutonium in the diluted form. Converting the diluted values back to the original sample, an average value of 88.14 per cent plutonium was found as compared to the true value of 88.19 per cent. The standard deviation on this set of values was ±0.63 per cent.

In Table II, results for low-level samples ranging from 10 p.p.m. to 1820 p.p.m.

TABLE II.—COMPARISON OF KNOWN VALUES AND X-RAY VALUES IN LOW-LEVEL SLUDGE

X-ray results, p.p.m. Pu	Known values, p.p.m. Pu
87	86
82	65
65	64
62	51
73	77
540	560
230	210
19	21
930	1000
980	1100
1820	1820
460	470
370	370

Standard deviation = ±9.92 per cent.

TABLE III.—COMPARISON OF X-RAY RESULTS WITH RADIOCHEMICAL METHODS ON LOW-LEVEL SLUDGE

X-ray, p.p.m. Pu	Radiochemical method, p.p.m. Pu
150	150
170	150
11	11
11	8
10	3
140	150
160	150

Standard deviation between the two methods = ±6.3 p.p.m.

are compared with the known values. The standard deviation between the observed and true value was ±9.92 per cent.

In Table III, X-ray values are compared with values obtained by complete dissolution of the sample followed by alpha radio analysis.

The comparison between the two methods shows a standard deviation of ±6.3 p.p.m.

Results are shown in Table IV for liquid samples whereby a comparison can be made between X-ray values and known values on liquid check samples. The standard deviation between the known and true values is ±1.24 per cent.

In Table V, values obtained by a spectrophotometric method and the X-ray fluorescence method on submitted samples are compared. The standard deviation between the two methods is ±0.62 g/l.

All samples were analyzed on a diluted basis in order to handle a minimum amount of plutonium and to keep the matrix as similar as possible. The particle size of solid samples has an important effect on the analysis. This can be reduced by grinding each sample for a given time. Yttrium was used as an internal standard to eliminate any absorption or enhancement from other elements present in the sample. Sample handling is not as convenient as for non-radioactive samples. All preparation equipment, i.e., mixer/mill, drying oven, muffle furnaces, and balances must be in vacuum glove boxes. The steel grinding vials are cleaned with sea sand and chunks of graphite. Little or no contamination has been experienced in samples or standards when the vials

TABLE IV.—COMPARISON OF X-RAY VALUE AND KNOWN CONCENTRATIONS OF Pu IN LIQUID SAMPLES

X-ray, g Pu/l.	Known values, g Pu/l.
7.4	7.2
9.8	9.9
10.6	10.6
14.0	14.1
20.1	19.8
23.7	24.3
26.0	26.0
40.0	39.6
44.8	44.9
49.3	49.5
82.4	81.8
87.6	86.6
98.9	98.9
153.0	152.8

Standard deviation = ±1.24 per cent.

TABLE V.—COMPARISON OF X-RAY AND SPECTROPHOTOMETRIC VALUE OF LIQUID SAMPLES

X-ray, g Pu/l.	Spectrophotometric, g Pu/l.
47.4	48
49.3	48.7
54.1	53.8
18.9	18.9
47.9	48.0
42.0	41.8
40.1	39.1
31.6	31.4
11.4	11.8
9.2	9.6

Standard deviation between the two methods = ±0.62 g/l.

are cleaned in this manner. Volumetric flasks are cleaned with dichromate cleaning solution and rinsed with water. The plastic bead used in the weighed samples serves as a pestle for mixing the sample. Tongue depressors are used as spatulas for transferring the mixed samples to the pipe caps. This saves time in cleaning a metal spatula and prevents any cross contamination.

The matrix of aluminum hydroxide and magnesium oxide was chosen because of the ease with which it can be handled and also because it does not dry as fast as regular magnesium oxide and water. Future work is planned to find different matrix materials, to simplify sample preparation, to study better methods of sample preparation for samples containing metal particles, and to study more completely the reproducibility and accuracy of the methods reported here.

The X-ray fluorescence method of analysis is rapid and accurate. In many cases, no analysis of plutonium content could be made by any other method because of poor solubility or interfering substances. This method is primarily used on samples where extreme accuracy is not needed but where a reasonably accurate method is necessary for process control.

Assembly line procedures are used for sample preparation where drying and grinding are required. Aside from sample preparation, about 10 min are required per sample for counting and making the calculation. Only a few minutes are required for preparing liquids and about 12 min for the preparation of low-level sludges.

SUMMARY AND CONCLUSIONS

It has been shown that X-ray fluorescence methods, using yttrium as an internal standard, may be extremely valuable for the determination of plutonium in low-level sludges, high-level solids and liquids. The method is almost completely free from interferences by other cations and anions. It is free from interference caused by the isotopic content of the metal. A standard deviation of ±0.63 per cent has been found for high-level oxide samples. A standard deviation of ±1.24 per cent has been found for liquid check samples. For low level sludges containing from 10 p.p.m. to 1820 p.p.m., the standard deviation was ±9.92 per cent.

Acknowledgements—The author wishes to recognize the work done by J. Ellis, R. Gaskins, and B. Scott in this study.

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THE DETERMINATION OF PLUTONIUM IN IRRADIATED URANIUM FUEL SOLUTIONS BY CONTROLLED-POTENTIAL COULOMETRY*†

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General Electric Company, Richland, Washington

Summary—Controlled potential coulometry has been applied to the determination of plutonium in solutions which contain plutonium within the range 0.05 to 50 g/l. The titrations are performed by direct electrode reactions at the controlled-potential electrode. No valence state adjustments or methods for detecting the end point of a titration are necessary. The electronic equipment and special cells necessary to prevent the spread of radioactivity are described in detail. The procedures are simple enough and the equipment dependable enough for routine application in control laboratories. The method has been applied to solutions containing approximately 20 g/l. of plutonium with a relative standard deviation of 0.05 per cent and with an accuracy of better than 0.1 per cent. The method has also been applied to the direct estimation of the plutonium content of solutions of irradiated natural uranium (dissolver solution) with a relative standard deviation of 0.5 per cent and an accuracy of at least 1.4 per cent, using samples containing between 100 and 200 μg of plutonium.

The titration curves follow the Nernst equation exactly for ions which undergo reversible electrode reactions. Therefore, if the concentration and half-wave potential of an interfering material are known, estimations can readily be made of the theoretical magnitude of the interference.

The method is remarkably free from interferences since there are few reversibly titratable ions which have standard electrode potentials near that of the plutonium^{IV} plutonium^{III} couple in an acid medium. When an ion with a standard redox potential near that of the plutonium couple is known to be present, the titration can usually be carried out by the selection of a complexing medium which increases the difference between the electrode potentials of the interfering substances and that of plutonium. Several such media have been investigated and are compared.

The high acid or salt content of the media used provides buffering action and prevents interference from variations in the acid content of the sample.

Details concerning the procedure can be obtained from document number HW-58491. A year of experience with the method has been obtained since the publication of this document and has led to a definite preference for the titration cell using the platinum working electrode. Electrode efficiencies and reaction reproducibility have not proven to be a problem as anticipated in HW-58491. The ease of cell construction and the simplicity with which remote titrations can be performed using this cell have proved to be of great advantage.

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* Work pertinent to this abstract performed at Hanford Atomic Products Operation. This paper is not reproduced in full in the Proceedings because the information contained therein is available in document number HW-58491.

† Work performed under Contract No. W-31-109-Eng-52 for the U.S. Atomic Energy Commission.

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Talanta, 1960, Vol. 6, p. 197. Pergamon Press Ltd. Printed in Northern Ireland

ANALYSIS FOR NEPTUNIUM BY CONTROLLED-POTENTIAL COULOMETRY*†

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Summary—An accurate and precise method for the determination of neptunium has been developed, based on a controlled-potential coulometric titration. The electrolysis cell contains a platinum working electrode at which the neptunium^{V}–neptunium^{VI} couple is titrated. A 1.0*N* sulfuric acid solution is used as a titration medium. The precision of the method ranges from 1 per cent relative standard deviation for 20 μg samples to 0.5 per cent relative standard deviation for samples of neptunium approximately 1 mg or larger in size. With care, as little as 2 μg of neptunium can be detected and 7 μg can be titrated with a relative standard deviation of 6 per cent. Under ordinary conditions, large excesses of plutonium, iron and uranium can be tolerated or the interference calculated. The general procedure is to first oxidize the neptunium to neptunium^{VI} with cerium^{IV}, then electrolytically reduce the neptunium^{VI} and excess cerium^{IV} to neptunium^{V} and cerium^{III} and, finally, coulometrically oxidize the neptunium^{V} to neptunium^{VI}. The integrated current in the last step is used to calculate the concentration of the neptunium.

The solutions can be analyzed for the concentrations of neptunium in different oxidation states with the coulometer, using a platinum electrode cell. The neptunium^{VI} is determined by a coulometric reduction to neptunium^{V}. The neptunium^{V} is then oxidized coulometrically; the difference between these two titrations being the concentration of the neptunium^{V}. The total neptunium concentration is determined by the method described in the preceding paragraph, and the neptunium^{IV} is then calculated from the difference between the concentrations of neptunium^{V} plus neptunium^{VI} and the total neptunium. This analysis depends upon the fact that neptunium^{IV} is not oxidized at a significant rate during the coulometric oxidation of the neptunium^{V}. All substances which undergo oxidation or reduction at the applied potentials interfere and must be removed or masked in order to carry out this determination. The accuracy and precision depend, of course, on the total neptunium concentration and the concentrations of neptunium in the various oxidation states.

A simple and rapid method to determine oxidation–reduction potentials, using the controlled-potential coulometer, is described. In this method, the same electrode system is used to measure potentials and to adjust the concentrations of the element in various valence states by coulometric titrations. Some formal oxidation potentials are given for iron, neptunium and plutonium couples.

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* AEC Reports HW-58212 and HW-59447. Work performed under contract with the Atomic Energy Commission.

† The full text of this paper is not included in the Proceedings because the information contained therein is available in documents numbered HW-58212 and HW-59447.

ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

SECTION IV. THE ANALYSIS OF FISSION-PRODUCT MIXTURES

Talanta, 1960, Vol. 6, pp. 201 to 208. Pergamon Press Ltd. Printed in Northern Ireland

QUANTITATIVE GAMMA-RAY SPECTROMETRIC ANALYSIS OF NUCLIDE MIXTURES CONSECUTIVE STANDARD SOURCES NULLIFICATION*

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Summary—Conventional methods for analysing fission product mixtures are lengthy and difficult. Gamma scintillation spectrometry shortens the analysis time and gives a visible picture of what is being counted. However, for complex spectra, the graphical representation and interpretation of data requires tedious plotting and data reduction time. In the proposed method a sample of mixed fission products is scanned by a 256 channel gamma-ray spectrometer. Instrumental analysis of this spectrum is made, using complement nuclide subtraction technique. Specific activities are determined for each nuclide using standard sources. The time required to make an analysis where four isotopes are present would be about 30 min. Statistical evaluation of the method has been made for Ce^{144}, Ru^{106}, Cs^{137} and Nb^{95} in the experimental work. Since standard sources are required for the analysis, this method is limited to reasonably long half-lived fission products. A similar method for other nuclides was published in *Analytical Chemistry* at the time this paper was being written.

INTRODUCTION

CONVENTIONAL radiochemical separation methods[1,2,10,11] for analyzing fission product mixtures are lengthy and difficult. Gamma scintillation spectrometry both shortens analysis time and provides visible identification of individual nuclides from their characteristic spectra. However, to obtain routine quantitative results of methods from decomposition of spectra into components and the interpretation of data as described by Heath[4] requires tedious plotting and considerable data reduction time. Automatic subtraction of Compton events employing two crystals[6,7,8,9] has been used for removing unwanted pulses in photopeaks by a different method of analysis. Gamma-ray abundance from the photopeak area has been determined using digital information to give direct quantitative evaluations.[3,4]

A method will be described in this paper which utilizes the magnetic memory of a time conversion pulse analyser to decompose a complex gamma spectrum with good precision. This represents a considerable saving in time. A sample of mixed fission products is scanned by a 256 channel gamma-ray spectrometer. Addresses in the memory contain counts ranging in value from 0 to 65,535. These values are complemented giving new numbers of 65,535 — the original. From standard sources representing particular nuclides, a number of counts are fed to the proper address which is indicated when the index photopeak disappears and that address count drops to zero. Compton pulses associated with each nuclide are automatically subtracted along with the photopeak. The time required to remove each isotope by the process gives a direct and unbiased (corrected for high energy Compton reactions) quantitative measure of isotope abundance. Effects of geometry and detector configuration are removed since the standard and unknown are measured under identical conditions.

At the time of writing this report, a method similar to the proposed analyses was published[5] in which different media and isotopes were used.

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* Work done under Contract AT(10-1)-205 to the U.S. Atomic Energy Commission.

APPARATUS

An Argonne Type 256 Channel Analyzer (Fig. 1) with an automatic dead-time correction circuit was used. Experimental samples were timed into the analyzer with the instrument's automatic dead-timer. Removal times were measured with a precision time clock, and dead time corrections were applied for each standard according to its specific activity. A precision high voltage supply with a specified regulation of 0.0006 per cent change in output per 1 per cent change in input, with stability of better than 0.01 per cent per hour, was employed. A 3 × 3-in. NaI (Tl) crystal was used as a gamma detector (Fig. 2).

This detector unit is housed in a 2 × 2 × 2-ft. lead gamma-shield lined with cadmium and copper (Fig. 3).

EXPERIMENTAL

Standardization of solutions

Tracer solutions were prepared to contain approximately 1×10^6 photopeak gamma rays per minute. Mounts of the tracers were calibrated by gamma-ray spectrometry. Three independent calibrations were made on each mount. Gamma results were verified by 4π beta counting.

Method

Prepare mounts of the samples in the same manner as was used for standards. Scan at a fixed distance for a known time.

Assume that a visual inspection of the scope spectrum indicates the presence of four nuclides *A*, *B*, *C*, and *D*, with gamma-ray energies increasing from *A* to *D*. Complement the information in the memory. Replace the sample with a standard mount of nuclide *D* and determine the time required to remove the photopeak. The equivalence point is indicated when all the pulses from a nuclide have been removed. When the gaussian disappears to the base line the equivalence point has been reached. This can be seen with good accuracy after a little experience has been gained by the operator. Gain shifts cause some difficulty but compensation can be made and good data obtained.[5]

Remove the photopeaks from nuclides *C*, *B*, and *A* by the same process. A careful inspection of the spectrum will reveal any nuclides which have been masked by the abundant emitters. Quantitative removal of these peaks can now be made. A ratio of the removal time by the standard to the accumulate time of the unknown multiplied by the calibration of the standard gives the emission rate for any given nuclide. As an example, a fission product sample is scanned for 2 minutes and found to have a photopeak at 0.51 MeV and another 0.66 MeV peak broadened on the low energy side. Cesium and ruthenium are the nuclides which are present. The data are complemented. When the sample is replaced with a cesium standard whose disintegration rate was found to be 1×10^6 d/m, it required exactly 1 minute to remove the cesium peak. Now the 1×10^5 d/m ruthenium standard removes all the remaining peaks in 10 minutes. Therefore, the cesium disintegration rate is

$$\frac{\text{removal time}}{\text{accumulate time}} \times \text{d/m of Standard or } \frac{(1)}{(2)}\,(1 \times 10^6) = 5 \times 10^5 \text{ d/m},$$

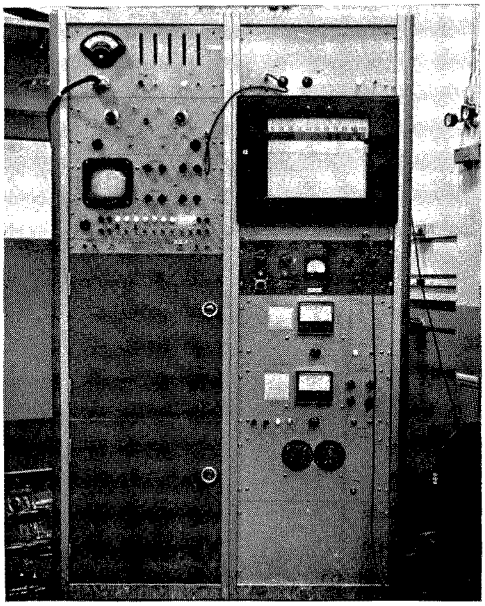

FIG. 1.—Gamma scintillation spectrometer.

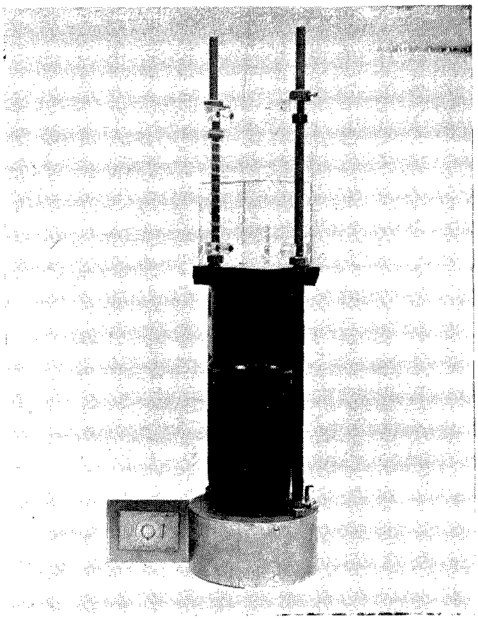

FIG. 2.—Detector, sample holder and sample.

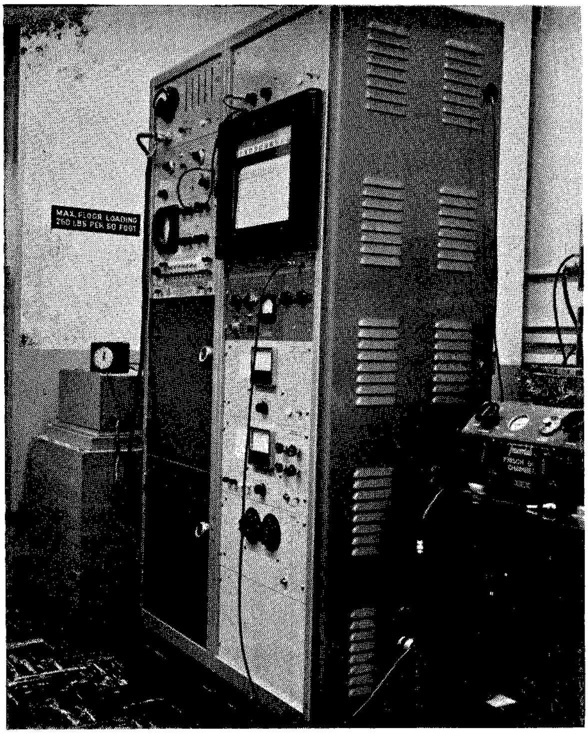

FIG. 3.—Gamma shield.

while the ruthenium is

$$\frac{(10)}{(2)}(1 \times 10^5) \text{ or } 5 \times 10^5 \text{ d/m.}$$

Reliability

A series of sixteen synthetic samples was prepared from standard tracer solutions of Ce^{144}, Ru^{106}, Cs^{137} and Nb^{96}. Each nuclide was varied between approximately 2 and 70 per cent of the gross activity. The total activity ranged from 9×10^5 to 4×10^6 gamma-rays per minute on the mount. Concentrations of all nuclides were known. Mounts were scanned for 124 sec at a distance of 10 cm from a 3 × 3-in. NaI (Tl) crystal, (Fig. 4). The data were then complemented (Fig. 5). A timed removal of the Nb^{95} peak was made (Fig. 6). The Cs^{137}, Ru^{106}, and Ce^{144} peaks were removed in order (Figs. 7, 8, 9). The results are summarized in Table I.

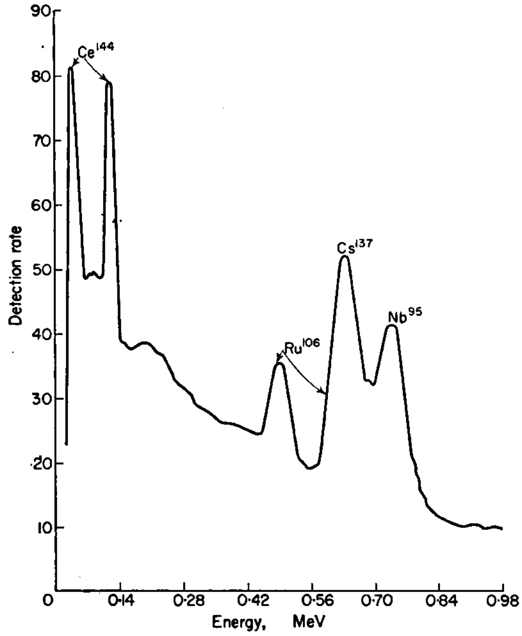

Fig. 4.—Initial scan.

In this group of 16 samples a statistical analysis of the data was made to determine the effects of each component on relative deviation from known content. It was found that there was no appreciable bias on all nuclides. The uncertainty appeared to increase with energy. Since the photopeak area decreases with energy, for a given number of disintegrations, it would appear that the error is associated with the number of events occurring in the photopeak.

A second group of analyses was made increasing the specific activity of Cs^{137} and Nb^{95}. The uncertainty associated with each nuclide agreed very well with the findings of the first experiment (Table II). The peak area was apparently not the reason for the error.

Eight more samples were prepared and analyzed (Table III). In the previous two analyses the emitters were removed according to their abundance starting with the

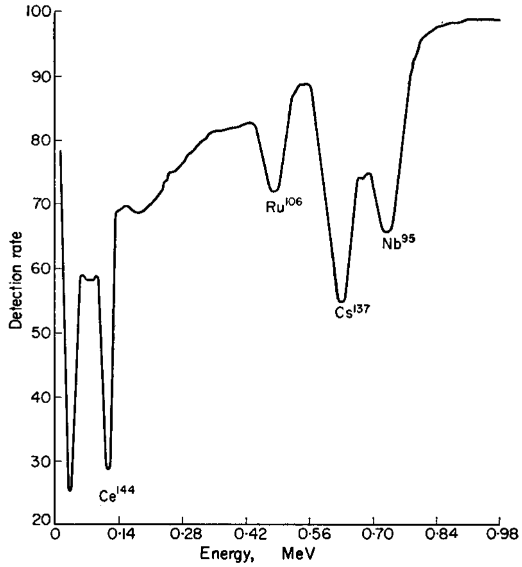

FIG. 5.—Completed spectrum.

TABLE I

Sample No.	Ce		Ru		Cs		Nb		Total γ/m/Sample
	Spiked	Recovered	Spiked	Recovered	Spiked	Recovered	Spiked	Recovered	
1	2.64×10^5	2.70×10^5	1.83×10^6	1.81×10^6	6.00×10^4	5.96×10^4	5.94×10^4	5.70×10^4	2.21×10^6
(%)	11.9*	+2.3**	82.8	−1.1	2.71	−0.7	2.69	−4.0	
2	2.64×10^5	2.70×10^5	3.65×10^5	3.72×10^5	2.40×10^5	2.37×10^5	2.38×10^5	2.50×10^5	1.11×10^6
(%)	24	+2.3	33	−1.9	22	−1.2	21	+5.0	
3	2.64×10^5	2.61×10^5	9.12×10^4	9.60×10^4	1.70×10^6	1.21×10^6	0	1.42×10^4	1.56×10^6
(%)	17	−1.1	6	+5.3	77	+0.8	0	<1% of Gro.	
4	2.64×10^5	2.62×10^5	7.30×10^5	7.03×10^5	4.80×10^5	5.44×10^5	1.67×10^6	1.57×10^6	3.14×10^6
(%)	8	−0.8	23	−3.7	15	+13.3	53	−6.0	
5	5.28×10^5	5.01×10^5	1.83×10^6	1.80×10^6	1.20×10^6	1.19×10^6	4.76×10^5	4.38×10^5	4.03×10^6
(%)	13	−5.1	45	−1.7	30	−0.8	12	−8.0	
6	5.28×10^5	5.19×10^5	3.65×10^5	3.50×10^5	4.80×10^5	5.50×10^5	1.19×10^6	1.17×10^6	2.57×10^6
(%)	20	−1.7	14	−4.0	23	+14.5	46	−1.7	
7	5.28×10^5	5.42×10^5	9.12×10^4	9.63×10^5	6.00×10^4	4.93×10^4	2.38×10^5	2.24×10^5	0.917×10^6
(%)	58	+2.65	10	+5.6	7	−18	26	−5.9	
8	5.28×10^5	5.59×10^5	7.30×10^5	7.25×10^5	2.40×10^5	2.31×10^5	5.94×10^4	4.86×10^4	1.56×10^6
(%)	34	+5.9	47	−0.7	15	−2.9	4	−1.8	
9	6.60×10^4	7.00×10^4	1.83×10^6	1.80×10^6	4.80×10^5	4.63×10^5	2.38×10^5	1.92×10^5	2.61×10^6
(%)	2.5	+6.0	70	−1.6	18.4	−3.5	9.1	−19	
10	6.60×10^4	7.06×10^4	3.65×10^5	3.54×10^5	1.20×10^6	1.11×10^6	5.94×10^4	5.75×10^4	1.69×10^6
(%)	4	+7.0	22	−2.5	71	−7.5	3	−3.2	
11	6.60×10^4	7.19×10^4	1.82×10^5	2.07×10^5	2.40×10^5	2.44×10^5	1.19×10^6	1.14×10^6	1.59×10^6
(%)	4	+8.95	6	+13.7	15	+1.6	75	−3.3	
12	6.60×10^4	7.14×10^4	7.30×10^5	7.35×10^5	6.00×10^4	5.63×10^4	4.76×10^5	4.67×10^5	1.33×10^6
(%)	5	+8.2	55	+0.7	4.5	+6.2	36	−1.9	
13	1.32×10^6	1.27×10^6	1.83×10^6	1.85×10^6	2.40×10^5	2.14×10^5	4.76×10^5	4.52×10^5	3.87×10^6
(%)	34	−3.8	47	+1.1	6	−10.8	12	−5.0	
14	1.32×10^6	1.34×10^6	3.65×10^5	3.66×10^5	6.00×10^4	5.60×10^4	1.19×10^6	1.18×10^6	2.94×10^6
(%)	45	+1.5	12	0.27	7	−6.7	40	0·84	
15	1.32×10^6	1.30×10^6	9.12×10^4	8.36×10^4	4.80×10^5	5.13×10^5	5.94×10^4	4.80×10^4	1.95×10^6
(%)	68	−1.5	5	−9.0	25	+11.5	3.0	−19.2	
16	1.32×10^6	1.35×10^6	7.30×10^5	7.09×10^5	1.20×10^6	1.15×10^5	2.38×10^5	1.96×10^5	3.49×10^6
(%)	38	+2.3	21	−2.9	34	−4.2	7	−17.6	

* Per cent spiked—fraction of the gross sample activity.

**Per cent recovered—per cent deviation from the actual emission rate.

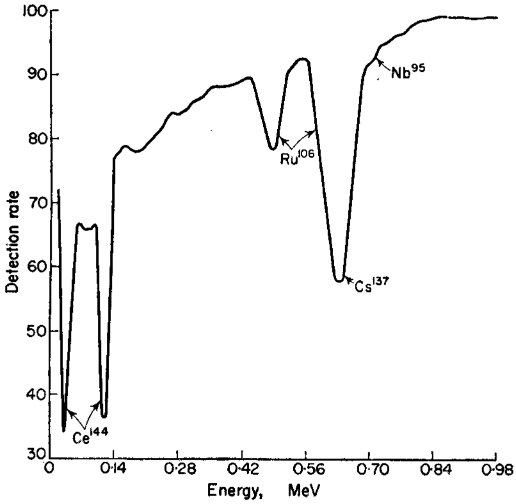

FIG. 6.—Nb^{95} removed.

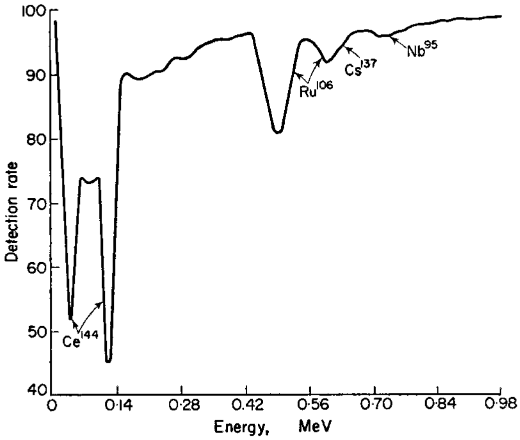

FIG. 7.—Nb^{95}, Cs^{137} removed.

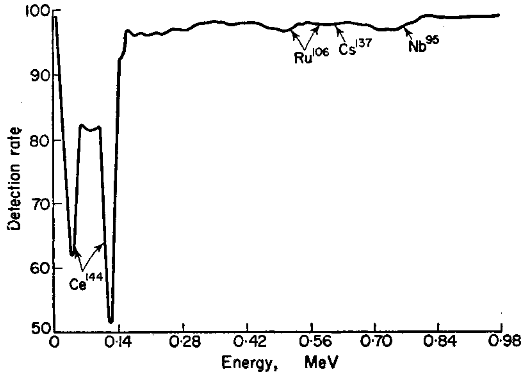

FIG. 8.—Nb^{95}, Cs^{137}, Ru^{106} removed.

greatest. No attempt was made to correct over or under removals. Careful inspection of the first sample after analysis indicated the Cs^{137} and Nb^{95} had been over-removed. What appears to be the equivalence point in the initial subtraction evidently is biased by other nuclide contributions. After the removal of greater than 90 per cent of the activity (Fig. 9), a final correction for under-removals or over-removal was made (Fig. 10). These corrections were considered when making the final calculation of this nuclide. This set of data gave the following precision expressed as 95 per cent confidence limits of each component.

TABLE II

Sample No.	Ce		Ru		Cs		Nb		Total γ/m/Sample
	Spiked	Recovered	Spiked	Recovered	Spiked	Recovered	Spiked	Recovered	
1	6.93×10^5	6.73×10^5	9.85×10^5	9.83×10^5	3.19×10^6	3.20×10^6	6.90×10^4	7.66×10^4	4.94×10^6
(%)	14.0	−2.9	19.9	−0.2	64.6	+0.3	1.5	+11.0	
2	3.46×10^5	3.58×10^5	3.94×10^5	3.82×10^5	1.60×10^5	1.76×10^6	1.38×10^6	1.41×10^6	2.28×10^6
(%)	15.1	+0.35	17.2	−3.0	7.2	+10.0	60.5	+2.2	
3	8.65×10^4	8.54×10^4	1.97×10^5	2.03×10^5	1.28×10^6	1.27×10^6	2.76×10^5	2.67×10^5	1.85×10^6
(%)	4.8	−1.3	10.8	+3.0	69.2	−0.8	14.9	−3.3	
4	1.73×10^6	1.72×10^6	8.65×10^4	8.91×10^4	6.39×10^5	6.21×10^5	5.52×10^5	5.31×10^5	3.01×10^6
(%)	57.5	−0.6	2.9	+3.0	21.0	−2.8	18.3	−3.8	

Per cent spiked—fraction of the gross sample activity.
Per cent recovered—per cent deviation from the actual emission rate.

TABLE III

Sample No.	Ce		Ru		Cs		Zr	
	Spiked	Recovered	Spiked	Recovered	Spiked	Recovered	Spiked	Recovered
1	7.6×10^4	7.54×10^4	1.83×10^5	1.8×10^5	1.18×10^6	1.19×10^6	2.43×10^6	2.41×10^6
(%)	1.9	−1.0	4.7	−1.0	30.5	+1.0	62.8	−1.0
2	3.04×10^5	2.89×10^5	3.66×10^5	3.53×10^5	2.96×10^6	3.04×10^6	1.22×10^5	1.40×10^5
(%)	8.1	−4.9	9.7	−3.6	78.9	+2.7	3.3	+14.7*
3	6.08×10^5	6.25×10^5	9.15×10^5	9.06×10^5	1.48×10^5	1.50×10^5	4.86×10^5	4.88×10^5
(%)	28.2	+2.9	42.3	−1.0	6.9	+1.4	22.6	+0.4
4	1.52×10^6	1.54×10^6	4.58×10^4	4.69×10^4	5.92×10^5	6.40×10^5	9.72×10^5	9.14×10^5
(%)	48.6	+1.3	1.5	+2.4	18.9	+8.3	31.1	−6.0
5	7.60×10^4	8.31×10^4	9.15×10^5	9.19×10^5	1.18×10^6	1.16×10^5	4.86×10^5	4.84×10^5
(%)	2.9	+9.3	34.4	+0.4	44.4	−1.7	18.3	−0.4
6	3.04×10^5	2.76×10^5	3.66×10^5	3.55×10^5	1.48×10^5	1.61×10^5	2.43×10^6	2.53×10^6
(%)	9.3	−9.2	11.3	−3.0	4.6	+8.8	74.8	+4.1
7	6.08×10^5	5.90×10^5	4.58×10^4	4.43×10^4	2.96×10^6	2.98×10^6	1.22×10^5	1.22×10^5
(%)	16.3	−3.0	1.2	−3.2	79.1	+0.6	3.3	0.0
8	1.52×10^6	1.51×10^6	3.66×10^5	3.60×10^5	5.92×10^5	6.03×10^5	9.72×10^5	9.62×10^5
(%)	44.1	−0.7	10.6	−1.6	17.2	+1.9	28.2	−1.0

* Rejected as an outlier by an objective test.
Per cent spiked—fraction of the gross sample activity.
Per cent recovered—per cent deviation from the actual emission rate.

Nuclide	*Precision*
Cerium	±13 per cent
Ruthenium	±4.8 per cent
Cesium	±8.8 per cent
Niobium	±7.3 per cent

Time of analysis

To perform one analysis using chemical separations, with a mixture of four nuclides, requires approximately 8 hours. The time to analyze this same sample by the suggested method is approximately 20 minutes.

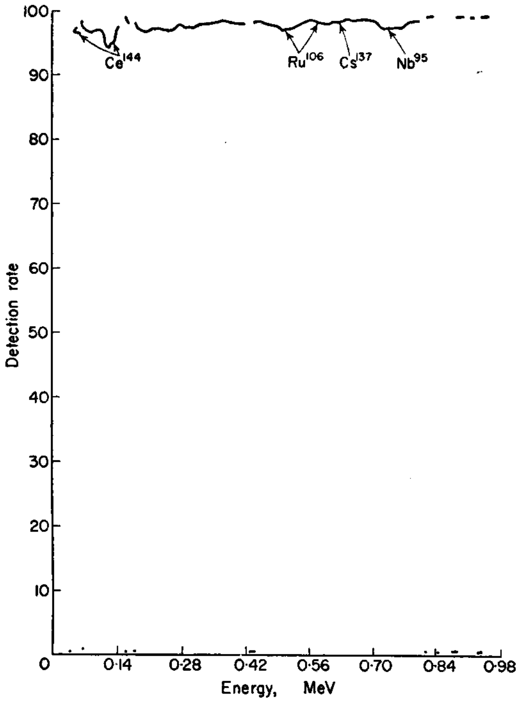

FIG. 9.—>90 per cent nullification.

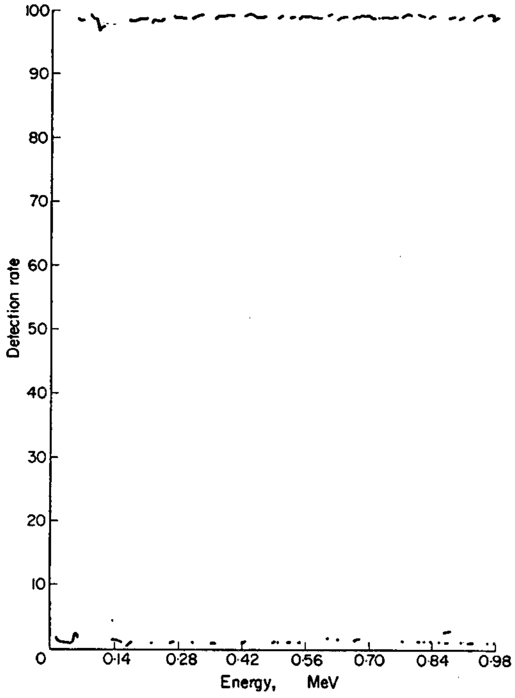

FIG. 10.—Complete nullification.

Anticipated adaptations in method

The major difficulty in this method is keeping a stock of standard nuclides on hand, especially when short half-lives are involved. Equipment has been ordered which should provide a solution to this difficulty. It is anticipated that the typical spectrum of any nuclide can be recorded on a continuous belt magnetic tape. This tape will then represent an endless source of gamma-ray pulses which, when fed back into the analyzer, will be identically equivalent to the spectrum of the original recorded nuclide. By controlling the speed and time of play-back, a quantitative number of events can be introduced, making this recording equivalent to a standardized source of this nuclide, which is now free from half-life deterioration. Any nuclide which has a half-life sufficiently long to be analyzed can be recorded and kept as a reference source. Initial plans are to have from 6 to 8 nuclides recorded on one belt. Delivery is to be made in January 1960 of this magnetic read-out–read-in equipment.

Acknowledgements—The author wishes to express gratitude to Dr. F. H. Tingey for his assistance in the statistical analysis of data, and to Mr. R. C. Shank, Director of the Analytical Section, for permitting and lending encouragement to this study.

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Talanta, 1960, Vol. 6, pp. 209 to 214. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROCHEMICAL ANALYSIS OF 'FISSIUM' FOR CERIUM AND LANTHANUM*

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Summary—'Fissium' is a synthetic spent Pu-rich reactor fuel which has a nominal weight per cent composition of 2.5 Fe, 0.7 Ce, 1.3 La, 0.7 Mo, 1.3 Ru, and 0.8 Zr. It is used as a stand-in for irradiated fuel in the study of pyrometallurgical methods of treatment for the removal of fission products. To evaluate the Ce and La contents of the fuel alloy as well as the by-products of this treatment, a spectrochemical method was developed which has a coefficient of variation of 6 per cent and comparable accuracy when amounts ranging from 40 to 200 μg are determined.

The recommended procedure involves the following steps: dissolution of the solid sample in HCl, HNO_3, or $HClO_4$; oxidation of Pu to the hexavalent state with $HClO_4$; separation of Ce and La from Pu and other elements by precipitating them as the fluorides along with Eu which is added as a coprecipitant; conversion to an HCl medium; spectrographic analysis of the sample and a set of standards, utilizing spark excitation with copper electrodes; photometry of suitable spectral lines, including those of the internal standard, Eu, on a calibrated emulsion to evaluate the concentrations by conventional means. After dissolution of the sample, the succeeding steps can be readily completed for six samples in duplicate by the expenditure of 8 man-hours of work. The least practical amount of element to process is 10 μg.

A factorial experiment involving Ce, La, Nd, Pu and other fissium element concentrations indicated that bias existed for Ce and La determinations at the 20-μg level of each, but not at the 50-μg and higher levels. No significant difference is observed when the relative proportions of Ce and La are varied tenfold in the absence of Nd. Erratic and incomplete recovery of Ce is noted if the concentration of $HClO_4$ is less than $1N$ during the F^- precipitation; $HClO_4$ in concentrations up to $3N$ gives satisfactory results. Processing of standards, both with and without the fission elements, by the recommended procedure yields data which are not significantly different spectrographically from those observed for unprocessed aliquants.

INTRODUCTION

IN conjunction with the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE), a development program was set up to study pyrometallurgical methods for purifying spent plutonium fuel. As a stand-in for irradiated fuel, a synthetic spent alloy named 'fissium' was selected. On the basis of 10 per cent fuel burnup, nominal composition of this alloy was about one per cent each of cerium, lanthanum, molybdenum, ruthenium, and zirconium along with $2\frac{1}{2}$ per cent of iron and the remainder of plutonium. The iron was present to represent a component of the raw fuel. To evaluate the effectiveness of the studies, considerable analytical chemistry was required to make rather complete analyses of the treated material and associated by-products for at least six elements in addition to plutonium.

The determination of lanthanum was undertaken by emission spectrographic methods. The evaluation of cerium was investigated mainly by spectrophotometry until later and was successfully determined by a method which will be reported in another paper presented at this conference.[1]

'Fissium,' in the early testing, contained sufficient lanthanum to permit the direct application of spectrographic methods for its determination. No chemical processing,

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* Work performed under contract with the U.S. Atomic Energy Commission.

other than dissolution of sample or removal of substances likely to attack copper electrodes, was needed. Usually, plutonium is to be avoided in the electrode sample; in this instance, it served as a useful internal standard. The amount placed on the electrode was not critical; about 50 μg was a convenient amount. Excitation by a copper spark technique provided the exposure needed to determine the lanthanum-to-plutonium weight ratio. The concentration of plutonium was required to calculate the lanthanum concentration and was usually determined by a radiometric method. The rapid spectrographic method just described showed fair precision with a coefficient of variation of about 10 per cent, but because its limit of detection was 0.1 per cent, it was not applicable to materials obtained in later treatments.

Meanwhile, a spectrophotometric method for the determination of cerium was developed which utilized fluoride precipitation to remove cerium from 'fissium' after oxidation of the plutonium to the hexavalent state. Lanthanum was added to serve as a co-precipitant. Similar processing was considered as a means of removing lanthanum and other rare earth elements from 'fissium' prior to their determination by spectrographic methods. Europium was selected as the co-precipitant, mainly because it was not likely to be included in 'fissium.' The method developed primarily for the reliable determination of lanthanum and secondarily for cerium, is presented below.

OUTLINE OF METHOD

Usually, sufficient solid sample is dissolved in a hydrochloric–perchloric acid mixture to provide aliquant portions for all the analyses required. To an aliquant containing between 40 and 100 μg of either lanthanum or cerium, 1 mg of europium is added to provide a carrier precipitate and to serve as an internal standard for the spectrography. The plutonium present is oxidized to plutonium^{VI} by strong heating in the presence of perchloric acid. Cerium, lanthanum, and europium are precipitated as fluorides by addition of hydrofluoric acid. The precipitate is dissolved in perchloric acid and the solution is heated to dryness to remove excess acid. After the residue is dissolved in hydrochloric acid, aliquots are dried on the ends of copper electrodes, and are then excited by a spark discharge. Spectra of the sample and accompanying standards are photographed on a calibrated plate. Selected spectral lines of the elements sought and the internal standard are photometered and the measurements are converted to concentrations by means of the usual calibrations.

EQUIPMENT AND OPERATING CONDITIONS

In Table I are shown the pertinent spectrographic equipment and the operating conditions found to be satisfactory. The usual list of more or less conventional parameters is included.

The operating conditions were first established as being satisfactory by measuring the reproducibility of exposures made of three standards containing both lanthanum and cerium. They contained 1 mg per ml of europium and were used subsequently for testing of the chemical processing. On each of 8 plates two samples of each standard were exposed and measured to obtain intensity ratios. The data shown in Table II indicated adequate precision for the operations used.

SEPARATION OF LANTHANUM AND CERIUM

The processing required for separation of lanthanum and cerium from 'fissium' was developed by application of the method outlined to standard solution samples containing at first only lanthanum and europium. The contents of the test samples were progressively altered by addition of iron, other elements, and plutonium to approach the composition of 'fissium' after lanthanum had been sucessfully determined following each change in composition. Fairly precise results with good recoveries were obtained for additions up to as much as twice the nominal concentration of plutonium. This method for the determination of lanthanum appeared promising; the prospect of including cerium seemed favorable.

TABLE I.—EQUIPMENT AND OPERATING CONDITIONS

Spectrograph	Jarrell-Ash 3.4-m Wadsworth 15,000 grooves/in. grating
Sample	50 μl. divided between two electrodes
Electrodes	Copper, 1/4-in. dia., with carefully-machined end
Excitation	4-amp R.F., 600 μH, 7.5 milli μF, residual resistance, 8 discharges per half cycle, 2.5-mm analytical gap
Exposure time	30 sec
Slit width	15 microns
Emulsion	Kodak 103-0
Wavelengths	3800 to 4500 Å, second order
Emulsion calibration	Iron line-group method, 4200 to 4350 Å
Analytical lines	La 4322.5 and 4333.7; Ce 4186.6; Eu 4237.5
Photometer	Jarrell-Ash recording microphotometer

TABLE II.—PRECISION DATA OBSERVED WITH UNPROCESSED STANDARDS

Concentration, *μg/ml*	Coefficient of variation, % La	Ce
20	7.0	5.3
70	2.6	2.5
200	3.3	4.0

Two exposures of each concentration were made on each of eight plates.

With only lanthanum, cerium and europium in the test samples, satisfactory recovery of both elements was noted. This was not the case when more than a few mg of plutonium were present. Cerium recovery was significantly less than 100 per cent; the degree of recovery was inversely proportional to the plutonium concentration. Yet the recovery of lanthanum was as complete as observed in prior experiments.

The effect of plutonium was counteracted by increasing the perchloric acid concentration from a few tenths of normal to greater than 1*N* prior to fluoride precipitation. Further studies showed that cerium could be determined quantitatively in the presence of as much as 100 mg of plutonium and with the perchloric acid concentration ranging from 1 to 3*N*.

Inter-element effect among the rare-earth elements during spark excitation was tested by a statistical experiment made on samples containing lanthanum and cerium at three concentration levels, and neodymium at two concentration levels, along with a fixed amount of europium. Controls containing either lanthanum or cerium were exposed on each plate. Table III summarizes the data in terms of recovery and precision. At the 20-μg level, the recovery is greater than at the other levels and is considered to be significantly biased.

Another part of the statistical experiment just mentioned involved five factors. In addition to the three rare-earth elements, plutonium, and the other 'fissium' elements as a unit group were included for study. Seventy-two test solutions were treated by the procedure to determine both lanthanum and cerium by means of control standards exposed on each plate. The results given in Table IV show excellent recovery for both elements at the 70- and 200-μg levels but a significant bias is indicated at the 20-μg level. The bias found for lanthanum was unexpected because standards containing equal amounts of lanthanum, cerium and neodymium at the levels discussed above have been processed many times with and without plutonium to yield good recovery of lanthanum. Cerium had been observed to give incomplete recovery or a negative bias when the plutonium content was greater than 100 mg. A breakdown of the statistics for the inter-element experiment showed that effects significant at the 95 per cent confidence level were either directly related to neodymium or with interaction of neodymium with lanthanum and with cerium. The possibility that neodymium might be added to 'fissium' was the reason for including it in the experiment. Since the addition of neodymium did not materialize, it was omitted from the lanthanum-cerium standards and its effects removed.

TABLE III.—FACTORIAL EXPERIMENT INVOLVING LANTHANUM, CERIUM AND NEODYMIUM*

Element	Taken, μg	Found, μg	Recovery, %	Coefficient of variation, %
La	20	21.9	109.5	8.1
	70	72.0	103.0	5.5
	200	203.4	101.7	3.1
Ce	20	21.5	107.5	7.7
	70	73.1	104.4	6.4
	200	203.0	101.5	5.7

* Nd was present in amounts of 20 and 200 μg for each amount of La and Ce taken.

TABLE IV.—FACTORIAL EXPERIMENT INVOLVING LANTHANUM, CERIUM, NEODYMIUM, PLUTONIUM AND OTHER 'FISSIUM' ELEMENTS*

Element	Taken, μg	Found, μg†	Recovery, %	Coefficient of variation, %
La	20	23.6	118.0	8.6
	70	70.7	101.0	4.7
	200	198.3	99.2	3.4
Ce	20	21.5	107.5	7.4
	70	69.3	99.0	7.8
	200	201.3	100.7	7.5

* Amounts of elements: Nd, 20 and 200 μg; Fe, 0 and 2.5 mg; Pu, 0 and 100 mg; Mo, Ru and Zr, 0 and 1 mg each.

† Each result represents the average of 24 samples, exposed in duplicate.

Since bias was not observed at the 70-μg level, and subsequently not at a 50-μg test, the practice followed in analysis has been to take an amount of sample which will contain 40 to 100 μg of the element of interest. Better precision is also obtained.

The effect of plutonium at low concentration was shown by adding 500 mg of plutonium to standards containing 7.2 μg each of lanthanum and cerium. Analysis of 12 portions showed an average recovery of 6.6 μg of lanthanum and no indication of cerium.

TABLE V.—ANALYSIS OF SYNTHETIC 'FISSIUM'
(Concentrations are expressed as μg/ml)

Sample	La taken, μg	La found (a) Spect., μg	Ce taken, μg	Ce found (a) Spect., μg	Ce found (b) Color., μg
59-8(c)	100	96.0	100	101.5	95.2
59-0(c)	40	39.4	20	21.4	18.5
59-10(c)	20	19.4	40	42.4	37.4
59-11(d)	10	9.9	10	10.4	9.3

(a) Each value represents the average of four processed aliquots, each of which was analyzed spectrographically in duplicate.
(b) Each value represents the average results for six processed aliquots.
(c) Plutonium concentration is 10 mg/ml.
(d) Plutonium concentration is 5 mg/ml.

TABLE VI.—ANALYSES OF 'FISSIUM': SPECTROGRAPHIC VS. SPECTROPHOTOMETRIC

	La, %	Ce, %			La. g/l	Ce, g/l	
Sample	Spect.	Spect.	Color.	Sample	Spect.	Spect.	Color.
48-1	2.10	0.82	0.77	57-B	0.45	0.46	0.45
48-2	1.64	0.84	0.74	90-1	0.64	0.23	0.223
48-3	1.58	0.76	0.72	90-2	0.16	0.11	0.100
48-4	1.74	0.79	0.73	13-2	0.22	0.11	0.104
78-1	0.30	0.15	0.15	14-3	0.14	0.080	0.068
78-2	0.30	0.12	0.15	14-4	0.025	0.005	0.005
78-3	0.29	0.14	0.16	19-4	0.60	0.26	0.22
78-4	0.32	0.12	0.15	19-5	0.68	0.32	0.33
78-5	0.31	0.14	0.17	19-6	0.15	0.095	0.088

The reason for low cerium recovery in the presence of considerable plutonium is not understood. Only indirectly has it been investigated, by trying other oxidants and acid media. No fruitful results have been observed.

ANALYSIS OF SAMPLE

The present practice allows the taking of six samples, each in duplicate, from the 'as dissolved' step to the reporting of results in about eight man-hours. The estimated precision is a ±6-per cent coefficient of variation for the average of duplicate portions. For reliable cerium determination, the amount of plutonium present during processing should not exceed 100 mg; for lanthanum, much more plutonium can be tolerated. Sensitivity of lanthanum is 5 μg with up to 100 mg of plutonium present. Cerium sensitivity is 6 μg in the absence of plutonium and 10 μg in the presence of 100 mg of plutonium.

In Table V are shown spectrographic and spectrophotometric analyses of four synthetic 'fissiums.' Except for the top sample, the spectrographic results are as high as the spectrophotometric are low.

In Table VI results are tabulated from some typical 'fissium' samples. Those expressed on a percentage basis are metal samples; those expressed in grams per liter represent solution samples of by-products.

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A QUANTITATIVE DETERMINATION OF SEVERAL SHORT-LIVED IODINE, BARIUM AND STRONTIUM FISSION PRODUCTS IN GAS-COOLED REACTOR EFFLUENTS

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Summary—Gamma scintillation spectrometry is used as a basis for the quantitative determination of absolute disintegration rate values for I^{131}, I^{132}, I^{133}, I^{134}, I^{135}, Ba^{139}, Ba^{140}, Sr^{91} and Sr^{92} collected from reactor effluent air on activated coconut charcoal. After chemical separations for the various elements have been made, the complex γ-spectra resulting are treated mathematically, resulting in the solution of simultaneous linear equations to yield d/m values for the specific isotope. Corrections are made for any absorber between the source and NaI(Tl) crystal, for the total absolute detection efficiency for the counting geometry used, for the peak to total ratios for the particular photopeak, for the decay scheme, and for any internal conversion, thus obviating the need for standard plates of the isotope in question. The method is applicable to γ-emitters in general, providing values for corrections to be applied are available.

INTRODUCTION

The operation of a nuclear reactor requires continuous monitoring of the coolant for fission products in order to maintain safe working conditions for operating personnel, and to control direct radiation and radiation contamination to the surrounding area. Often a positive indication of fission product release to the coolant is sufficient to govern reactor operations. In other cases, knowledge of the quantity of fission products released is of value to evaluate the extent of damage to the core. Various devices, such as ionization chambers, scintillation counters, etc., have been used as indicators for release of radioactivity to the coolant. Spurious indication of fission products in the coolant may be given by the presence of activation products formed by neutron-induced reactions on reactor-structural or fuel-cladding materials. Since the above indicative devices measure total radioactivity, they will not discriminate between the activation and fission products. To alleviate this problem, Heath[10] has developed a system for the detection and measurement of active iodine from gross fission products in MTR coolant water by utilizing ion exchange resins to chemically separate the radioiodines from other radioactive species. The anion resin is observed with a scintillation spectrometer to obtain the spectrum of the iodine isotopes present. The ratio of the various iodine isotopes may then be determined. Other types of monitors for fission products in reactor coolant water have been used such as a direct gamma monitor,[10] delayed neutron monitor,[10] and an automatic gamma monitor used for Hanford reactor coolants.[7]

When a gaseous coolant is used, other types of monitoring systems are used, since the fission products present in the coolant may consist of noble gases, gaseous species of relatively high vapor pressure, such as I, Ru, etc., or fission product activity associated with particulate material. A continuous monitor for I^{131} has been described by Smith and Alkire[19] utilizing pulse discrimination with gamma scintillation counters to observe a gas flowing past the detector. Goslovich, Pingel, and Fish[8] sample the gas stream into an evacuated vessel and use scintillation counting to determine the isotopes present.

Many other systems have been used, such as scrubbing the gases with caustic[12] or aqueous silver nitrate;[9] absorbing the iodine on soda lime, silver-coated slag wool, silver nitrate-impregnated filter paper[18], or collecting radioactive particulate material on CWS filters.[12]

Another system for gaseous coolant monitoring utilizes the adsorption of iodine, krypton, and xenon on activated charcoal traps. Advantages of this system are (a) quantitative retention of iodine on the first inch of the charcoal sampling trap, even at 100°C,[8,9] (b) ability to sample large volumes of coolant gases, (c) ability of charcoal to act as a particulate filter, and (d) partial retention (dependent upon trap temperature) of krypton and xenon,[1,2,3,9,13,15,17] allowing subsequent decay of the short-lived gaseous isotopes into rubidium and strontium, and cesium and barium isotopes, respectively. Since the retention of xenon and krypton on charcoal is highly dependent upon temperature, the traps are often cooled in liquid nitrogen, or in a dry ice–1, 1, 1-trichloroethane mixture. If the coolant gas contains significant water vapor, the trap must not be cooled to such low temperatures, since ice will form and plug the traps.

In most cases, absolute disintegration rate determinations of short half-life fission products present in carbon traps require chemical separations. The leaching of carbon with various reagents does not remove iodine completely.[6,20] The wet ashing of carbon with nitric, sulfuric and perchloric acids is a long tedious procedure. This laboratory has found the burning of carbon in an oxygen stream supplies a rapid method for destroying carbon, and, coupled with an effluent gas scrubber, gives quantitative recovery of iodine. The isotopes of barium and strontium are retained in the ash from the carbon, and are easily processed by chemical separation.

Gamma scintillation counting with a multichannel analyzer and a sodium iodide crystal detector provides a convenient method for counting mixed gamma-emitting isotopes. Heath[11] describes a rapid, versatile and accurate method of determining absolute disintegration rates, utilizing peak to total ratios, and absolute efficiencies.[21] The determination of a specific isotope may be accomplished by the subtraction of spectra of other isotopes present in the sample. Many multi-channel analyzers have circuitry arrangements to allow the 'subtracting' of a peak using an alternate gamma source of the desired energy.[14] However, such a procedure is impractical when short-lived isotopes such as I^{132}, I^{133}, I^{134}, I^{135} are present since the substitution of longer-lived isotopes having the same major peak energy will not duplicate the complicated spectra of the short-lived isotopes. The use of standard spectra of the desired isotope obtained under carefully standardized conditions provides an accurate means for subtraction of the standard isotope spectrum from the mixed isotope spectrum, but the process is rather laborious. When many samples of mixed isotopes are processed, the time involved in the calculation becomes prohibitive.

This laboratory has developed a rapid procedure for correcting for the effect of interfering isotopes by utilizing empirical calculations for the area under specific photopeaks derived from spectra of pure isotopes, and utilizing peak height ratios within the spectrum of a given isotope. Under carefully controlled counting conditions, this procedure, as used in the calculation of I^{134} and I^{135}, requires only the major peak heights of the isotopes present to calculate the disintegration rate.

EXPERIMENTAL AND PROCEDURE

Sample

The air samplers commonly used are made from $\frac{3}{4}$-in. i.d. stainless steel pipes, 14 in. long and containing −20, +30 mesh activated coconut charcoal (Barneby-Cheney Co., Columbus, Ohio). A small stainless steel screen holds the carbon in place. Desired trap lengths of from 5 in. to 14 in. may be obtained. These traps may be operated at room temperature, or chilled with dry ice–1,1,1-trichloroethane mixture, ice or liquid nitrogen. The flow rate is measured with flowmeters.

Iodine separation

A sample of the charcoal from the trap is weighed into a platinum crucible after thorough mixing to insure homogeneity. Standardized barium, strontium, and iodine carriers are added (~10 mg each), and burned in a tube furnace with oxygen in the quartz apparatus shown in Fig. 1. The effluent gas is scrubbed through a 0.25*M* Na_2SO_3 solution contained in a heavy-wall 40-ml centrifuge tube. After burning is complete, the quartz tube is rinsed with water, and the washings combined with the scrubber solution. This solution is acidified with concentrated HNO_3, and CCl_4 is added. Crystalline $NaNO_2$ is then added until the H_2SO_3 is destroyed and the iodide is oxidized to iodine. The iodine is extracted into CCl_4 and the organic layer transferred to another centrifuge tube. The iodine is stripped into a 1*M* HNO_3–H_2SO_3 solution and the aqueous layer transferred to another tube. The process of extraction and stripping is again repeated. The final stripping solution (just acid with HNO_3) is heated to boiling, $PdCl_2$ solution added (~10 mg/ml), and the precipitate filtered on a weighed glass filter paper, washed with water, acetone, dried in an oven at 110°C, weighed as PdI_2, mounted on 2 × 3 in. cardboard for counting, and the chemical yield calculated.

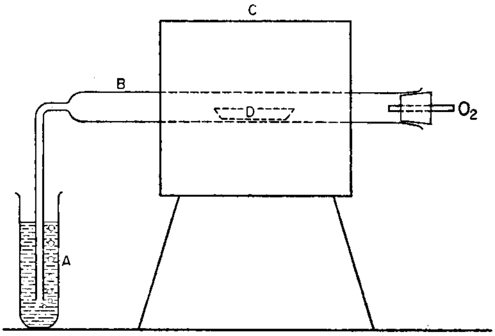

FIG. 1.—Combustion apparatus.
A 40 ml centrifuge tube containing 0.25*M* Na_2SO_3
B quartz ignition tube
C tube furnace
D Pt boat or folded crucible containing carbon sample.

Barium and strontium separations

The ash remaining in the platinum boat from the iodine separation is fused with Na_2CO_3. The melt is dissolved in dilute HNO_3. The solution is made basic with NaOH, and saturated Na_2CO_3 is added to precipitate the barium and strontium carbonates. The carbonates are dissolved in dilute HNO_3, and the nitrates are precipitated twice from fuming HNO_3. The nitrates are dissolved in water, and the solution is subjected to a ferric hydroxide scavenging step. Strontium and barium are then precipitated as the carbonate with saturated Na_2CO_3. After dissolution and dilution, barium is precipitated as the chromate from an ammonium acetate–acetic acid buffered solution. Additional separation of barium from strontium is accomplished by dissolving the chromate precipitate in dilute HCl, adding 10 mg strontium holdback carrier, and reprecipitating the barium as the chromate. The precipitate is filtered on a weighed glass filter paper, washed, dried, weighed as $BaCrO_4$, mounted, and the chemical yield calculated.

Strontium is precipitated from the first supernate from the barium separation by making the solution basic with concentrated NH_4OH and adding saturated oxalic acid. The precipitate is filtered on a weighed glass filter paper, washed, dried, weighed as $SrC_2O_4{\cdot}H_2O$, mounted, and the chemical yield calculated.

Counting system

All counting is done with a multichannel gamma-ray spectrometer consisting of the following components:

1. Radiation Counter Laboratory 256 Channel Analyzer with logarithmic converter and digital printer. Channel widths of 5 and 10 keV are generally used in scanning mounted chemical separations.
2. A Mosely XY Recorder, Model 4.
3. A 3 × 3 in. NaI (Tl) crystal optically coupled to a Dumont 6363 photo-multiplier tube.
4. A light-weight Lucite sample holder supported only by the scintillation crystal.
5. An iron shield.

The glass filter paper mounts are counted at known distances from the scintillation crystal (usually 3 or 10 cm) for a pre-set lifetime. The gamma spectra are recorded automatically on 3-cycle semilog graph paper with the XY recorder. A digital print-out on paper tape is also taken for each sample for use in summing up the total counts in the photopeaks.

A switch installed in the decimal decorder of the analyzer prevents the readout system from resetting to zero each time a new channel is read out. This permits the system to give a sub-total of all the previous counts each time it prints out a channel count. Therefore, to sum up the counts in any given photopeak the sub-total at the low energy side of the peak is subtracted from the sub-total at the high energy side of the peak. It has been a practice in our laboratory to obtain both an 'add' print-out and the 'regular' (not add) print-out tape. The channels at which the valleys occur can easily be determined from inspection of the recorded spectrum and the counts at the peaks can also be recorded. This latter figure is used in some of the calculations.

The iron shield that houses the scintillation crystal assembly is made from a 30 in. section of a surplus 16 in. Navy rifle barrel. The top and bottom of the shield are made from 7-in. thick armor plate. This system gives a peakless background that is less than half that of an equivalent lead shield for the gamma energy region 0.010 MeV to 2.56 MeV.

RESULTS AND DISCUSSION

The procedures are rapid enough to allow separations to be made for short-lived isotopes such as I^{134} in ample time to obtain good counting statistics. Absolute disintegration rates for I^{134}, I^{135}, Ba^{139}, Ba^{140}, Sr^{91} and Sr^{92} can be given within two hours from receipt of a trap in the laboratory by control analysts.

Determination of I^{131} and I^{133} on separations made shortly after reactor coolant sampling will give low results since these isotopes have some rather long-lived Te precursors (30-h Te^{131} and 63-m Te^{133}). These iodine isotopes are sufficiently long-lived (8 day and 21 hr) to allow separation and counting two days after sampling. This delay allows all the Te^{132} and most of the Te^{131} to decay into their daughters. A second separation of I^{131} and I^{133} is therefore usually made at this time. Studies indicate little difference between I^{131} results obtained on separations made at two days and five days after sampling. Since I^{134} has such a short half-life, such a delay is not possible. Determination of I^{132} can be made on the I^{131}, I^{133} separation.

An investigation has shown that with a linear face velocity of 100 ft/min and at 0°C, the first five inches of charcoal in the 14 in. trap contains 95 per cent of the total iodine in the trap, approximately 80 per cent of the barium isotopes (arising from direct yield as well as from the decay of xenon precursors), while the strontium isotopes are more generally distributed throughout the trap.

The exchange of radioiodine with iodine carrier is usually a slow and uncertain process, even when the iodines are in the same valence state. Since the valence state of the fission product iodine collected on the charcoal is not known, it was desirable to check the recovery of radioiodine, when present in the oxidized or reduced state. Accordingly, experiments with carrier-free I^{131} added to the charcoal as I^-, I_2 and IO_3^- were carried out using the described burning procedure. These experiments gave >98 per cent recovery of the I^{131}, indicating good exchange of the radioiodine with the iodine carrier, as well as a dependable method for its separation from carbon. The data are presented in Table I(a).

TABLE I(a)—RECOVERY OF VARIOUS IODINE OXIDATION STATES

Specie	Original	Separation	% Recovery
IO_3^-	6.33×10^4	6.38×10^4	101
I_2	1.81×10^5	1.92×10^5	106
I^-	2.95×10^5	2.93×10^5	98

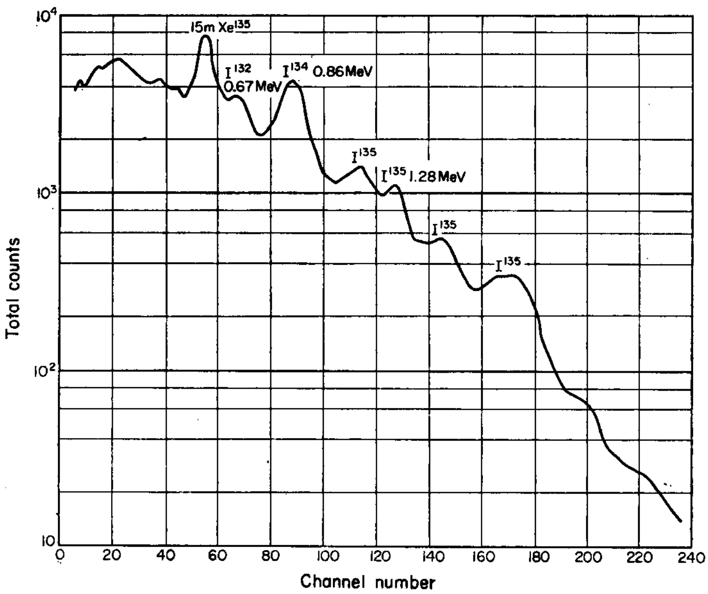

FIG. 2.—Mixture of I^{132}, I^{134} and I^{135}. 3 × 3 in. NaI (Tl) crystal. 10 keV per channel.

Following are details for calculating the disintegration rates of the short-lived isotopes, after the counting procedures utilizing the multichannel analyzer have been completed:

(a) I^{134} *and* I^{135}

An early gamma spectrum of an iodine separation of fresh fission products shown in Fig. 2 contains I^{132}, I^{134}, and I^{135}. (I^{131} and I^{133} are also present but their comparatively low specific activities make them no problem in making the I^{134} and I^{135} calculation). This resulting complex gamma spectrum causes difficulties in analyzing for a specific isotope. This difficulty has been eliminated, however, by correcting for the effects of the gamma spectra of each isotope on that of the others. This was accomplished by obtaining unique gamma spectra curves for each of the three radioisotopes with the crystal used in the analysis. These are shown in Figs. 3, 4 and 5. The effects of the gamma spectrum of each iodine isotope on the peak heights of the other two are then calculated. An example of a typical calculation is as follows:

Photopeaks to be used in calculations:
I^{132}—0.67 MeV
I^{134}—0.86 MeV
I^{135}—1.28 MeV

TABLE I(b)—DATA FROM THE UNIQUE GAMMA SPECTRUM CURVE OF EACH OF THE THREE ISOTOPES

I^{132} Curve	I^{134} Curve	I^{135} Curve
A_2 = counts at 0.67 MeV = 5465	A_4 = counts at 0.67 MeV = 1316	A_5 = counts at 0.67 MeV = 285
B_2 = counts at 0.86 MeV = 780	B_4 = counts at 0.86 MeV = 2405	B_5 = counts at 0.86 MeV = 325
C_2 = counts at 1.28 MeV = 350	C_4 = counts at 1.28 MeV = 150	C_5 = counts at 1.28 MeV = 297

If A, B, and C represent the peak heights of a composite sample of I^{132}, I^{134}, and I^{135} at 0.67 MeV, 0.86 MeV and 1.28 MeV, respectively, less background at those peaks, then:

$$A = A_2 + A_4 + A_5 \qquad (1)$$

$$B = B_2 + B_4 + B_5 \qquad (2)$$

$$C = C_2 + C_4 + C_5 \qquad (3)$$

but: $$\frac{A_4}{B_4} = \frac{1316}{2405} \qquad \text{or, } A_4 = 0.548B_4 \text{ from the } I^{134} \text{ Std. Curve.}$$

Similarly:

$$\frac{A_5}{C_5} = \frac{285}{297} \qquad \text{or, } A_5 = 0.960C_5 \text{ from the } I^{135} \text{ Std. Curve.}$$

also:

$$B_2 = 0.143A_2,\ B_5 = 1.094C_5,\ C_2 = 0.0640A_2 \text{ and } C_4 = 0.624B_4.$$

$\therefore$ Equation (1) becomes: $A = A_2 + 0.548B_4 + 0.960C_5.$

Similarly,

(2) becomes: $B = 0.143A_2 + B_4 + 1.094C_5$

also,

(3) becomes: $C = 0.0640A_2 + 0.0624B_4 + C_5.$

Solving these three simultaneous equations gives A_2, B_4 and C_5 in terms of only A, B and C.

$$A_2 = 1.11A - 0.581B - 0.430C \qquad (4)$$

$$B_4 = 1.12B - 0.0856A - 1.14C \qquad (5)$$

$$C_5 = 1.10C - 0.0656A - 0.0326B \qquad (6)$$

The use of these equations will thus allow the determination of count rates of I^{132}, I^{134} and I^{135} from a composite mixture of the three. Extreme care must be taken when peak heights are used for calculations because the shape of the photopeak is affected by (a) the scintillation crystal used, (b) the photomultiplier-crystal combination, (c) the gamma-energy per channel calibration, (d) the beta-absorber thickness, and (e) the intensity of the sample being counted. If any of these items are changed, the constants used in equations (4), (5), and (6) must be adjusted accordingly.

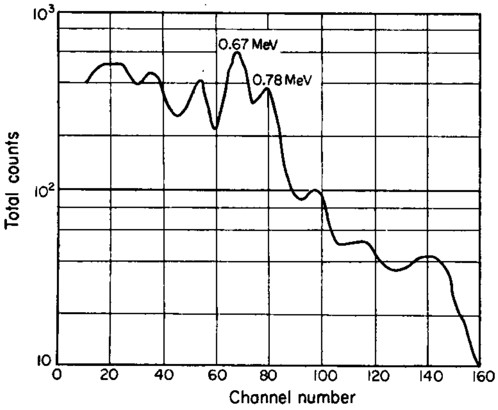

FIG. 3.—I^{132} spectrum milked from Te^{132} 3 × 3 in. NaI(Tl) crystal. 10 keV per channel.

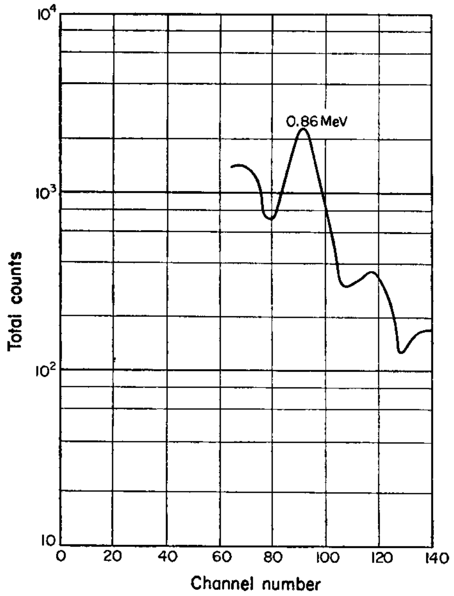

FIG. 4.—I^{134} spectrum. 3 × 3 in. NaI(Tl) crystal. 10 keV per channel.

Equation (4) is for reference only since an iodine separation is made later for the determination of I^{131}, I^{132}, and I^{133}. I^{132} will be in equilibrium with its Te precursor at this time.

It has been determined experimentally and verified periodically that for an I^{135} gamma-spectrum curve the total counts in the 1.28 MeV photopeak is $= (10.2)(C_5)$. This is accomplished by obtaining an I^{135} spectrum and subtracting the counts due to the Compton scattering of the higher energy peaks from the spectrum in the 1.28 MeV region. The resulting count under the 1.28 MeV peak is divided by the original 1.28 MeV peak height, giving a ratio of 10.2. Similarly for I^{134} the total counts in the 0.86 MeV photopeak is $= (9.19)(B_4)$. Thus, equations (5) and (6) when used to determine absolute disintegration rates, become:

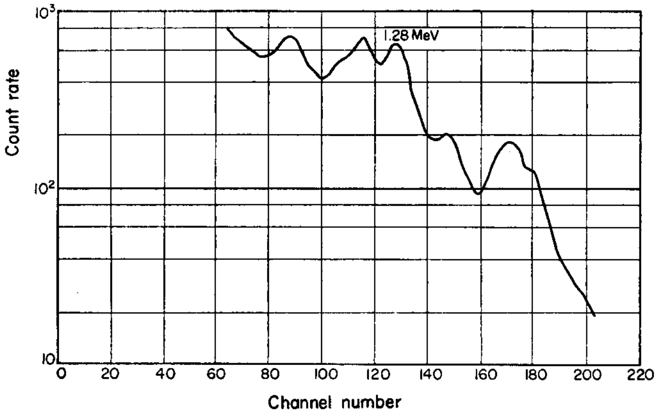

FIG. 5.—I^{135} spectrum above 0.60 MeV. 3 × 3 in. NaI(Tl) crystal. 10 keV per channel.

$$I^{134} = \frac{(9.19)[(1.12)B - (0.0856)A - (1.14)C]}{DEFGHIJL} = \text{d/m/g carbon} \tag{7}$$

$$I^{135} = \frac{(10.2)[(1.10)C - (0.0656)A - (0.0326)B]}{DEFGHIJL} = \text{d/m/g carbon} \tag{8}$$

where:

D = correction for factor for any absorber between source and crystal

E = total absolute detection efficiency for geometry used

F = peak to total ratio for photopeak used

G = decay scheme correction

H = internal conversion coefficient correction (1.00 for I^{134} and I^{135})

I = count time in minutes

J = chemical yield

L = sample weight (g).

(b) I^{131}, I^{132}, *and* I^{133}

A second iodine separation is made two days after the initial iodine s eparation. The early gamma spectrum of this separation shown in Fig. 6 will show I^{132} if Te^{132} is present in the trap. The I^{132} disintegration rate is determined at this time from the 0.67 MeV photopeak using equation (9). After the I^{132} decays out the mount is counted again, this time for I^{133}, which is determined from the 0.53 MeV photopeak using equation (10). A spectrum is shown in Fig. 7.

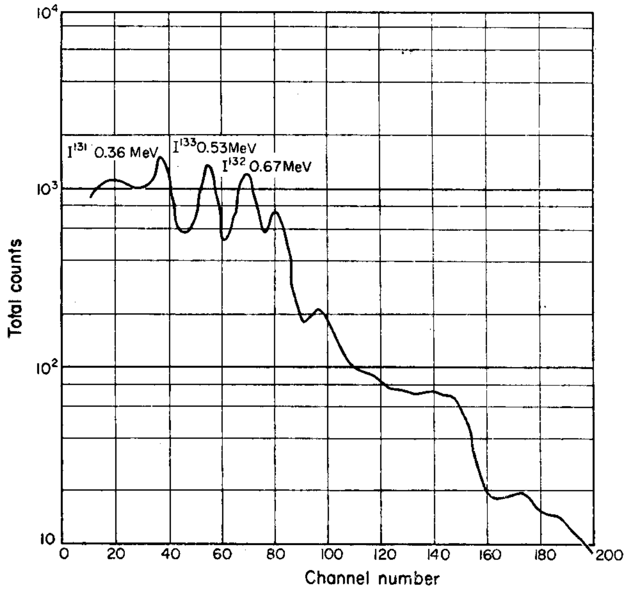

FIG. 6.—Early spectrum of I^{132}, I^{133}, I^{131} separation. 3 × 3 in. NaI(Tl) crystal. 10 keV per channel.

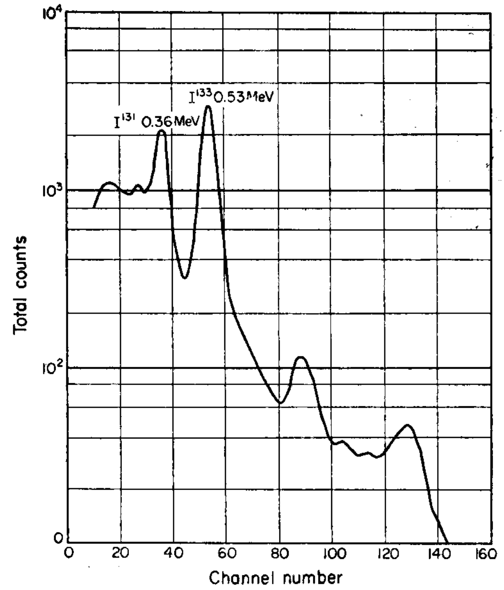

FIG. 7.—I^{131}, I^{133}, spectrum after I^{132} decay. 3 × 3 in. NaI(Tl) crystal. 10 keV per channel.

I^{131} is determined by counting the same iodine separation mount again as soon as the I^{133} is gone. (See equation 11).

$$I^{132} = \frac{K_p - [(0.15)K_2 + K_b]N_2}{DEFGHIJL} = \text{d/m/g carbon} \qquad (9)$$

K_p = total count in 0.67 MeV peak

K_2 = 0.67 MeV peak height (0.15K_2 gives contribution per channel of higher energy I^{132} peaks to the 0.67 MeV peak)

K_b = average background per channel at 0.67 MeV

N_2 = number of channels used in determining K_p.

$$I^{133} = \frac{(K_p - [(0.01)K_1 + K_b]N_3}{DEFGHIJL} = \text{d/m/g carbon} \qquad (10)$$

K_b = total counts in 0.53 MeV peak

K_1 = the I^{131} 0.36 MeV peak height (0.01K_1 gives I^{131} contribution per channel to the 0.53 MeV peak)

K_b = average background per channel at 0.53 MeV

N_3 = number of channels used in determining K_p.

$$I^{131} = \frac{K_p - [(0.007)K_1 + K_b]N_1}{DEFGHIJL} = \text{d/m/g carbon} \qquad (11)$$

K_p = total counts in 0.36 MeV peak

K_1 = the I^{131} 0.36 MeV peak height (0.007 K_1 gives contribution per channel to 0.36 MeV peak from the Compton counts from the I^{131} 0.64 MeV peak)

K_b = average background per channel at 0.36 MeV

N_1 = number of channels used in determining K_p.

In actual practice it was determined that I^{133} had negligible effect on the I^{131} determinations when the I^{133} 0.53 MeV peak height was as much as 20 per cent as high as the I^{131} 0.36 MeV peak height.

(c) Ba^{139}

Ba^{139} is determined by counting the Ba mount as soon after the separation as possible. The amplifier gain is increased to give 5 keV per channel for this determination since the Ba^{139} 0.16 MeV photopeak falls close to the front end of the spectrum. A typical spectrum is shown in Fig. 8. The factors used for correcting for the effects of Ba^{140} as shown in the equation (12) were determined from a Ba^{140} gamma spectrum containing no Ba^{139}.

$$Ba^{139} = \frac{K_p - K_4K_5 - K_bN}{DEFGHIJL} = \text{d/m/g carbon} \qquad (12)$$

K_p = total counts in 0.16 MeV peak

K_4 = Ba^{140} 0.54 MeV peak height

K_5 = a factor relating the Ba^{140} 0.54 MeV peak height to counts in 0.16 MeV peak N channels wide as determined from a Ba^{140} gamma spectrum. Factors used are $K_5 = 18.1$ for $N = 28$ channels, $K_5 = 19.8$ for $N = 34$ channels, etc.

K_b = average background counts per channel at 0.16 MeV for a gain of 5 MeV per channel.

N = number of channels counted for K_p.

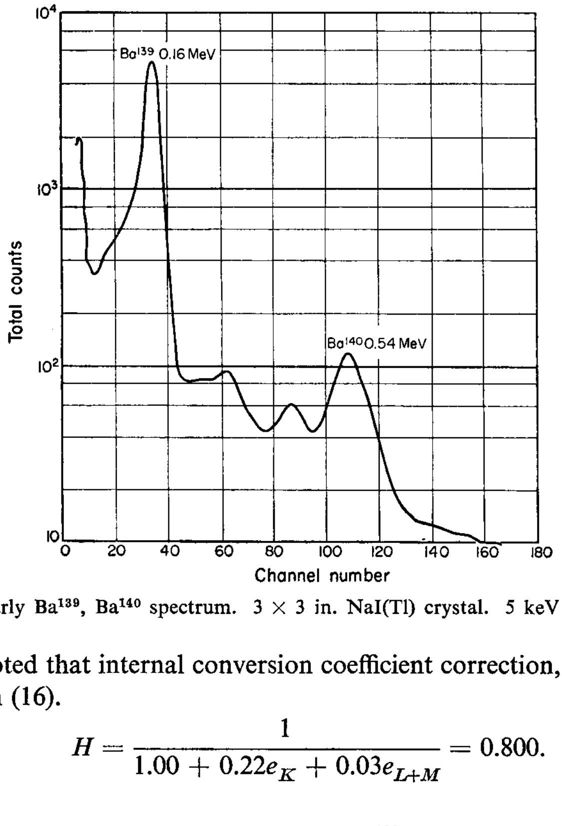

FIG. 8.—Early Ba^{139}, Ba^{140} spectrum. 3 × 3 in. NaI(Tl) crystal. 5 keV per channel.

It should be noted that internal conversion coefficient correction, H, is significant for this calculation (16).

$$H = \frac{1}{1.00 + 0.22e_K + 0.03e_{L+M}} = 0.800.$$

(d) Ba^{140}

The same Ba mount that was counted for Ba^{139} is counted again—this time with a gain of 10 keV per channel. Ba^{140}, shown in Fig. 9, is calculated from equation (13). The correction factor for Ba^{139} is calculated from a Ba^{139} gamma spectrum which is obtained by taking a spectrum rich in Ba^{139} and subtracting out Ba^{140}.

$$Ba^{140} = \frac{K_p - K_6K_7 - K_bN}{DEFGHIJL} = \text{d/m/g carbon} \tag{13}$$

K_p = total counts in 0.54 MeV peak

K_6 = correction factor for Ba^{139} for N channels

K_7 = 0.16 MeV peak height

K_b = average background counts per channel at 0.54 MeV

N = number of channels counted for K_p.

Ba^{140} can also be calculated by waiting until it is in equilibrium with its daughter La^{140} and counting the sample for La^{140}.

(e) Sr^{91}, Sr^{92}

The Sr mount is counted as soon after the separation as possible for Sr^{91} and Sr^{92}. (See Fig. 10 for a typical spectrum.) Sr^{91} is calculated from equation (14); Sr^{92} is calculated from equation (15).

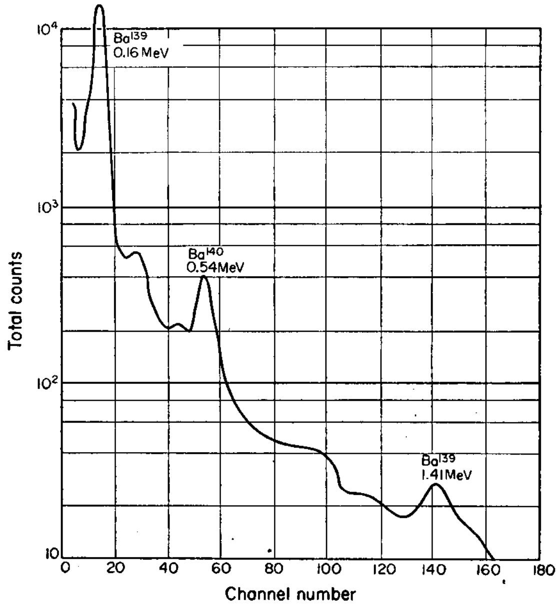

FIG. 9.—Ba^{139}, Ba^{140} spectrum. 3 × 3 in. NaI(Tl) crystal. 10 keV per channel.

$$Sr^{91} = \frac{K_p - [(0.30)(K_8) + K_b]N}{DEFGHIJL} = \text{d/m/g carbon} \tag{14}$$

K_p = total counts in 1.02 MeV peak

K_8 = Sr^{92} 1.37 MeV peak height ($0.30K_8$ gives Sr^{92} contribution per channel to the Sr^{91} 1.02 MeV peak)

K_b = average background per channel at 1.02 MeV

N = number of channels counted for K_p.

$$Sr^{92} = \frac{K_p - K_bN}{DEFGHIJL} = \text{d/m/g C} \tag{15}$$

K_p = total counts in 1.37 MeV peak

K_b = average background at 1.37 MeV

N = number of channels used in determining K_p.

The precision available for repetitive radioiodine, radiobarium, and radiostrontium isotope absolute disintegration rate determinations was studied. Separate samples of carbon from the same trap were run according to the procedures outlined. All chemical separations were made by routine laboratory control analysis with no special precautions over those ordinarily exercised. The results on 10 separations for these isotopes are listed in Table II. In addition, a single mount was counted repetitively with the counting systems described. These results are listed in Table III.

It is noted that the precision of repetitive counting of a single mount is better than that for the repetitive chemical separation followed by counting. This is expected since only a portion of all the errors that may accumulate during the whole process of sample burning to counting the chemically separated radioactivity are being compared. The contributing accumulated errors would consist of (a) the inaccuracy in initially mixing and weighing the carbon sample prior to burning, (b) the incomplete drying of the mounted filter paper containing the precipitated radioisotope, (c) the inaccuracy in weighing the filter paper before and after mounting, (d) the inaccuracy in standardizing and adding pertinent carrier solutions, (e) the statistical randomness of radioactive decay, and (f) the instability of electronic components within the multichannel analyzer.

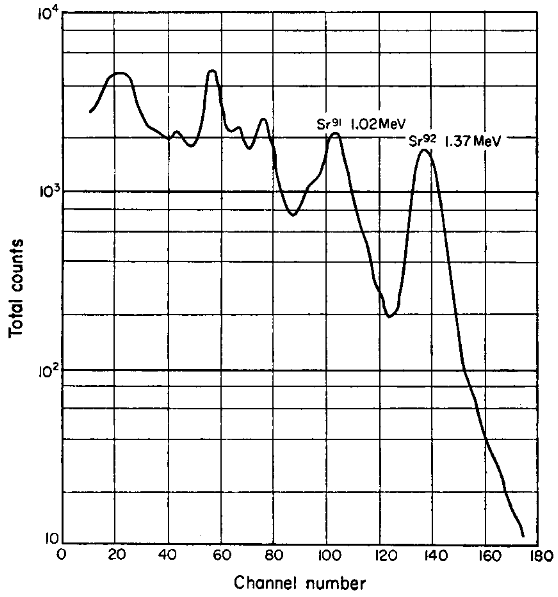

FIG. 10.—Sr^{91}, Sr^{92} spectrum. 3 × 3 in. NaI(Tl) crystal. 10 keV per channel.

SUMMARY AND CONCLUSION

Methods have been described for the determination of absolute disintegration rates of I^{131}, I^{132}, I^{133}, I^{134}, I^{135}, Ba^{139}, Ba^{140}, Sr^{91} and Sr^{92} present in gas-cooled reactor effluents. A gas sampler consisting of activated charcoal was used to collect the radioactivities, and standard radiochemical methods were adapted to this collecting system. The recovery in iodine of various oxidation states of iodine through the chemical separation was studied, resulting in >98 per cent recovery of all stages. The standard deviation of replicate analyses for the radioactivities when performed by routine laboratory analysts on large numbers of samples has been determined. Finally,

TABLE II.—PRECISION ON REPETITIVE ABSOLUTE DISINTEGRATION RATE DETERMINATION

Isotope	Number of determinations	Mean, d/m/g C	Standard deviation
I^{131}	10	2.48×10^6	0.20×10^6
I^{135}	10	7.93×10^5	1.23×10^5
Sr^{91}	10	1.67×10^5	0.15×10^5
Sr^{92}	10	1.56×10^4	0.15×10^4
Ba^{140}	10	7.19×10^4	0.70×10^4

TABLE III.—REPETITIVE COUNTING OF A SINGLE MOUNTED SEPARATION FOR I^{131}

Number of determinations	Mean, d/m/g C	Standard deviation
10	6.85×10^6	0.017×10^6

counting techniques utilizing 'spectrum subtraction' methods and solution of simultaneous linear equations for contributions of interferences of one radioisotope on another at the gamma peaks used for decay rate determinations in the complex spectra are discussed. Disintegration rate values for I^{134}, I^{135}, Sr^{91}, Sr^{92}, Ba^{139} and Ba^{140} can be obtained within two (2) hours from receipt of the carbon trap in the laboratory by routine laboratory analysts.

Acknowledgements—The authors express with thanks the assistance of C. L. Grover, J. O. McFarlin, M. A. Hiatt who supplied the data for the calculation of chemical separation statistics, to Miss E. M. Livingston for the counting and calculation of all absolute disintegration rates, and to A. R. Harbertson for his contributions in the initial phases of the work.

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A RADIOCHEMICAL TECHNIQUE FOR DETERMINING FISSIONABLE MATERIAL CONTAMINATION ON COMPLETED REACTOR FUEL ASSEMBLIES*

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Summary—A nondestructive method is described for the determination of the extent to which the cladding of reactor fuel assemblies is contaminated with U^{235}. The method involves the irradiation of the assemblies in a test reactor at an extremely low power level. Subsequent to the irradiation, the fission product (Cs^{138}) is separated by tetraphenylboron extraction. The concentration of this fission product is used as a measure of the extent to which the cladding is contaminated with U^{235}.

INTRODUCTION

The method to be discussed here was developed for the determination of U^{235} contamination on cladding surfaces of U^{235} fuel elements. The method is applicable to the determination of any fissionable contaminant on a fuel cladding surface and may be applicable to such a determination on other surfaces. The primary point of control of cladding contamination by U^{235} is, of course, during the actual fuel cladding process. At this point, samples of the cladding material and process environment may be analyzed destructively by any one of a number of techniques for the detection of U^{235}. At the completion of the cladding process, individual fuel elements can be nondestructively scanned for surface U^{235} contamination by α-counting techniques. Fuel plate assemblies, consisting of a welded assembly of individual elements and representing a large fraction of the total reactor core, offer a unique problem in nondestructive analysis for U^{235} contamination. It is in answer to this problem that the present method finds valuable application.

The many ramifications of fuel-element surface contamination, especially with respect to water-cooled reactors, need not be discussed here. It will suffice to note that such contamination results in excessive fission-product contamination of the circulating primary coolant water during reactor operation at any significant power level.

In order to show the extremely minute quantities of U^{235} required to produce significant fission product concentration in the primary coolant of a power reactor, consider the following hypothetical reactor power plant system:

Specific power: 2000 watts/g of U^{235}
Coolant volume: 5×10^6 ml
U^{235} contamination over total fuel surface: 1 mg.

We may take Cs^{138} ($T_{\frac{1}{2}} = 32$ min) as a convenient example of a typical fission product which is produced in high yield. At equilibrium, the coolant of this reactor would show a concentration of Cs^{138} of about 5×10^4 d/m per ml, assuming a fission yield of 5.7 per cent and total release to the coolant of all the cesium formed during fission. Accordingly, we may wish to maintain total fuel contamination at 0.1 mg. If each

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* Work performed under contract with the U.S. Atomic Energy Commission.

fuel assembly constitutes one tenth of the core, then we must detect as little as 10 μg of U^{235} distributed over the surfaces of a fuel assembly.

PRINCIPLES OF THE METHOD

In this method microgram amounts of U^{235} on fuel cladding surfaces are detected by fissioning some of this U^{235} by means of a short irradiation in a moderate neutron flux, followed by subsequent concentration and measurement of a suitable fission product, i.e. Cs^{138}. The irradiation flux and time are minimized to prevent excessive activation of the bulk fuel inside the cladding, which would seriously hamper subsequent handling. To assure fissioning proportional to that to be expected in the final reactor, the fuel assembly is irradiated in a low-power test reactor whose flux distribution closely matches that of the power reactor in which the fuel is to be used. During the irradiation, the fuel assembly is enclosed in a polyethylene container filled with a measured volume of redistilled water. Great care is taken to avoid introduction of U^{235} from sources other than fuel surface contamination. At the end of the irradiation, the water is drained from the container and a large volume of this water is analyzed for the 32 min Cs^{138}. This isotope is formed as a product of the fission of U^{235} and is a member of the decay chain:

$$5.8 \text{ sec } I^{138} \rightarrow 17 \text{ min } Xe^{138} \rightarrow 32 \text{ min } Cs^{138} \rightarrow \text{stable } Ba^{138}.$$

Many other isotopes of cesium are formed as fission products. Most of these are of no interest in the present consideration because of their extremely long or extremely short half-lives. The only cesium isotope of significance as an interference in the determination of Cs^{138} is the 9.5 min Cs^{139}. This isotope is allowed to decay and produces a negligible error to the Cs^{138} measurement in the method employed here.

Cesium-138 is chosen as the fission product best indicating the amount of U^{235} surface contamination for a number of reasons: it possesses a high fission yield (5.7 per cent) and short yet workable half-life (32 min). These two properties tend to make this isotope a sensitive indicator of U^{235} fission over short irradiation periods. As an alkali metal, it forms highly soluble compounds and because of its single oxidation state, its chemical behavior is rather simple and reliably predictable. These latter properties tend to make this isotope amenable to chemical analysis in that it will favor distribution in the water rather than on fuel and container surfaces and can be separated from other activities by simple rapid procedures. Because of this favorable chemical behavior, these distribution and separation properties are not expected to be critical functions of minor environmental changes.

The cesium is separated from the other fission products and induced activities by extraction into isoamylacetate, using sodium tetraphenylboron. The cesium is then back extracted into hydrochloric acid, precipitated as the nickel ferrocyanide complex, and mounted for β-counting. Exposure of known quantities of uranyl nitrate under the same flux conditions with subsequent Cs^{138} determination provides a correlation between Cs^{138} concentration and total U^{235} contamination of the fuel assembly surfaces.

PROCEDURAL DETAILS

Irradiation

In preparation for irradiation, the fuel assemblies are inserted in a heavy walled polyethylene container fitted with tubing, also polyethylene, for the introduction of water. The container is lowered into the test reactor and the contained assembly becomes an integral portion of the reactor's active mass. Using a leveling bottle, the container is then filled with redistilled water until the assembly is completely submersed. Twenty-liter polyethylene bottles are used to transport the redistilled water from the source of supply to the reactor prior to irradiation. The same bottles are used repeatedly with redistilled water rinses between each use. The bottles are initially rinsed with redistilled nitric acid and flushed with redistilled water to prevent interference by any environmental U^{235} contamination—bearing in mind that as little as one μg of U^{235} would be detected in the subsequent irradiation and analysis. After filling the container, the reactor is taken to a predesignated power level and held constant for exactly 30 min. In the work described here, the thermal neutron flux was 7.6×10^7 n/cm^2 per sec and corresponded to a power generation of 5.3 W in the fuel assembly.

Sampling

At the completion of the irradiation period the reactor is scrammed. At scram time, a stop watch is started for use in the Cs^{138} analysis to be described later. After a 5 min waiting period to allow for decay of short-lived induced activities—which produce a rather intense radiation field around the reactor for a short period of time after scram—the reactor area is entered and the water inside the polyethylene container surrounding the fuel assembly is allowed to drain into a 20 l. polyethylene bottle. This bottle contains about 10 μg of stable Cs^{133} to serve as a carrier and reduce the probability of the loss of Cs^{138} by adsorption on container surfaces. After the water is drained from the fuel assembly (this operation usually consumes 3–5 min) it is moved to the laboratory for analysis. Two 3600-ml samples are taken, using 5-l. graduates, for extraction of Cs^{138}. The total volume of water surrounding the fuel assembly during the irradiation and subsequently drained into the 20-l. bottle is measured. The volume does not normally vary significantly from 14.0 l.

Cesium extraction

The cesium extraction procedure used here is an adaptation of a procedure described by H. L. Finston of Brookhaven National Laboratory.

The details of the procedure used are as follows.

(1) Sodium citrate, 530 g, are placed in each of two 4-l. separatory funnels.

(2) Post-irradiation water (3600 ml) is placed in each funnel. Motor driven glass agitators are inserted in the funnels and vigorous agitation is initiated.

(3) As the citrate begins to dissolve, 57 ml of concentrated nitric acid are added to each funnel.

(4) When the citrate has completely dissolved or at scram time plus 15 min, 400 ml of 0.05M sodium tetraphenylboron in isoamylacetate are added to each funnel. The agitation is increased to the maximum permissible rate to insure complete dispersion of the organic and aqueous phases. This agitation is maintained for 5 min.

(5) The two phases are allowed to separate for a minimum of 2 min. At scram time plus 25 min, the lower aqueous phase is separated and discarded. This timing of the organic–aqueous separation with respect to scram time is necessary in order repetitively to maintain the contribution of the 17-min Xe^{138} to the observed Cs^{138} concentration.

(6) The 400-ml organic phases are successively contacted with the same 50-ml volume of $3M$ hydrochloric acid in order to back extract the Cs^{138} into an aqueous solution. This back extraction is performed, using manual agitation and two 500-ml separatory funnels.

(7) The $3M$ hydrochloric acid phase is transferred to a 100-ml centrifuge tube containing 10 ml of $6M$ NaOH. The contents of the tube are agitated to assure completion of the partial neutralization.

(8) One ml of $0.2M$ $Ni(NO_3)_2$ is added and the solution agitated. With continued agitation, 1 ml of $0.1M$ $Na_4Fe(CN)_6$ is added and agitation continued for 5 min. A light-green colored, nickel-cesium-ferrocyanide compound is precipitated.

(8) One milliliter of $0.2M$ $Ni(NO_3)_2$ is added and the solution agitated. With continued agitation, 1 ml of $0.1M$ $Na_4Fe(CN)_6$ is added and agitation continued for 5 min. A light-green colored, nickel-cesium-ferrocyanide compound is precipitated.

(9) The mixture is centrifuged at a high velocity and filtered through two 2.4-cm glass-mat filter papers. The precipitate is extremely fine and tends to clog the paper. For this reason, most of the supernatant solution is filtered rapidly and the ferrocyanide compound agitated into the final few ml of the supernatant and passed to the filter. Quantitative transfer of the precipitate is completed with a small volume of water.

(10) The filter is sucked dry and the precipitate on the paper is washed with a few ml of ether.

(11) The top filter paper is dried under a heat lamp and mounted on a cardboard mount with acrylic tape.

The use of the nickel ferrocyanide compound is adapted from the work of Burns[1] and others[2] at Hanford who used this compound in a large scale Cs^{137} recovery process.

Inclusion of the extensive buffering procedure is probably not necessary in the analysis of water used for the fuel assembly irradiations because this water was, of necessity, carefully prepared. The extraction is based on the formation of a cesium tetraphenylboron compound favoring organic phase distribution and does not involve a change in hydrogen-ion concentration. The original procedure by Finston was designed for the analysis of acid solutions. Because of the fact that this adaptation of an extraction procedure involving large volumes of solution had to be developed on an extremely urgent basis, the use of a non-buffered system was not investigated.

By means of a series of extractions, using a large volume of sample, a standard Cs^{137} tracer solution and large volumes of extractant, the recovery was demonstrated to equal 74 per cent. This factor was included in interpreting the observed results.

Counting technique

The counting rate determinations were performed, using standard end-window G-M tubes. A standard $Sr–Y^{90}$ source prepared by a caustic-carbonate precipitation of a NBS standard solution was used as a reference for the determination of the counting yield factor

$$\frac{\text{Disintegrations/min}}{\text{Counts/min}} .$$

Since the maximum β energies emitted by Sr–Y^{90} do not correspond to those emitted by Cs^{138}, the quotation of Cs^{138} d/m values are inaccurate to an extent determined by the energy dependence of the G-M tube.[3] This inaccuracy may be as large as 10–15 per cent and the bias is positive. This does not appear in the U^{235} measurements since it is eliminated by the calibration technique used. This technique will be discussed in more detail below.

The samples were counted on the first shelf of the β-counter at intervals of 5 min, using a counting time of 4 min. The observed counting rates were plotted as a function of time after scram, the 32-min half-life period of Cs^{138} was extrapolated back to scram, and the result was calculated as shown in Fig. 1. The experimental points obtained at a minimum of 70–80 min after scram were used to extrapolate back to time zero on the 32-min decay line. Experimental points observed before the 70–80 min cooling time are biased high due to the 10-min Cs^{139}.

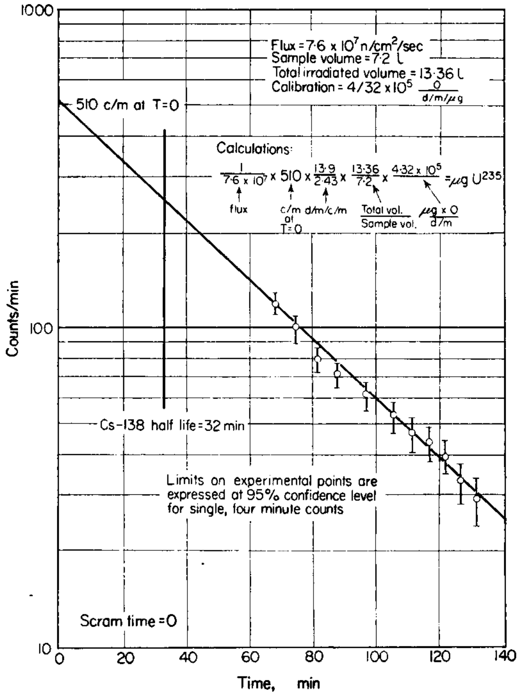

FIG. 1.—Cs^{138} determination.

Calibration

A relationship between Cs^{138} d/m and U^{235} concentration was obtained by irradiation of a uranyl nitrate solution of known concentration in a known flux in another test reactor which had a higher flux. The extraction of Cs^{138} was performed in the same manner as for the fuel assembly irradiations. Since the volume of water involved in the calibration experiments was only about 200 ml, rather than the 3.6 l. sample volumes involved in the fuel assembly irradiations, the small volume was diluted to 3.6 l. before extraction in order carefully to reproduce the fuel assembly irradiation measurements. A few extractions were also performed to provide calibration data for samples of small volume. When this was done a correction was applied for the 90-per cent recovery observed for the extraction of 200-ml samples as compared to 74-per cent recovery observed in the extractions of 3.6-l. samples. Since the thermal neutron flux used in the irradiations of the standard uranyl nitrate solutions was not the same as the flux used for the fuel assembly irradiations, the Cs^{138} d/m vs. U^{235} μg relationship was expressed in terms of a constant, C:

Where ϕ = Flux

$$C = \frac{\phi}{\text{disintegrations/min}/\mu g}$$

$$\text{and } \mu g\ U^{235} = \frac{C \cdot \text{disintegrations/min}}{\phi}.$$

The calibration data obtained is shown in Table I.

TABLE I.—CALIBRATIONS

Neutron flux, n/cm²/sec = 1.73×10^8

Run No.	U^{235} irradiated, μg	Disintegrations/ min per μg at $t = 0$	C
1	154.8	320	5.40×10^5
2	77.4	434	3.99×10^5
3	54.2	483	3.58×10^5
4	77.4	423	4.09×10^5
5	77.4	379	4.56×10^5
			Average 4.32×10^5

Limitations

A number of variables affect the accuracy of this method in its application to the determination of the absolute concentration of U^{235}. Probably the two most significant of these variables are the loss of Xe^{138}, the gaseous precursor of Cs^{138}, and the loss of cesium by adsorption on exposed surfaces. The contribution of Xe^{138} to the observed Cs^{138} concentration is controlled by maintaining a constant Xe–Cs separation time in the analytical scheme. The loss of Xe^{138} is fairly well standard between the calibration and fuel assembly irradiations. This loss is, at least, not extremely variable since an acceptable reproducibility of Cs^{138} recovery is obtained within a single series of irradiations. The standardization data of Table I indicate the magnitude of this variation.

The possible loss of Cs by adsorption on the surfaces of the fuel assembly offers a problem that is not amenable to easy experimental definition. A series of experiments performed during a period when U^{235} contamination was determined by this method on a large number of fuel assemblies showed Cs^{138} losses by adsorption varying from 10 to 50 per cent. A sorption factor of 1.65

$$\left(F_s = \frac{\text{true } Cs^{138} \text{ disintegrations/min}}{\text{observed } Cs^{138} \text{ disintegrations/min}}\right)$$

was used for correcting the U^{235} values so obtained. This corresponds to a loss by adsorption of 40 per cent of the Cs^{138}. Later work by Eiland *et al.*[4] at K.A.P.L. showed that this sorption factor may be high. This latter work indicated that a sorption factor of 1.2–1.35 is more reasonable, corresponding to a 16–20 per cent sorption loss.

The sensitivity of the method is, of course, a direct function of the power generated in the fuel assembly during the irradiation and is dependent also upon irradiation time. For example, it would be possible to detect easily a millimicrogram of U^{235} in the power reactor described previously if the reactor were operated at 100 per cent power for 30 min. However, the generation of extremely high power levels in these fuel assemblies for the determination of U^{235} contamination prior to final reactor installation is not practical. Such power generation would produce extremely high concentrations of fission products within the fuel and create difficult handling problems during the subsequent reactor installation. For this reason, the power generation utilized for this analytical technique and the length of the irradiation period must be held to a minimum consistent with minimum sensitivity requirements. For the fuel assemblies and irradiation period used in the work described herein, exposure levels at the fuel assembly surfaces after irradiation were of the order of 1 r/hr and decayed to less than 6 mr/hr within 24 hr.

When the method presented here was first proposed as a means for determining contamination of a fuel assembly before loading it into a power reactor, it was expected to be accurate within a factor of two. The method was applied to two reactor fuel loads and the Cs^{138} levels observed at full power agreed with those predicted by this method well within this margin of error. The accuracy may, therefore, be better than a factor of two, but because of the sources of error previously pointed out, this is not assured.

Acknowledgements—All the reactor irradiation aspects of this analytical technique were performed by the K.A.P.L. Reactor Physics group, headed by Dr. J. S. King. This entire group performed all irradiations of the fuel assemblies. Special mention should be made of the contributions of D. R. Bach and R. E. Slovacek of Physics and Miss B. Thompson of G.E.L. who performed the test reactor calibration and sorption study irradiations. Dr. A. E. Lessor of G.E.L. assisted in setting up the Cs extraction procedure and performed a large number of fuel assembly analyses. Other members of K.A.P.L. Radiochemistry, D. Dutina and H. M. Eiland, also performed a number of fuel assembly analyses. Dr. Eiland studied the sorption problem in detail. This work will be issued separately.

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Talanta, 1960, Vol. 6, pp. 237 to 245. Pergamon Press Ltd. Printed in Northern Ireland

THE SPECTROPHOTOMETRIC DETERMINATION OF ALLOYING AND FISSION PRODUCT ELEMENTS IN NONIRRADIATED PLUTONIUM 'FISSIUM' ALLOYS*

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Summary—In the development of fuel processing methods for purifying Pu–Fe or Pu–Co fuel alloys, methods of chemical analysis were required for the alloying element and representative fission product elements. The initial Pu fissium alloy, which represented 10 per cent burnup after 130 days of fast fission, contained 2.5 per cent Co or Fe, 0.7 per cent Ce, 1.3 per cent La, 0.7 per cent Mo, 0.03 per cent Nb, 1.3 per cent Ru, and 0.8 per cent Zr. The concentration of many of these elements was reduced in the fuel processing to less than 0.01 per cent. It was necessary to devise chemical methods for determining each element in these concentration ranges except La, which was determined spectrographically. Dissolution of these alloys is accomplished by a sealed-tube technique, using HCl which contains a few drops of $HClO_4$ as a solvent, or by heating the sample with HCl and $HClO_4$ in a distillation apparatus until the Ru distills as the tetroxide. Cerium is separated from Pu^{VI} by precipitation of Ce^{IV} fluoride, after which it is determined spectrophotometrically as Ce^{IV}. Cobalt is determined in the presence of Pu by means of the color formed by Co in an HCl–acetone medium. Iron is determined by measuring the absorbancy of the ferrous-*o*-phenanthrolate complex, either in the presence of Pu or after separation by extraction of $FeCl_3$. Molybdenum and Zr are each determined colorimetrically as the chloranilates after separation of Mo by hexone extraction from HCl solution and precipitation of Zr as the *p*-bromomandelate. Niobium is extracted into hexone from an H_2SO_4–HF medium and estimated by means of the color formed by Nb with hydroquinone in H_2SO_4. Ruthenium is distilled as the tetroxide and estimated colorimetrically as Ru^{IV} chloride. In the higher concentration ranges, the relative standard deviation for the determination of each element is less than 2 per cent. At lower concentrations, relative standard deviations of 5 per cent are acceptable.

INTRODUCTION

IN THE investigation of pyroprocessing and other methods for removing fission product elements from plutonium-rich fuel alloys, synthetic spent fuel or 'fissium' was prepared by dissolving representative fission product elements in a molten plutonium alloy containing 9.5 atomic per cent iron or 12 atomic per cent cobalt. For initial experiments, each element was added at a concentration that corresponded approximately to the concentration of the element in a fuel having undergone 10 per cent burnup after 130 days of fast fission. Later, a synthetic spent fuel was prepared to correspond to 2 per cent burnup. A typical analysis of the plutonium–iron 'fissium' corresponding to 10 per cent burnup is shown in Table I. In the various fuel processing steps the concentration of some of the fission product elements is reduced to less than 0.01 per cent. To establish the efficiencies of the fuel processing methods, it was necessary to analyze the 'fissium' initially and after each processing step. In addition, to obtain material balances and to determine the distributions of the fission product elements, their concentrations were determined in various side products, such as oxide or halide skulls, residues after filtration, halide salt mixtures, and amalgams. In order to analyze these samples, new spectrophotometric methods were developed, or existing methods

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* Work performed under contract with the U.S. Atomic Energy Commission.

were adapted, for the determination of iron, cobalt and each fission product element except lanthanum which is determined spectrochemically. Naturally, these methods are only applicable for analyzing nonirradiated or synthetic fuels. Radiochemical methods, which are not discussed here, are utilized in the determination of the fission products in irradiated fuel.

TABLE I.—COMPOSITION OF IRON–PLUTONIUM "FISSIUM" ALLOY REPRESENTING 10 PER CENT BURNUP

Element	Concentration, %
Pu	92.3
Fe	2.76
Ce	0.74
La*	1.31
Mo	0.74
Nb	0.03
Ru	1.28
Zr	0.82

* Excess lanthanum was added as a stand-in for all rare-earth fission-product elements except cerium.

DISSOLUTION

Complete dissolution of the 'fissium' alloys representing 10 per cent burnup is not easily accomplished. From an investigation of various types of fusions or acid systems as solvents for 'fissium', two satisfactory methods were evolved: (1) the 'sealed-tube' method of Wichers[15], and (2) dissolution in a hydrochloric–perchloric acid solvent mixture from which ruthenium is distilled.[14]

In the 'sealed-tube' method, 7 ml of 12*M* hydrochloric acid is added to a 1–2 g sample in a 10-mm i.d. quartz tube approximately 18 in. long which is sealed at one end. Four drops of 70% perchloric acid are added, and the tube is sealed and placed in a steel shell (Fig. 1). Before screwing the cap on tightly, a calculated amount of dry ice

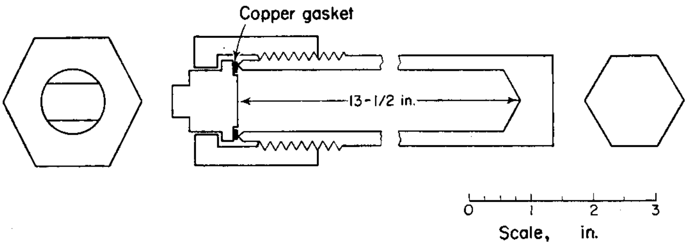

FIG. 1.—Steel shell for protection of sealed tube.

is added, partially to equalize the pressure inside and outside the quartz tube. Then the tube is heated at 300–325°C for about 2 hr or until dissolution is complete. A quartz tube must be used to avoid contaminating the sample with zirconium which is present in glass, and the hydrochloric acid must be 12*M* to dissolve zirconium.

In the second method, which is generally used, the sample is reacted with hydrochloric acid in a quartz still and excess acid and water are removed by evaporation. About 10 ml of 60% perchloric acid are added, an air-cooled condenser and a trap containing 3*M* sodium hydroxide are attached, and the reaction mixture is heated to strong fumes. A slow flow of air, bubbled through the boiling mixture, carries the ruthenium tetroxide that is formed into the trap. A 1–2 g sample is usually dissolved in about 40 min, and the ruthenium is quantitatively separated from the remainder of the sample. If large amounts of plutonium oxide are present, dissolution is not complete. In that case, the mixture in the still pot is centrifuged, and the residue is dissolved by heating in hydrofluoric, nitric and sulfuric acids. The 'sealed-tube' method is preferred for oxidized samples.

SPECTROPHOTOMETRIC METHODS

Ruthenium

One of the methods investigated for dissolving the residue remaining after treating 'fissium' alloy with hydrochloric acid consists of refluxing the residue with a perchloric acid–hydrochloric acid mixture. Although this proved to be an unreliable dissolution method, it was observed that the solution formed was intensely colored. The absorption spectrum varied from sample to sample, however, presumably due to variation in the oxidation state of the ruthenium, and methods for obtaining uniformity in color development were investigated. By reducing all the ruthenium to the Ru^{III} oxidation state with sulfurous acid, and then oxidizing the ruthenium in 6*M* hydrochloric acid solution to the Ru^{IV} valence state with chlorine, reproducible results were obtained. The absorbance of the ruthenium chloro compound is a maximum at 485 mμ where the molar extinction coefficient, or molar absorptivity, is about 5300. Beer's Law is obeyed up to a ruthenium concentration of 15 μg/ml.

The fission-product elements and iron at concentrations equal to the ruthenium do not interfere. Thus, ruthenium in 'fissium' solutions can be determined without separation.[11] Nitrate and larger amounts of iron, however, interfere with the determination. With the advent of iron–plutonium 'fissium' and nitrate-containing dissolver solutions, the method failed and a separation of the ruthenium became necessary.

By using the dissolution method in which ruthenium is distilled into 3*M* sodium hydroxide, separation of the ruthenium is achieved. In addition, all the ruthenium is converted to one oxidation state which may be reduced by hydrochloric acid to form the highly colored Ru^{IV} chloro complex. Possible reactions for this reduction are shown in Table II. Equation 4 shows that excess acid increases the stability of ruthenium tetrachloride. Spectra for the ruthenium chloro compound formed by sulfurous acid reduction–chlorine oxidation of a ruthenium solution and by hydrochloric acid reduction of ruthenium tetroxide are identical, as shown in Fig. 2. It was concluded that the end product is the same by either method of formation.

TABLE II.—REACTIONS OF RUTHENIUM IN SODIUM HYDROXIDE AND HYDROCHLORIC ACID

Equation no.	Reaction
1	$RuO_4 + 2OH^- \rightleftharpoons RuO_4^{2-} + H_2O_2$
2	$RuO_4 + 6HCl \rightleftharpoons H_2RuO_2Cl_4 + 2H_2O + Cl_2$
3	$H_2RuO_2Cl_4 + 2HCl \rightleftharpoons RuCl_4 + Cl_2 + 2H_2O$
4	$RuCl_4 + H_2O \rightleftharpoons Ru(OH)Cl_3 + HCl$

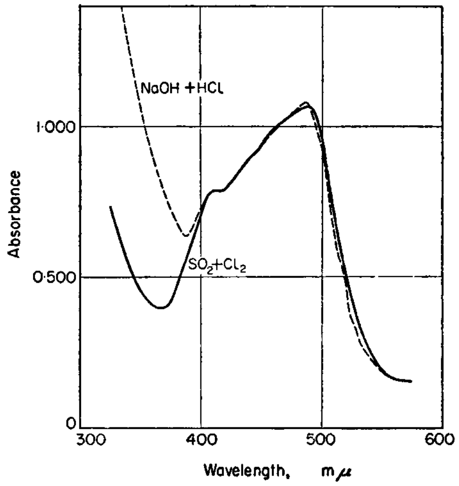

FIG. 2.—Absorption spectra of Ru^{IV} chloride.

Based upon this Ru^{IV} chloride formation and the distillation method of dissolution, ruthenium is determined using the procedure described in Table III.[4] For sixteen determinations of 70–280 μg of ruthenium, the coefficient of variation was 0.9 per cent.

TABLE III.—DETERMINATION OF RUTHENIUM

(1) Dilute solution in trap to known volume.
(2) Add 10 ml of 12*M* HCl to an aliquot containing 25–400 μg of Ru.
(3) Dilute to 25 ml and heat on a steam bath for 20 min.
(4) Cool, and measure absorbance at 485 mμ.

Variations of ±1 ml in the volume of 3*N* sodium hydroxide or 12*M* hydrochloric acid added do not affect the results. None of the other fission product elements distill with ruthenium, and osmium, which does distill, causes no interference in the spectrophotometric measurement.

Cobalt

A spectrophotometric method, based upon the absorbance of Co^{II} in a hydrochloric acid–acetone solution, was developed for the determination of Co in plutonium.[4] This method is rapid, requiring no separation of the cobalt, and reliable at the cobalt concentrations of 0.5–3 per cent which are encountered in the plutonium–cobalt fuel alloys being investigated. However, application of this method for the determination of trace amounts of cobalt in plutonium is limited by the relatively low molar extinction coefficient of approximately 565 at 665 mμ for the Co^{II} colored compound. Pu^{III} also absorbs at 665 mμ in the hydrochloric acid–acetone medium, but the molar extinction coefficient is small (about 14.5) and equal to the molar extinction coefficient of the plutonium at 785 mμ. As shown in Fig. 3, Co^{II} does not absorb at the higher wavelength. The difference, therefore, between the absorbances at 665 and 785 mμ is the absorbance of the Co^{II} complex alone at the lower wavelength. The spectra in Fig. 3 were obtained by using two solutions, one of which contained only cobalt, and the other, only plutonium. The relative concentrations of cobalt and plutonium are the same as for a binary alloy containing 1.8 per cent cobalt. The absorbance of the Co^{II}

may also be measured at about 695 mμ where Pu^{III} does not absorb significantly, and no correction need be applied. Cobalt is less precisely determined from the absorbance at this wavelength than from the absorbance measurements at 665 and 785 mμ, and the latter technique involving the correction for Pu^{III}, is preferred.

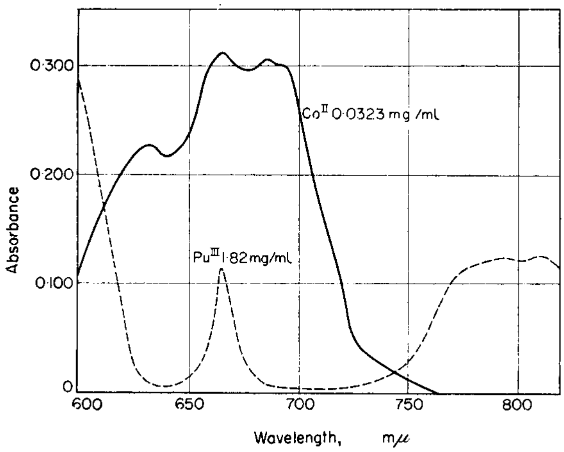

FIG. 3.—Absorption spectra of Pu^{III} and Co^{II} in hydrochloric acid–acetone.

The simplicity of the method is evident from the brief description of the procedure given in Table IV.

TABLE IV.—OUTLINE OF THE PROCEDURE FOR THE DETERMINATION OF COBALT

(1) Remove an aliquot containing 3–18 mg of Co.
(2) Add 0.2 ml of 70% $HClO_4$ and evaporate to incipient dryness.
(3) Add 4 ml of 25% $NH_2OH{\cdot}HCl$ and warm for 15 min.
(4) Add 5 ml of 12*M* HCl.
(5) Dilute to 25 ml with acetone.
(6) Measure absorbances at 665 and 785 mμ.
(7) Subtract A_{785} from A_{665}.

For cobalt concentrations of 0.5, 1 and 3 per cent relative to the plutonium concentration, coefficients of variation of 1.4, 1.2 and 0.3 per cent, respectively, were obtained with solutions of known concentrations. Analyses of three aliquots of a sample solution may be performed in 1 hr.

The metals in "fissium" do not interfere with this determination of cobalt. The error caused by various ions in the concentrations listed in Table V is less than 2 per

TABLE V.—ION CONCENTRATIONS CAUSING LESS THAN 2 PER CENT ERROR

Ion	Ion/cobalt weight ratio
Sr^{2+}	1.0
Ce^{4+}, Cs^{+}, Ru^{4+}, Na^{+}, Zr^{4+}	1.7
Fe^{3+}, La^{3+}, Mo^{6+}	2.5
K^{+}	3.3
Nd^{3+}	7.5
PO_4^{3-}	2000
SO_4^{2-}	2000

cent. Volatile anions such as fluoride or nitrate are eliminated in the evaporation step. The absorbance of the cobalt^{II} complex is constant over a 24-hr period, but the reagent blank develops a light yellow color which does not interfere in the determination.

Cerium

Cerium and lanthanum represent the rare-earth elements in the 'fissium' alloy. Lanthanum is determined spectrochemically, and the spectrophotometric determination of cerium described by Medalia and Byrne[6] was adapted for use with plutonium.[9] As outlined in Table VI, the cerium is separated by oxidizing the plutonium to the Pu^{VI} valence state with persulfate and precipitating the cerium as the fluoride, using lanthanum trifluoride as a carrier. After dissolving the precipitate in sulfuric acid, the cerium is oxidized with silver and persulfate, and the absorbance of the Ce^{IV} is measured at 320 mμ. The Ce^{IV} is then reduced with peroxide and the absorbance is remeasured to determine the blank (Table VI, 9).

TABLE VI.—DETERMINATION OF CERIUM

(1) Dilute an aliquot containing 50 mg of Pu to 10 ml with 1*N* H_2SO_4.
(2) Oxidize with Ag^+ and persulfate.
(3) Add La carrier solution (1 mg La) and 0.5 ml of 48% HF.
(4) Centrifuge, decant the supernate and wash the precipitate with 2 ml of 1*M* HF.
(5) Add 0.1 ml of 18*M* H_2SO_4 to the precipitate and heat at 200°C for 20 min.
(6) Add 7 ml of 1*N* H_2SO_4, 0.2 ml of 0.25% $AgNO_3$, and 1 ml of 2.4% $(NH_4)_2S_2O_8$.
(7) Heat in steam bath, cool and dilute to 10 ml.
(8) Measure the absorbance at 320 mμ.
(9) Add two drops 3% H_2O_2 and measure the absorbance at 320 mμ.

For plutonium alloys containing 0.01 per cent cerium, the coefficient of variation is 5 per cent, but for 0.3 per cent cerium, the coefficient of variation is only 1 per cent. No interference results from a twelve-fold excess, with respect to the cerium, of molybdenum, zirconium and ruthenium; a twenty-four-fold excess of neodymium; a thirty-six-fold excess of cobalt, tantalum and iron; or a forty-four-fold excess of potassium. Large amounts of ruthenium are removed by an initial fuming with perchloric acid. For samples containing less than 0.05 per cent cerium, cells with 10-cm light paths are used to measure absorbance; for higher concentrations, cells with 1-cm light paths are used. At the 0.05 per cent concentration level for cerium, the coefficient of variation of the determination is 1.4 per cent, using cells with 10-cm light paths, as compared to 5.3 per cent when measurements are made using cells with 1-cm light paths.

Iron

This element is determined, without separation from plutonium, as the ferrous-*o*-phenanthrolate complex. One ml of 25% hydroxylamine is added to an aliquot containing 2–40 μg of iron and less than 50 mg of plutonium. After 1 hr, 1 ml of 20% sodium acetate and 1 ml of 0.5% *o*-phenanthroline are added and the solution is diluted to 10 ml. After standing for 1 hr, the absorbance of the solution is measured at 515 mμ. The coefficient of variation of the method is 1–2 per cent.

For plutonium to iron ratios greater than 1000, which are generally not encountered in 'fissium' alloys, a correction for the absorbance of the Pu^{III} is required. This correction is determined from the absorbance of an aliquot of the sample containing all reagents except *o*-phenanthroline. Alternately, the iron may be separated before the spectrophotometric determination by extracting Fe^{III} from 6*M* hydrochloric acid into hexone or other organic solvent, or the plutonium may be precipitated and removed as the oxalate.

Molybdenum

A method was developed in which molybdenum is extracted into hexone from a 6*M* hydrochloric–0.4*M* hydrofluoric acid solution and then determined spectrophotometrically as the chloranilate.[12] In early work, using samples of plutonium–cobalt alloys, the method proved to be very satisfactory, but an additional step in the procedure was required to eliminate interference caused by iron when the method was applied to plutonium–iron alloys. The final procedure is described briefly in Table VII. The molybdenum–chloranilate complex is formed instantly and is stable for several hours, but the absorbance is dependent upon the acidity which must be carefully controlled. Although bismuth, tin and tungsten cause interference in these determinations, none of the 'fissium' elements interfere. For aliquots of known solutions containing 19–96 μg of molybdenum, the coefficient of variation is 1.6 per cent.

TABLE VII.—DETERMINATION OF MOLYBDENUM

(1) Evaporate an aliquot containing less than 100 μg of Mo to dryness with H_2SO_4.
(2) Dissolve the residue in 10 ml of 6*M* HCl–0.4*M* HF containing 0.3% SO_2.
(3) Extract the molybdenum into one 10-ml and two 5-ml portions of hexone.
(4) Back extract into three 5-ml portions of water.
(5) Evaporate the water extract to dryness, acidify, and dry again.
(6) Dissolve the residue in two drops of HCl, add NaOH until basic and warm.
(7) Remove $Fe(OH)_3$ by filtration, and then evaporate the filtrate.
(8) Add 7 ml 2*M* perchloric acid and 3 ml of chloranilic acid solution (9 mg/ml).
(9) Measure the absorbance at 350 mμ and correct for absorbance of blank.

Niobium

This element is separated by extraction into hexone from hydrofluoric–sulfuric acid solution and determined spectrophotometrically using hydroquinone in 18*M* sulfuric acid as the chromogenic reagent.[13] The stepwise procedure is outlined in Table VIII.

Evaporation of the hexone fractions (Table VIII, 3) without first adding base causes charring. Even after the extracts are made alkaline, slight discoloration sometimes occurs, and the final sulfuric acid solutions must be decolorized by oxidation with persulfate.

An absorbance of about 5.5 units/mg of niobium in 10 ml is obtained. For absorbances greater than 0.1, the coefficient of variation of the method is about 2 per cent. Tantalum interferes seriously with the determination. The platinum metals, manganese, molybdenum, titanium and vanadium, also interfere if present in significant

TABLE VIII.—DETERMINATION OF NIOBIUM

(1) Evaporate an aliquot containing 0.025–1 mg of Nb to fumes with H_2SO_4.
(2) Extract the Nb into hexone from a $6.3M$ H_2SO_4–$1.6M$ HF solution.
(3) Add NaOH and evaporate the extract to dryness.
(4) Dissolve the residue in dilute HF.
(5) Add H_2SO_4 and evaporate to fumes.
(6) Cool, and add 3 ml of hydroquinone reagent (55 mg/ml H_2SO_4).
(7) Dilute to 10 ml with H_2SO_4.
(8) Measure the absorbance at 410 mμ.

amounts, but these interfering elements can be eliminated by a second extraction. Because of the unfavorable concentration ratio of molybdenum to niobium of 25 to 1 in 'fissium' alloys, a double extraction is usually necessary.

Zirconium

Spectrophotometric methods for the determination of zirconium based upon the colored complex formed with chloranilic acid have been described by several authors.[2,7,10] Other metals, however, including iron and molybdenum, interfere with this colorimetric method, and separation of the zirconium is necessary. Precipitation of zirconium as the mandelate or halogenated mandelate has been reported.[3,5,8] This method of separation was not previously applied to small samples of zirconium. Preliminary work indicated that 15–100 μg of zirconium could be precipitated quantitatively with *p*-bromomandelic acid from solutions 0.1–$0.2M$ in hydrochloric acid. To eliminate coprecipitation of Pu^{IV}, hydroxylamine is added prior to the precipitant to reduce the plutonium. To obtain a complete separation of the zirconium, a double precipitation is necessary. Based upon these conditions, the stepwise procedure outlined in Table IX was developed.[1]

TABLE IX.—DETERMINATION OF ZIRCONIUM

(1) Dilute an aliquot containing less than 100 μg of Zr to 3 ml.
(2) Adjust acidity to 1–$2M$.
(3) Add 2 ml of 10% hydroxylamine and heat (90°C) for 30 min.
(4) Add 5 ml of 2% *p*-bromomandelate and heat for 30 min.
(5) Centrifuge and wash the precipitate.
(6) Dissolve in seven drops of 70% $HClO_4$ and two drops of HNO_3.
(7) Heat to 200°C, cool, repeat the precipitation.
(8) Dissolve the precipitate in three drops of 70% $HClO_4$ and two drops of HNO_3.
(9) Dilute to 25 ml with $2M$ $HClO_4$.
(10) Add 7 ml of solution to 3 ml of 0.09% chloranilic acid.
(11) Measure the absorbance at 350 mμ.

For less than 20 μg of zirconium the entire solution of the final precipitate is diluted to 7 ml and 3 ml of chloranilic acid solution are added. An absorbance of 9.7 units/mg of zirconium is obtained by this method. For more than 15 μg of zirconium, the recovery is about 98.4 per cent and the coefficient of variation is about 3 per cent. Hafnium is the only known interfering metal.

In summary, two dissolution methods for 'fissium' alloys, and spectrophotometric methods for the determination of most of the elements in plutonium-rich 'fissium' have been described. The spectrophotometric methods are summarized in Table X.

TABLE X.—SUMMARY OF SPECTROPHOTOMETRIC METHODS

Element	Separation	Color-forming reagent	Range, μg	Coefficient of variation, %
Ce	F^- precipitation	$S_2O_8^{2-}$ oxidation	5–150	5–1
Co	None	HCl–acetone	3–18 mg	1.4–0.3
Fe	None	*o*-Phenanthroline	2–40	2
Mo	Hexone extraction	Chloranilic acid	20–100	1.6
Nb	Hexone extraction	Hydroquinone–H_2SO_4	25–1000	2
Ru	RuO_4 distillation	HCl	25–400	0.9
Zr	*p*-Bromomandelate precipitation	Chloranilic acid	15–100	3

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FISSION-PRODUCT ANALYSIS OF FAST-REACTOR PLUTONIUM FUELS*

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Summary—For the purpose of evaluating the pyrometallurgy program at Los Alamos for the reprocessing of fuels from fast reactors, it was necessary to determine fission products in the presence of large amounts of plutonium, especially when low-burnup fuels were to be analyzed. From results of a testing program in which classical analytical methods originally developed for uranium fuels were used to determine fission products, it was shown that adequate decontamination from plutonium and americium was not achieved in a number of cases. New or modified methods were developed for zirconium, niobium, ruthenium, rhodium, cerium, neodymium and praseodymium. All procedures were designed to utilize sample aliquots containing as much as 50 mg of plutonium and to give α-decontamination factors of not less than 10^5 and as high as 10^9, when from 10–50 mg of carrier were added. Ion-exchange methods proved to be the most effective for removing plutonium and americium, in those cases where these elements caused interference. Up to this time, methods for fourteen fission products have been tested or devised for use in the analysis of plutonium fuels.

THIS work was undertaken to test the adequacy of classical fission-product analyses when applied to low-burnup plutonium fuels. The need for this arose in connection with the LAMPRE (Los Alamos Molten Plutonium Reactor Experiment) program, particularly in that part of it directed to developing successful methods for the reprocessing of fast reactor plutonium fuels by both pyrometallurgical and aqueous solution methods. These processes were aimed at reducing fission-product levels in spent fuel to the point where the fuel was suitable for re-use in a reactor.

In order to avoid the necessity of using shielded facilities during the development stages of the reprocessing program, small samples of plutonium weighing 100 mg were exposed to short periods of neutron irradiation, giving an average of 10^{14} fissions per sample. This corresponds to a burnup of 5×10^{-5} per cent, which is extremely low, yet results in sufficient fission-product activity to permit measurement of decontamination of the fuel through a particular reprocessing method. At the same time, analytical procedures are required which will give high α-decontamination values for each fission product which is analyzed. Figure 1 illustrates typical fission-product activities compared to the plutonium activity for such a sample at various periods of time after irradiation. In most cases, α-decontamination factors of 10^6 or greater are necessary. In general, the requirements set up for the fission product analyses were the following: (1) The method should permit the use of aliquots containing up to 50 mg of plutonium, depending on the relative activity of the fission product being analyzed; (2) α-contamination of the separated nuclide should not be greater than 1 per cent of the total β-activity; (3) reproducibility should be within 5 per cent, and (4) the chemical yield should not be less than 50 per cent. In addition, it was desired that no more than 8 hr should be required to perform duplicate analyses by means of a particular method, exclusive of counting time.

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* Work performed under contract with the U.S. Atomic Energy Commission.

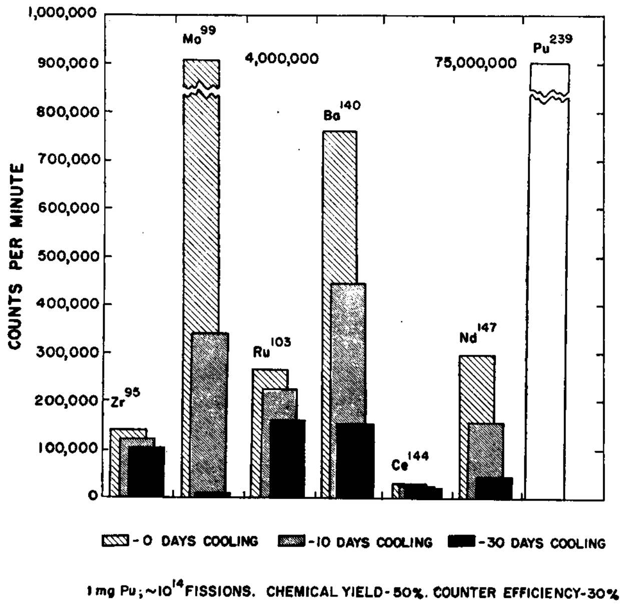

FIG. 1.—Comparison of typical fission-product and plutonium activities.

Up to this time, existing procedures have been tested, or new procedures developed, for the analysis of the following fission products in plutonium fuels; strontium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, cadmium, tellurium, iodine, cesium, barium, cerium, neodymium and praseodymium. The procedures which are described are those which are new, or in which modifications were made in order to meet the requirements outlined above.

SAMPLE PREPARATION

Dissolution

The irradiated plutonium metal disk, weighing 100 mg, was placed in a 100-ml volumetric flask and dissolved by the dropwise addition of several ml of 12*M* hydrochloric acid. After the plutonium was completely dissolved, the solution was made up to 100 ml with 6*M* hydrochloric acid. This was the stock solution from which all aliquots were taken.

Preliminary plutonium removal

In the early part of the development work, it was necessary to perform many of the fission-product analyses on open bench tops. In order to reduce the hazard of handling milligram quantities of plutonium in such a manner, a procedure was adopted to lower the plutonium in the sample aliquot to a low-microgram level. This procedure, which is based on the adsorption of Pu^{IV} on an anion-exchange resin similar to Dowex-1,[8] is outlined below.

Appropriate fission product carriers are added to an aliquot of the stock solution, and the mixture is then evaporated to dryness four times with 16*M* nitric acid. Half an ml of 1*M* hydroxylamine nitrate is added to the moist residue and warmed gently under an infrared heat lamp for 10 min, after which 1½ ml of freshly prepared 1*M* potassium nitrite is added to the mixture to obtain Pu^{IV}. After standing for 10 min, the solution is made $8M$ in nitric acid and passed through a 1 by 10 cm column of Dowex-1-X4 resin in the nitrate form, which had been previously equilibrated with $8M$ nitric acid. The column is then washed with $8M$ nitric acid until a total of 25 ml is collected (sample effluent plus wash solution). The combined effluent contains the fission products, about 0.1 per cent of the plutonium, and any americium originally present in the sample aliquot.

After dry boxes became available for the fission-product analyses, this step was omitted for all procedures except the procedure used in the cerium method.

ZIRCONIUM

Previous methods for the analysis of fission-product zirconium have been based on the precipitation of barium fluozirconate from solutions containing excess fluoride, the presence of which was considered essential to obtain complete exchange between carrier and radionuclide.[3] More recently, Bricker and Waterbury demonstrated the quantitative separation of microgram quantities of zirconium from milligram amounts of plutonium by precipitation with *p*-bromomandelic acid.[1] The method presented herein, which is based on the use of this reagent, has the advantage of avoiding the use of fluoride solutions. Ten milligrams each of zirconium, cerous and tellurium carriers are added to the sample aliquot; the mixture is evaporated to dryness twice with hydrochloric acid. The residue is taken up in $3M$ hydrochloric acid, heated in a boiling water bath, and then saturated with sulfur dioxide gas. Tellurium metal, which is precipitated, is discarded. Enough $12M$ hydrochloric acid is added to the supernatant liquid to make it $5M$ with hydrochloric acid, after which the solution is heated, and $0.01M$ *p*-bromomandelic acid is added to precipitate the zirconium. After a 15 min digestion period, the centrifuged precipitate is dissolved with a minimum of dilute ammonium hydroxide, and zirconium hydroxide is precipitated from this solution by adding $12M$ sodium hydroxide. After centrifuging and removing the supernatant liquid, the precipitate is dissolved in $5M$ hydrochloric acid, tellurium and cerium carriers are again added, and the tellurium, zirconium *p*-bromomandelate and zirconium hydroxide precipitations are performed a second time. The second zirconium hydroxide precipitate is dissolved, cerium carrier is added, and a third *p*-bromomandelic acid precipitation is made from the hot $5M$ hydrochloric acid solution. The precipitate is removed by filtration and washed successively with $5M$ hydrochloric acid, water, ethanol and ether. After drying for 15 min at 110°C, it is weighed as zirconium tetrabromomandelate to determine the yield, and then mounted for β- or γ-counting.

The elements most likely to interfere are tellurium, americium and plutonium. Tellurium is eliminated by the two scavenging steps, and also by performing the *p*-bromomandelic acid precipitations from $5M$ hydrochloric acid. At lower acid concentrations, increasing amounts of tellurium coprecipitate. Plutonium is most effectively eliminated by insuring that it is in the trivalent state during the *p*-bromomandelic acid precipitation; this reduction is accomplished by the sulfur dioxide added during the tellurium precipitation. The addition of a cerous hold-back carrier is essential for decontamination from americium. Typical tests showed that americium contamination is likely to be 10^3 times greater in the absence of a cerium hold-back carrier.

The average yield is 70–80 per cent. Four aliquots may be analyzed simultaneously in 5 hr. The standard deviation for a single determination is 2 per cent. Parallel analyses made by this method and the fluoride method gave results which agreed within 1 per cent, which indicates that isotopic exchange is satisfactory. The α-decontamination factor is 10^7.

NIOBIUM

This procedure is a modification of one described by Morris and Scargill[7], in which a general separation is first achieved by niobic acid precipitation, followed by extraction of the niobium into tributyl phosphate from a fluoride solution to eliminate any zirconium coprecipitated with the niobic acid.

Ten milligrams of niobium carrier (in oxalic acid) is added to the irradiated plutonium aliquot, plus ten milligrams each of zirconium and tellurium hold-back carriers. After allowing the solution to stand for 15 min, an equal volume of $16M$ nitric acid is added, the mixture is heated and 0.5 g of sodium bromate is added to destroy the oxalate and allow niobic acid to precipitate. The niobic acid is centrifuged and washed once with $8M$ nitric acid. It is then dissolved in 1 ml of saturated oxalic acid, and 10 mg of copper carrier is added. The solution is then adjusted to $1M$ with hydrochloric acid, heated, and copper sulfide is precipitated by bubbling hydrogen sulfide through the solution for 2 min. The copper sulfide is removed by centrifugation and discarded. Ten milligrams tellurium carrier is added to the supernatant liquid, and the acidity is adjusted to $3M$ with hydrochloric acid, after which the solution is heated in boiling water, and saturated with sulfur dioxide to precipitate tellurium in the elemental form. After centrifuging and discarding the tellurium metal, the supernatant liquid is made $8M$ in nitric acid, and 0.5 g of sodium bromate is added to precipitate niobic acid. The precipitate is removed by centrifugation and dissolved in 2 ml of $12M$ sulfuric acid plus two drops of $27M$ hydrofluoric acid, after which the solution is transferred to a polyethylene tube. Two ml each of $27M$ hydrofluoric acid and tributyl phosphate is added, and the tube is stoppered and shaken vigorously for 30 sec. After the phases have separated, the tributyl phosphate phase is transferred to a clean polyethylene tube to which 5 ml of $7.5M$ ammonium hydroxide is slowly added and stirred until the acid is neutralized. The mixture is cooled, then shaken with 5 ml of petroleum ether, and the aqueous phase plus precipitate are transferred to a clean tube and centrifuged to separate the niobic acid. This is washed once with 5 ml of $7.5M$ ammonium hydroxide and 5 ml of petroleum ether, and centrifuged. The niobic acid is then slurried and transferred to a platinum crucible with 2 ml of water, dried, and ignited at 800°C for 15 min. The niobic oxide is then slurried with water, filtered onto a Whatman No. 42 filter paper, washed with ethanol and ether, vacuum-dried at room temperature and weighed to determine the yield, after which it is mounted for counting.

The most troublesome contaminants encountered during the development of this procedure were tellurium and antimony. These are removed efficiently by the tellurium metal and copper sulfide scavenging steps. When the procedure was performed on freshly separated zirconium-95, less than 0.3 per cent of the original activity was found in the final niobic oxide, and most of this could be accounted for by growth of niobium-95 during the interval between the final zirconium separation and the initial niobic acid precipitation. Yields range between 60 and 80 per cent, while the standard deviation for a single determination is 3 per cent. The α-decontamination factor is about 10^6. Four simultaneous analyses can be performed in a period of 4 hr.

RUTHENIUM

During the early part of this program, ruthenium analyses were performed by the well-known method involving the distillation of ruthenium tetroxide. Later, while tests were being made of an iodine procedure, it was noticed that under certain conditions considerable amounts of ruthenium accompanied the iodine when it was extracted into carbon tetrachloride. This observation led to the procedure described below.

Ten milligrams of ruthenium carrier is added to the irradiated plutonium aliquot in a small separatory funnel, plus 10 mg of zirconium hold back carrier, and the solution is diluted to 10 ml with water. Sodium hydroxide ($12M$) is added dropwise until a precipitate forms; then ten more drops are added. Ten drops of 5% sodium hypochlorite are added to oxidize the ruthenium, and the vessel is stoppered and set aside for 1 hr to insure complete exchange. Hydrochloric acid is then added dropwise until the olive-green mixture turns yellow. This change in color occurs at a pH of 4, and indicates the formation of ruthenium tetroxide. Ten ml of redistilled carbon tetrachloride is added, and the vessel is stoppered and shaken vigorously to extract the ruthenium. After the phases have separated, the carbon tetrachloride is withdrawn into a second separatory funnel, and the remaining aqueous phase is extracted with a second portion of 5 ml of carbon tetrachloride. The carbon tetrachloride portions are combined and washed with 10 ml of water containing two drops of 5% sodium hypochlorite, after which the organic layer is transferred into a clean separatory funnel. The ruthenium is extracted from the carbon tetrachloride by shaking it with 10 ml of $3M$ sodium hydroxide containing one drop of $1M$ sodium bisulfite. The sodium hydroxide solution is transferred to a 25-ml volumetric flask, and diluted to volume with water. The chemical yield is determined by measuring the absorbance at 485 mμ of the $\mathrm{Ru^{IV}}$ chloro complex[4], prepared by diluting 1 ml of the sodium hydroxide solution to 25 ml with $5M$ hydrochloric acid and heating the solution on a steam bath for 15 min. The radioactivity is determined by reducing the ruthenium in a 20-ml portion of the sodium hydroxide solution with 2 ml of ethanol, producing ruthenium hydroxide, which is filtered, washed with water and alcohol, and dried at 110°C before mounting for β- or γ-counting.

The chief advantage of this method is the elimination of the classical distillation step by substitution of the rapid and nearly quantitative extraction step; this is possible because of the favorable distribution ratio of 58 shown by ruthenium tetroxide between carbon tetrachloride and water.[5] The only contaminant encountered during the development of this procedure was zirconium which contaminated the ruthenium when no hold-back carrier was added prior to extraction. Iodine is not extracted under these conditions. Yields are generally greater than 95 per cent, and the α-decontamination factor is 10^5. The standard deviation of a single determination is 1 per cent. Four determinations may be performed simultaneously in a period of 3 hr which includes 1 hr required to effect oxidation and exchange.

RHODIUM

This procedure was adapted from a combination of two methods, one described by Stevenson *et al.*[10], and the other by Seiler[9]. It is the only one of several tested which gives good decontamination from tellurium and plutonium. Of these two contaminants the most troublesome is tellurium, which is not removed completely by any one step, but only by the combination of steps described herein, ending with the final potassium rhodium nitrite precipitation.

Ten milligrams each of rhodium and palladium carriers is added to the sample of irradiated plutonium in hydrochloric acid, and the solution is heated to the boiling point to effect the isotopic exchange. The solution is then cooled to room temperature and diluted with enough water to make it $1M$ in hydrochloric acid. Palladium iodide is precipitated by adding about 0.4 ml of $0.5M$ potassium iodide. After standing for 5 min, the mixture is centrifuged, and the supernatant liquid, which contains the rhodium, is transferred to a small Erlenmeyer flask, along with an equal volume of $12M$ hydrochloric acid. Two grams of potassium iodide crystals are added to the solution which is then boiled gently on a hot plate for 20 min in order to attain complete precipitation and adequate coagulation. After removal of the precipitate by centrifugation, it is washed once with $6M$ hydrochloric acid and centrifuged again. Two ml of 72% perchloric acid are added to the precipitate, and the mixture is carefully heated over a flame to destroy the iodide and volatilize the ruthenium activity. The solution is fumed down to about 0.5 ml, 1 ml each of $16M$ nitric acid and 72% perchloric acid are added, and the mixture is again heated to strong fumes of perchloric acid. (This step also serves to convert the rhodium to the yellow-colored cationic form.) After cooling and diluting the solution to 25 ml with water, 5 ml of an aqueous slurry of Dowex-50-X2 resin is added. Chloride-free 50 to 100 mesh resin in the hydrogen form is used. The mixture is stirred and warmed gently until the yellow color of the rhodium disappears. The slurry of cation-exchange resin is then transferred to a column 1 cm in diameter which is filled to a height of about 1 cm with the same resin. The column is then washed with 10 ml of water followed by 10 ml of $0.5M$ hydrochloric acid. Rhodium is removed from the resin with 10 ml of hot $3M$ hydrochloric acid. The eluate is treated dropwise with $6M$ potassium hydroxide until a precipitate just starts to form. This precipitate is then dissolved with one drop of $12M$ hydrochloric acid. Potassium rhodium nitrite is then precipitated by adding 10 ml of $7M$ potassium nitrite and heating the solution for 15 min in a boiling water bath. After centrifuging, the precipitate is dissolved by heating it gently with 1 ml of aqua regia. The solution is then diluted to 15 ml with water, and the potassium rhodium nitrite is reprecipitated, after which it is filtered onto a Whatman No. 42 filter paper, washed with water, ethanol and ether, dried at 110°C, and weighed to determine the yield. The precipitate is then mounted on a suitable plate for counting.

The chemical yield of this procedure is about 70 per cent, with an average α-decontamination factor of 10^6. The standard deviation of a single determination is 4 per cent when β-counted and 3 per cent when γ-counted. Four samples may be analyzed in a period of 4 hr.

NEODYMIUM AND PRASEODYMIUM

Fission-product lanthanum is unsuitable as an indicator of rare-earth clean-up in a fuel reprocessing method because, owing to its genetic relationship to its parent, it tends to follow barium-140. Cerium also is unsuitable because of its 4+ valence. Praseodymium and neodymium are the next most abundant rare-earth fission products and may be expected to display behavior typical of rare-earth elements.

Rare-earth analysis in a plutonium fuel is a difficult problem because of the chemical similarity of plutonium and americium to the rare-earth elements. In the method described herein, the problem is attacked by dividing the analysis into three parts: (a) plutonium and americium are removed simultaneously from the fission products by adsorbing them on Dowex-1 resin from a thiocyanate solution[2]; (b) the rare-earth group is separated from the fission products by a series of fluoride and hydroxide precipitations; (c) the individual rare-earth elements are separated by elution from Dowex-50 resin with 1*M* lactic acid at a pH of 3.15 [6].

To an aliquot of the hydrochloric acid solution of the irradiated plutonium are added 10 mg each of praseodymium and neodymium carriers, plus 1 ml of 2*M* hydroxylamine hydrochloride, and the mixture is evaporated to dryness. The residue is dissolved in a small volume of water and again evaporated to dryness. This residue is dissolved in 5*M* ammonium thiocyanate, and passed through a column of Dowex-1-X8, 100- to 200-mesh resin, previously washed thoroughly with 5*M* ammonium thiocyanate. Americium and plutonium are both adsorbed, while the rare-earth elements and other fission products pass through. The column is washed with 20 ml of 5*M* ammonium thiocyanate, and this wash solution is combined with the sample effluent. The rare-earth elements are then precipitated once with ammonia, twice with hydrofluoric acid, and then twice again with ammonia. The last hydroxide precipitate is dissolved in several drops of perchloric acid, diluted to ½ ml with water and applied to a 0.5- by 30-cm column of Dowex-50-X4 resin in the ammonium form (the medium fraction, from a 200- to 400-mesh resin, which has a settling rate in water of 1–2 in./min, is used to fill the column). The rare-earth elements are eluted with 1*M* lactic acid, buffered at pH 3.15 with ammonia. Eluate fractions of about 1½ ml are collected. The neodymium peak is attained in about 14column volumes, while that of praseodymium is reached in 18 column volumes, as shown in Fig. 2. By adding 0.5 ml of saturated oxalic acid to each fraction in these regions, the fractions containing the two separated rare-earth elements may be identified. After rejecting fractions which show cross-contamination (by examination with a γ pulse-height analyzer), appropriate fractions are combined and the oxalate precipitates are removed by centrifugation. Each precipitate is then dissolved in a minimum of nitric acid, diluted with water

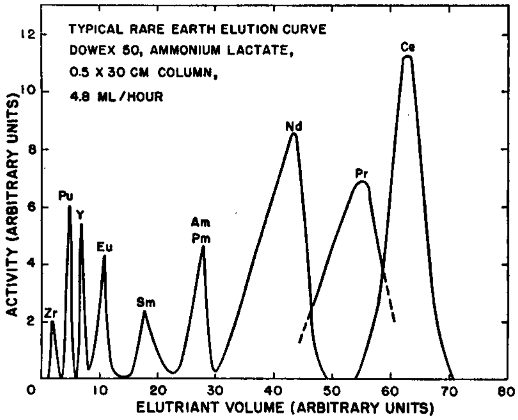

FIG. 2.—Typical rare-earth elution curve.

until the solution is 0.4*M* in nitric acid, and reprecipitated with oxalic acid. After filtering and washing the precipitate with water, ethanol and ether, each precipitate is vacuum dried at room temperature, and then weighed and counted.

Because of the rejection of cross-contaminated fractions, yields are low, ranging from 30 to 50 per cent. Even if neodymium alone is to be determined, it is necessary to use a praseodymium carrier, inasmuch as the praseodymium elution peak is shifted towards the neodymium elution peak if no praseodymium carrier is added. The standard deviation of a single determination is 3 per cent for either element. The α-decontamination factor is 10^6. Four determinations may be made in a period of 8 hr.

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CONCENTRATION OF RADIOACTIVITY AND DETECTION OF COBALT-60 AND ZINC-65 IN RAINOUT

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Summary—Ion-exchange resins have been used to concentrate, isolate and determine low levels of radioactive contaminants in rainwater. After the particulate and associated activities are removed by filtration, the ionic materials are retained on cation- and anion-exchange resin columns which are arranged in series.

This technique lends itself to the concentration of the low-level activities because the filtered rainwater contains a negligible amount of solids. Consequently, a large volume can be passed through the resin columns before the exchange capacity is approached.

Gamma scintillometry was used to identify the γ-emitters in each of the components in this concentration study. In addition to the expected fission-product activities in rainout, photopeaks attributed to Co^{60} and Zn^{65} were discernible. Despite the fact that the activity levels of these nuclides were very low, their photopeaks were considered to be significant. However, for positive identification, quantitative separation was required.

A sequential elution scheme based on the anionic adsorption of cobalt and zinc in solutions containing HCl in high concentration was used to separate the cobalt from the zinc, and from other anions adsorbed on the Dowex-1-(Cl) resin. Following elution, each nuclide was radiochemically isolated for quantitative measurement.

INTRODUCTION

THE determination of radioactive materials in environmental samples has become a problem of universal interest. A satisfactory analysis of rainfall, the major carrier of radioactive fallout, will indicate the concentration of radioactive nuclides. Analytical difficulty arises from the necessity of analyzing large sample volumes in order to obtain a significant value for the low levels of specific radionuclides present. Since the concentration of solutions of low ion content is one of the major functions of ion exchange resins, this property has been utilized in the determination of radionuclides in rain.

Basic ion exchange principles, kinetics and equilibrium phenomena have often been discussed in detail and will not be reviewed in this paper. Chemical separations of metallic elements in anion exchange systems have been intensively studied in recent years.[1,2,3] Adsorption and desorption of many metal complexes can be controlled by changing the acidity or anion content of influent solutions.

Adsorption equilibria in acid media and radiochemical separation of metal complexes by anion exchange resins are presented in several reports.[4,5,6] In these reports, practical separation schemes are discussed which provide quantitative chemical yields with radiochemical purity equivalent to that obtained in the most stringent analytical procedures. With a chemically pure eluate, any γ-emitter can be transferred directly to a scintillation spectrometer for assay and verification of purity. If additional radiochemical separation becomes necessary, simplified procedures can be employed, resulting in an increase in overall chemical yield.

To ascertain optimal separation conditions for the metal complexes on anion exchange resins, distribution coefficients over a wide range of conditions are usually required. Since this investigation was primarily concerned with concentrating, separating and identifying the induced radionuclides, Co^{60} and Zn^{65}, in Cincinnati rainout, the study was concentrated on these and on the most abundant interfering nuclides. Studies of the adsorption of these nuclides on an anion resin over the entire hydrochloric acid range, indicated that both cobalt and zinc can be completely absorbed on a Dowex-1 resin from a $12M$ HCl solution.[2] Cobalt can then be desorbed in $2M$ HCl, and zinc in $0.1M$ HCl.[3]

MATERIALS

Resins

Cation—Dowex-50W.

Anion—Dowex-1.

Table I lists the manufacturer's specifications and lot analyses of these two resins. Prior to use, both resins were washed consecutively with ethyl alcohol, ammonium hydroxide, hydrochloric acid and distilled water to remove excess amines and other impurities, and to convert the resins to their desired ionic form.

TABLE I.—SPECIFICATIONS OF DOWEX-50W AND DOWEX-1 RESINS

Type	Dowex-50W Strong acid	Dowex-1 Strong base
Cross linkage	8	8
Total exchange capacity		
Wet volume, mequiv./ml	2.2	1.3
Dry basis, mequiv./gm	5.2	3.7
Moisture content, %	54.1	42.4
Mesh size, mesh/in.	50–100	50–100
Lot No.	91273	20099

Tracers

Table II lists pertinent information on the γ-radionuclides used in this study. These tracers were not purified.

TABLE II.—TRACERS INVESTIGATED

Nuclide	Chemical form	Source	Half-life	Principal gamma energy, *MeV*
Co^{60}	$CoCl_2$	ORNL	5.3 years	1.17 and 1.33
Zn^{65}	$ZnCl_2$	ORNL	250 days	1.12
Zr^{95}–Nb^{95}	Oxalate solution	ORNL	65 days	0.72 and 0.76
Sr^{85}	$SrCl_2$	AECL Ottawa	65 days	0.51
Cs^{137}	CsCl	ORNL	33 years	0.66
Ce^{144}–Pr^{144}	$CeCl_3$	ORNL	282 days	0.134

Chemicals

All chemicals were of reagent grade and required no additional purification with the exception of zirconium which was received as the oxychloride and was converted to the nitrate.

EQUIPMENT

All γ-spectra were measured with a 100-channel analyzer (RIDL Model 3300) in conjunction with a 4 in. by 4 in. NaI (thallium activated) solid scintillation detector. Total γ-activities were determined with an RIDL Model 2001 scaler used in conjunction with a 2 in. by 2 in. NaI (thallium activated) solid scintillation detector. Beta measurements were made using an internal proportional gas flow counter (NMC Model PC-3A).

Initially, the tracer experiments involved passage of a single radionuclide through a small resin column. Both the resins and tracer solutions were γ-counted in 8-oz wide-mouth polyethylene bottles. To assure comparability of γ-measurements, these solutions were adjusted to the same sample volume before being scanned and counted. The sample bottles were placed directly on the solid detector and the γ emissions counted for a suitable time. As the sequential elution study progressed, each resin column was counted *in situ* to determine the removal of each nuclide after a specific operation, without disturbing the position of the nuclide on the resin.

For gross β determinations, the samples were dried under infrared lamps in aluminum planchets 2 in. in diameter and counted in an internal proportional counter.

EXPERIMENTAL

Gamma spectra of the dissolved radioactivity from 26 l. of Cincinnati rain concentrated on 10-g columns of Dowex-50W-(H) and Dowex-1-(Cl) in series are shown in Figs. 1 and 2. Readily discernible on the cation resins are the Ce^{144}–Pr^{144} peak at 0.14 MeV, the $Ru^{103-106}$ peak at 0.50 MeV, the Zr^{95}–Nb^{95} peak at 0.74–0.76 MeV, and the K^{40} peak at 1.4 MeV. Between 1.0 and 1.4 MeV, several smaller γ-photopeaks

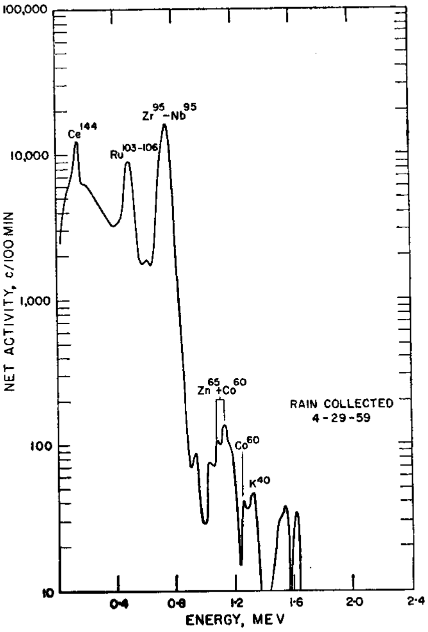

FIG. 1.—Dissolved radioactivity from 26 l. Cincinnati rain concentrated on 10 g Dowex-50W (H^+) cation resin.

are visible, but their significance as representing Co^{60} and Zn^{65} could not be determined without supplementary radiochemical separation. Similarly, the photopeak for Cs^{137} (0.66 MeV), if present, is masked by the very large Zr^{95}–Nb^{95} peak. Only with separation and radiochemical analysis would its existence be confirmed.

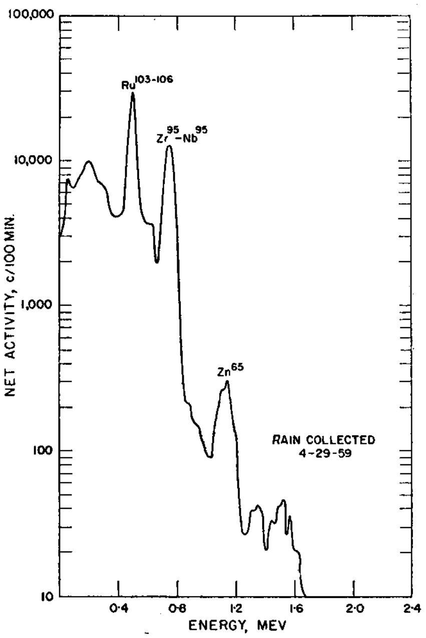

FIG. 2.—Dissolved radioactivity from 26 l. Cincinnati rain concentrated on 10 g Dowex-1 (Cl^-) anion resin.

The predominant photopeaks in the γ-spectrum of the anion resins are those associated with Zr^{95}–Nb^{95} and $Ru^{103-106}$. Inasmuch as the Zr^{95}–Nb^{95} is adsorbed on both the cation and anion resins, a separation scheme for a quantitative determination of these ions becomes complicated. Sequential elution would be facilitated if all the Zr^{95}–Nb^{95} could be complexed in such a manner as to cause its entire adsorption on the anion resin.

To ascertain the effect of chloride complex adsorption, concentrated HCl was used to elute the activities from the cation resin. The resultant acid concentration of the eluate (10*M* in HCl) was considered satisfactory for the adsorption of specific elements on the anion resin column. Ten column volumes (92 ml) of concentrated HCl eluted 100 per cent of the zinc, 95 per cent of the cobalt and 55 per cent of the zirconium–niobium from the Dowex-50W resin column, and 20 column volumes of 10*M* HCl passed through the anion exchange resin before zirconium and cobalt leakage occurred.

However, after investigating various HCl concentrations for the sequential elution of the Zr^{95}–Nb^{95}, Co^{60} and Zn^{65}, it soon became evident that the overlap between these nuclides was too great for a feasible quantitative separation scheme. In addition, the large volumes of strong acid required, made the operations impractical.

Zirconium–niobium were the interfering nuclides in this separation. Graphs[6] of distribution coefficients disclosed that they formed strong fluoride complexes in specific concentrations of HCl–HF. Further tracer studies with various HCl–HF mixtures resulted in a satisfactory sequential elution scheme for cobalt, zinc, zirconium and niobium. The activity eluted from the cation resin with concentrated HCl was passed over an anion resin column previously washed with 12*M* HCl. The zirconium activity, now complexed on the anion resin, was eluted with 5 column volumes of an 8*M* HCl–0.3*M* HF mixture. To remove all the HCl without leaving intermediate acid concentrations on the column, several column volumes of ether were passed through the resin column. The cobalt was eluted next with 5 column volumes of 0.5*M* HCl–0.3*M* HF; the zinc by 25 column volumes of 0.05*M* HCl–0.3*M* HF, and finally the niobium with 20 column volumes of 1.0*M* HNO_3. The elution curve as developed for these conditions is plotted in Fig. 3.

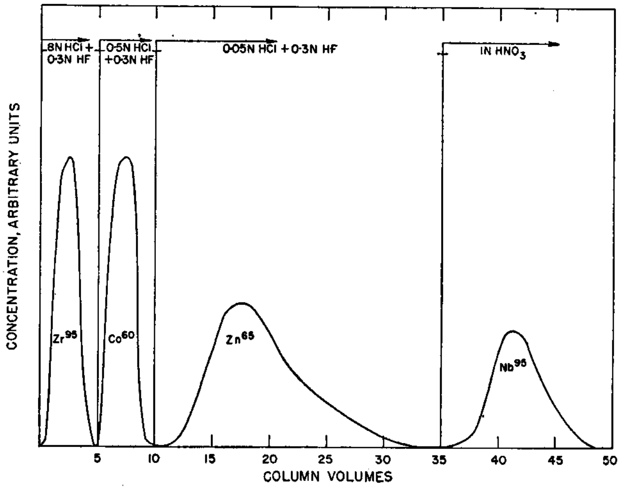

FIG. 3.—Sequential elution of Dowex-1. Method No. 1.

In a concurrent tracer study it was found that 10 column volumes of 0.1*M* HF quantitatively elutes the zirconium–niobium from the cation resin without affecting the cobalt, zinc or other cations present, and that in a 0.1*M* HF medium this Zr^{95}–Nb^{95} is completely retained on an anion resin. Subsequent studies showed evidence that when as little as 0.005*M* HF is present in a cation influent, the Zr^{95}–Nb^{95} passes through the cation resin and is retained on an anion resin. Other ions, not complexed by the HF, are adsorbed directly on the cation resin.

Based on these exploratory tracer studies, a more simple sequential separation scheme was developed. Of the tracer radionuclides under investigation, all the Zr^{95}–Nb^{95} was retained on the Dowex-1 resin, while all the Ce^{144}–Pr^{144}, Cs^{137}, Co^{60}, Zn^{65} and Sr^{85} was adsorbed on the Dowex-50W column. When the Dowex-50W column was eluted with concentrated HCl and this effluent was put through a new anion column, the cobalt and zinc, which form chloride complexes, were retained on the anion resin while all the other ions passed through.

Figure 4 depicts the elution technique as finally formulated. The cobalt activity is quantitatively separated from the zinc by passing 5 column volumes of 1*M* HCl through the anion resin, after which the zinc can be recovered in 20 column volumes of

1*M* HNO_3. Quantitative recovery of the Zr^{95}–Nb^{95} from the first anion resin column is similarly accomplished with 15–20 column volumes of 1*M* HNO_3.

In a corroborative study, using large volumes of influent, duplicate 20-l. samples of distilled water plus tracers and carriers were concentrated on the cation and anion exchange resins. In one carboy the solution was made 0.007*M* in HF*. After passage of the solutions through identical resin columns in series, the activity on each was identified and compared (Fig. 5). The resin spectra showed that only Zr^{95}–Nb^{95} is affected by the addition of dilute HF. In the presence of HF, the Zr^{95}–Nb^{95} is quantitatively adsorbed on the anion exchange resin, while it is only partially adsorbed without HF; part remains on the cation resin, and part leaks through the effluent. Gamma spectra subsequently recorded, following each of the sequential elutions of the resins, showed that the addition of HF to the influent did not alter the sequential elution efficiency.

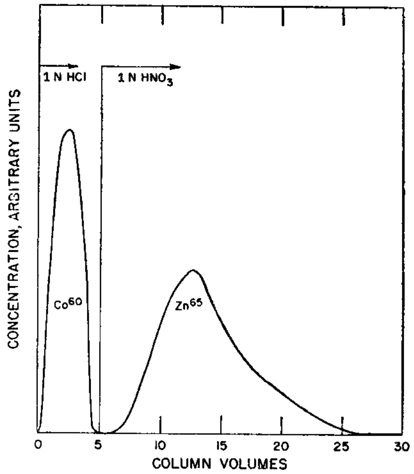

FIG. 4.—Sequential elution of Co and Zn on Dowex-1. Method No. 2.

CONCENTRATION OF RADIOACTIVITY IN LOCAL RAINOUT

Preliminary experiments indicated that the radioactive composition of the Cincinnati rains was predominantly Zr^{95}–Nb^{95}, $Ru^{103-106}$, $Ce^{141-144}$, Cs^{137}, Sr^{89-90}, and K^{40} (Figs. 1 and 2). Gamma spectra showed that other radionuclides, such as Co^{60} and Zn^{65}, might be present. Because of the very low levels of their activities, combined with the relatively poor sensitivity of gamma detection in the range 1.0–1.4 MeV, additional analysis was necessary to assure positive identification.

Large volumes of rain were deemed necessary to assure significant results for the individual radionuclides to be detected by the 100-channel analyzer. However, evaporation of such large volumes would be extremely tedious and precipitation of such large volumes is not practical on a laboratory basis. Consequently, ion exchange was utilized for concentrating the radionuclides.

Upon completion of the tracer studies to develop the most effective method for

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* The solution with no HF contained approximately twice the cerium activity as the other solution. All other nuclides were at approximately the same activity in each sample.

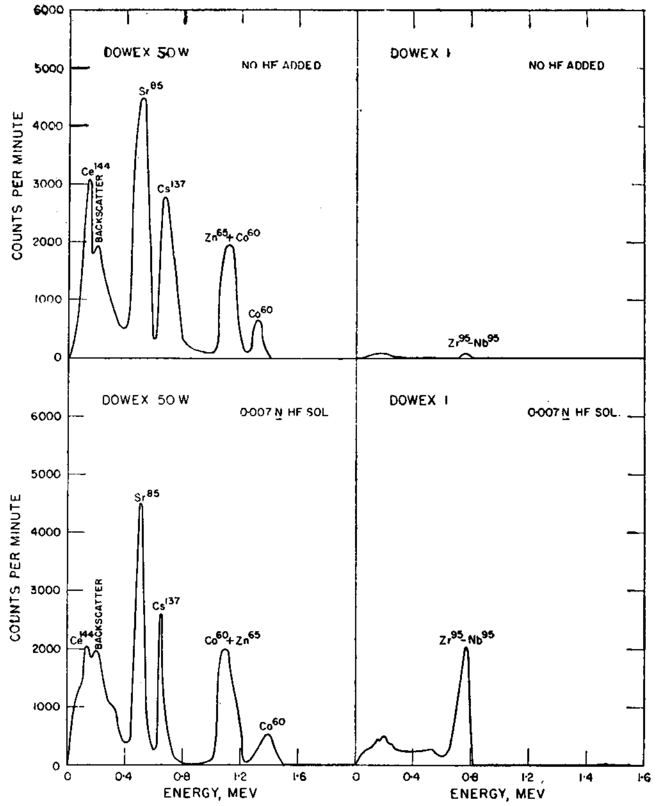

FIG. 5.—Comparison of tracer activity on 10 g cation and 10 g anion resin from 20 l. of spiked distilled water with and without addition of hydrofluoric acid.

sequentially separating the metal anion complexes, filtered (No. 41 Whatman filter paper) rain samples were concentrated on cation and anion exchange resin columns in series.

After removal of the particulates by filtration, the rain sample was put through the two resin columns at an average flow rate of 8–10 ml/min. With the insertion of a glass wool plug before and after each column, no clogging due to particulate matter was encountered. Addition of HF, as discussed previously, overcame the leakage of Zr^{95}-Nb^{95} noted in the initial runs, and concentration of the radioactivity from rainout became quantitative, provided the capacity of the resin column was not exceeded.

When it was ascertained that 10-g columns of Dowex-50W and of Dowex-1 resins satisfactorily concentrated up to 50 l. of filtered rain, all subsequent concentration studies were carried out with such columns. A sketch of the ion exchange apparatus is shown in Fig. 6.

To permit later chemical treatment for verification of the identity of the activity for quantitative assay and for determination of the chemical yield, the following carriers were added to each carboy:

Sr^{2+}	96.9 mg
Cs^{+}	39.6 mg
Zr^{4+}	51.5 mg

Co^{2+}	40.0 mg
Zn^{2+}	40.0 mg
Ce^{3+}	38.6 mg.

At the same time, 5 ml of concentrated HF was added per 20 l. of rain to complex the zirconium and niobium.

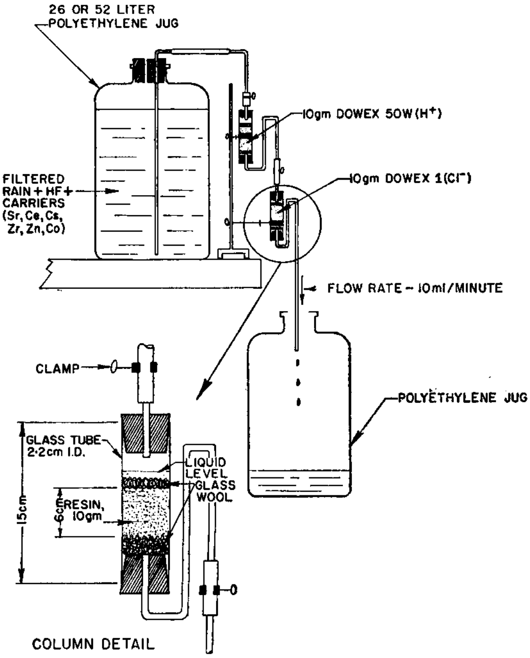

FIG. 6.—Ion exchange concentration apparatus.

Upon completion of the run, the total γ-activity and a γ-spectrum for each resin column was obtained. Figures 7 and 8 depict typical spectra of a Dowex-50W and a Dowex-1 resin after passage of 50 l. of local rain. It will be noted that there is no 0.74–0.76 MeV peak indicative of Zr^{95}–Nb^{95} on the cation resin in Fig. 7. These rains also contain a considerably smaller total activity than the earlier rains in Figs. 1 and 2, even though twice the volume of rain was concentrated. This can be attributed to the decay of nuclides of shorter half-life in the five month period between rain collections.

The previously developed elution procedure was followed for quantitative analyses of the rain. Although each 10-g resin column had a volume of 9.2 ml, an approximate value of 10 ml per column volume was used for convenience. All cations were first removed from the Dowex-50W resin by the passage of 20 column volumes of 12*M* HCl. When this Dowex-50W resin was gamma scanned, only ruthenium and some cerium remained on the column.

This 12*M* HCl eluate was passed very slowly (0.1–0.3 ml/cm^2 per min) over a second 10-g Dowex-1 resin, previously washed with 12*M* HCl. The cobalt and zinc were completely adsorbed on the anion resin while the rare-earth elements, cesium and strontium passed out in the effluent where they were analyzed by standard radiochemical techniques.[7] There was no zirconium or niobium present, since the HF in the original influent had prevented their adsorption on the cation resin.

Ten column volumes of 1*M* HCl eluted 95–98 per cent of the cobalt from the anion column, depending on the flow rate. Zinc was next eluted quantitatively by the passage of 30 column volumes of 1*M* HNO_3. To ascertain both chemical yields and levels of activity, the cobalt was precipitated with 1-nitroso-2-naphthol and ignited to the oxide while the zinc was precipitated as the sulphide (pH 2.5) and similarly ignited. Each precipitate was then counted in an internal proportional counter.

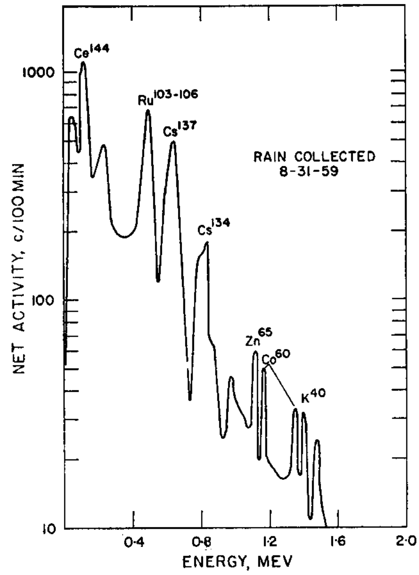

FIG. 7.—Dissolved radioactivity from 50 l. of Cincinnati rain + carriers + HF—concentrated on 10 g Dowex-50W (H^+) cation resin.

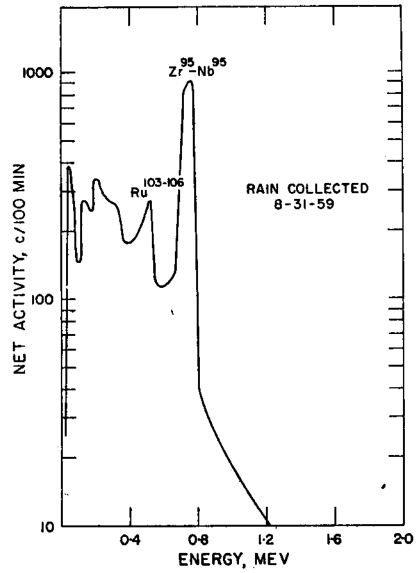

FIG. 8.—Dissolved radioactivity from 50 l. of Cincinnati rain + carriers + HF—concentrated on 10 g Dowex 1 (Cl^-).

The zirconium–niobium activity adsorbed on the original Dowex-1 resin was quantitatively eluted with 15 column volumes of 1*M* HNO_3. The zirconium was then directly precipitated with cupferron from the acid solution and counted as the oxide after ignition.

The analytical results obtained after concentrating the dissolved radioactivity in rainout are summarized in Table III. During 5 months of rain collecting, the gross β-activities associated with the soluble fraction decreased from 1500 μμc/l. to less than 100 μμc/l. During the same period, the Zn^{65} values dropped from 26.5 to 0.1 μμc/l. and the Co^{60} values from 5.5 to 0.5 μμc/l. Inasmuch as the radionuclide analyses were performed on a sample in excess of 20 l., these values must be considered significant and give valid proof of the presence of both Co^{60} and Zn^{65} in Cincinnati rainout.

TABLE III.—RADIOCHEMICAL ANALYSIS OF THE DISSOLVED ACTIVITY IN CINCINNATI RAIN

Date	Rain Concentrated, *l.*	Concentration, *μμc/l.*						
		Gross beta	Sr^{89-90}	Zr^{95}	Co^{60}	Zn^{65}	$Cs^{134-137}$	Total rare earths
4/27/59	26	1485	675	—	5.5	26.5	18.7	99
5/12/59	50	1170	460	20.6	3.5	17.9	8.4	112
6/22/59	73	145	22	4.1	0.5	0.5	8.6	17
7/17/59	50	136	29	1.2	0.6	0.1	1.3	62.5
8/31/59	46	53	9.2	0.5	0.5	0.1	0.9	11.8

SUMMARY AND CONCLUSIONS

The use of fluoride complexes in conjunction with ion exchange has made the concentration and subsequent separation of Co^{60} and Zn^{65} from a large volume of rain a relatively simple procedure.

With cation and anion resins in series, all the ions were adsorbed, provided the exchange capacity of the resins was not exceeded. Zirconium and niobium, which exist in both anionic and cationic states, were converted to their fluoride anionic complexes by making the solutions 0.007*M* in HF prior to the concentration. Thus, they are retained entirely on the anion resin, rather than being distributed over both columns as well as lost in the effluent. The cobalt and zinc, unaffected by this low fluoride concentration, are retained on the cation resin and then eluted with the concentrated HCl. The eluate is then passed through a new anion exchange resin column which retains the cobalt and zinc while passing uncomplexed cations.

By application of the serial elution technique for the desorption of the metallic anion complexes from a Dowex-1 resin, it was possible to collect each radionuclide in a pure condition. This study has shown that, with a definite volume of specific eluant (1.0*M* HCl or 1.0*M* HNO_3), the cobalt, zinc and zirconium fractions can be individually collected for analysis. Stable carriers were added to the original sample before concentration so that the fractions following the sequential elution could be radiochemically assayed, providing positive identification and quantitative results for each nuclide corrected for any losses. Since these nuclides are eluted essentially uncontaminated, simpler radiochemical procedures can be performed for each, assuring greater chemical yield of the analyzed ion. This anionic complexing technique has been successfully applied to rain samples where the particulate and dissolved solid concentrations are very low. It is anticipated that with some modification of the concentration and elution procedures, this sequential elution technique can be applied to other samples, such as stream effluents, which contain greater amounts of suspended and dissolved solids. Studies are proceeding in this direction.

Acknowledgement—This paper is based in part on work performed for the Atomic Energy Commission under Contract AT(49-5)-1288.

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THE DETERMINATION OF ZIRCONIUM-95 PLUS NIOBIUM-95 BY ANION-EXCHANGE SEPARATION FROM OTHER FISSION PRODUCTS*

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Summary—A rapid and simple anion-exchange method is described for the separation of Zr^{95} plus Nb^{95} from other fission products. The zirconium and niobium are adsorbed onto a 7 mm diameter column 100 mm in length of Dowex-1-X4, 100–200 mesh resin from a hydrofluoric acid solution of the fission products. The resin is counted directly, using a 3-in. NaI(Tl) well-type crystal and a gamma scintillation spectrometer. Yields of greater than 99.5 per cent are obtained. The activity levels of the major fission products (Ru^{106}, Cs^{137} and Ce^{144}) are reduced by more than 95 per cent.

Distribution coefficients were established for the adsorption of zirconium and niobium from HF solutions ranging from 0.1 to 6*M* in concentration. Elution characteristics are described for tracer amounts of Ru^{106}, Ce^{144} and Cs^{137} in HF solutions alone and in the presence of macro amounts of U, Fe and Al. The maximum amount of U which can be tolerated and an estimation of the error in counting caused by the displacement of Zr and Nb by U are given.

INTRODUCTION

SINGLE and multichannel energy analyzers have simplified analytical radiochemistry by limiting the need for complete separation of the radioelements and by allowing direct quantitative measurements of individual radioisotopes in radioactive mixtures.

In some cases where the quantity or energy spectrum of certain isotopes precludes the resolution of the characteristic energies of the isotope of interest, a simple and quantitative separation from the major fraction of the other radioelements is sufficient for accurate measurements. Such a method was desirable for the co-determination of zirconium-95 and niobium-95 in the presence of the longer half-lived fission products.

In one method for the separation of Zr^{95} plus Nb^{95}, niobic acid and zirconium phosphate are simultaneously precipitated by the addition of nitric acid and dibasic sodium phosphate.[1] A 3-hr waiting period is recommended for completion of the precipitation and yields average 64 per cent. These limitations were not compatible with our requirements of speed and completeness of recovery.

Elution constants for zirconium and niobium on Dowex-1 in HCl–HF mixtures[2] showed that these elements were more strongly adsorbed as the HCl concentration was reduced. This information suggested the adsorption of zirconium and niobium on Dowex-1 from HF as a means of separating them from other interfering fission product gamma activities.

An anion-exchange method was developed for the simultaneous separation of zirconium-95 and niobium-95 by adsorbing them onto Dowex-1 resin in the fluoride form from a 0.3*M* hydrofluoric acid solution of fission products. The resin was counted directly with a 3-in. NaI(Tl) well-type crystal and 256-channel energy analyzer. Average sample recoveries were 99.5 ± 0.7 per cent.

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* Work performed under Contract No. AT(45-1)-1350 between the Atomic Energy Commission and General Electric Company.

Cs^{137} and Ce^{144} activity levels were reduced by 99.9 per cent and tri- and tetravalent Ru^{106} was reduced by 95 per cent.

U^{VI} was strongly adsorbed while Fe^{III} and aluminium were only slightly adsorbed onto Dowex-1 from $0.3M$ hydrofluoric acid. The total uranium in the column influent must be limited to 400 mg to avoid the loss of zirconium and niobium by displacement on the 7 mm diameter column which is 100 mm long. A 4 per cent decrease in the counting efficiency occurred when 200 mg of uranium was present on the column. This decrease was attributed to the change in the geometry which occurred when the activity was displaced on the resin by the uranium.

DISCUSSION

*Zirconium and niobium distribution coefficients on Dowex-*1-*X*4, 100–200 *mesh in hydrofluoric acid*

A preliminary investigation was made in which it was shown that zirconium and niobium are strongly adsorbed onto a column of Dowex-1 from $1M$ hydrofluoric acid. Distribution coefficients were measured to determine the optimum hydrofluoric acid concentration for the adsorption. Zirconium-95 and Nb^{95} tracers were prepared by carrier precipitation from a fission-product waste solution. The Zr^{95} tracer was prepared just prior to use. The tracer emission rates were about 5×10^8 gammas/min/ml and contained about 1 mg/ml of carrier. Purity of the tracers was confirmed by gamma energy analysis.

The Dowex-1-X4, 100–200 mesh resin was washed with water to remove the fines, then with $1M$ hydrofluoric acid to convert it to the fluoride form and again with water until free of acid. The resin was then oven dried for 4 hr at 100°C and was desiccated in a vacuum for 48 hr prior to use.

The equilibrations were performed by contracting exactly 1 g of dried resin with 10 ml of diluted Zr^{95} or Nb^{95} tracer solutions of varying hydrofluoric acid concentrations. The resin and solutions were agitated in 1-oz polyethylene bottles for 16 hr with a mechanical shaker. One ml portions of each liquid phase were transferred to 10-ml tubes and counted in a 3-in. NaI(Tl) well-type crystal with a 256-channel energy analyzer. The original tracer solutions were assayed under the same sample volume and counting conditions. All subsequent counting measurements were made with this system.

The distribution coefficients were calculated by the equation:

$$K_D = \frac{(\text{Total c/m added} - \text{c/m in solution})}{\text{Grams of resin} \times \text{c/m ml in solution}}.$$

The distribution coefficients (Fig. 1) showed that, over the concentration range investigated, namely from 0.1 to $6M$ HF, the fluoro-complexes of zirconium and niobium are strongly adsorbed onto Dowex-1. The zirconium exhibited a maximum K_D of 3×10^4 at $0.3M$ HF while the distribution coefficient of niobium appeared to approach a maximum of about 7×10^4 at slightly less than $0.1M$ HF.

Elution characteristics of some fission products and macro sample constituents

In order to determine the degree of retention of Cs^{137}, Ce^{144} and Ru^{106} on Dowex-1, column elution studies were made, using the optimum concentration indicated by the distribution coefficients of 0.3M hydrofluoric acid as the elutriant. The columns were made of 7 mm i.d. fluorothene tubing cut in 20-cm lengths. Cotton plugs were used to support the resin. The columns were filled to a depth of 10 cm with Dowex-1-X4, 100–200 mesh resin in the fluoride form.

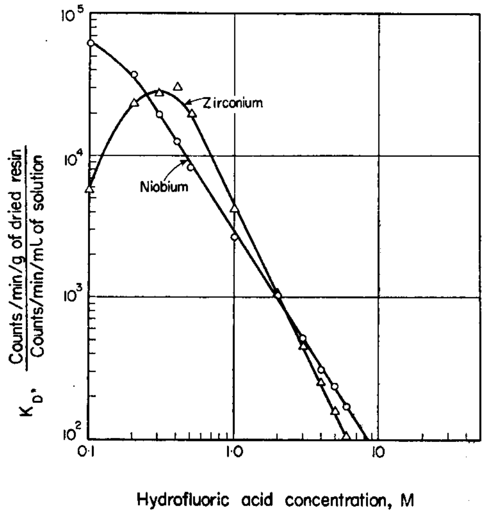

FIG. 1.—Distribution coefficients for zirconium and niobium on Dowex-1-X4, 100–200 mesh in hydrofluoric acid.

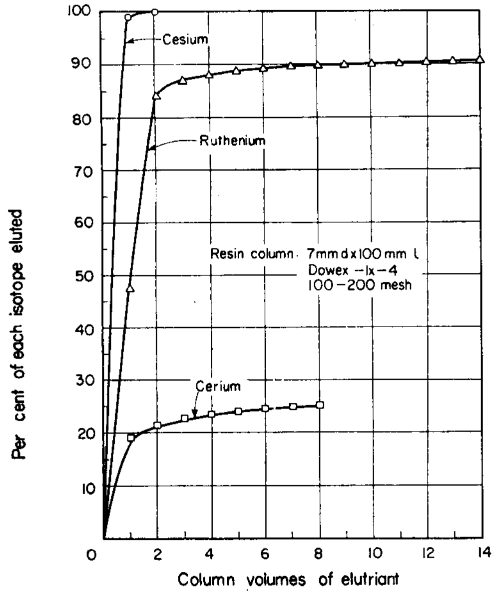

FIG. 2.—Elution of principle fission products with 0.3M hydrofluoric acid.

Cs^{137} *and* Ce^{144}. The Cs^{137} and Ce^{144} tracers were loaded directly onto the columns since only 10 λ of each tracer was required and the anions other than fluoride were considered to be negligible. Four ml fractions (1 column volume) of the eluant were collected and counted. The percentage of each isotope eluted versus the column volumes of eluant is shown graphically in Fig. 2.

The Cs^{137} was not adsorbed, 99 per cent being removed from the resin column in 1 column volume of elutriant. Only 25 per cent of the Ce^{144} was eluted in 8 column volumes of elutriant. The relatively large portion of Ce^{144} retained on the column was probably due to the formation of insoluble fluoride on the resin. In the final method, cerium activity was removed prior to loading the column by introducing a cerium carrier in addition to a zirconium and niobium carrier when converting a solution to the fluoride system. The ammonium hydroxide precipitation and hydrofluoric acid dissolution steps resulted in the formation of insoluble cerium fluoride which was removed by centrifugation.

Ruthenium-106. The Ru^{106} tracer, being in 6*M* HCl and requiring a volume of 200 λ, was converted to a fluoride system to eliminate any possible effect of the chloride. The tracer activity was carried on zirconium hydroxide and subsequently dissolved in 1 ml of 0.3*M* hydrofluoric acid in preparation for column loading. Four ml fractions of the 0.3*M* hydrofluoric acid eluant were collected and counted. From the results which are given in Fig. 2, Ru^{106} (present as Ru^{III} and Ru^{IV}) was shown to be 84 per cent eluted in 2 column volumes, after which the amount eluted increased slowly to 90 per cent in 10 column volumes of elutriant.

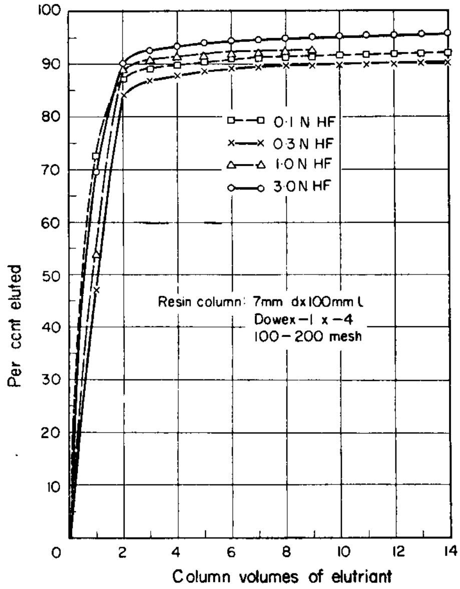

Fig. 3.—Elution of ruthenium with hydrofluoric acid.

Additional column elutions were made with Ru^{106} to measure the variation, if any, in the percentage of ruthenium eluted with various concentrations of hydrofluoric acid. A 5 per cent gain in the total ruthenium eluted was realized when 3*M* hydrofluoric acid was used as the elutriant, as shown in Fig. 3. At that concentration, the distribution coefficients of zirconium and niobium were sufficiently high to insure the retention of these elements on the resin.

Uranium^{VI}, *iron*^{III} *and aluminum.* Since macro quantities of U^{VI}, Fe^{III} and Al are frequently present in samples, the effect of the adsorption and elution characteristics of these elements on the adsorption of zirconium and niobium was of interest. Twenty milligrams each of U^{VI}, Fe^{III} and Al was separately converted to a fluoride system by precipitating with ammonium hydroxide and dissolving the precipitate in a minimum quantity of 0.3*M* hydrofluoric acid. The solutions were loaded onto separate columns of resin 7 mm in diameter and 100 mm in length and were then eluted with 0.3*M* hydrofluoric acid. The elutions of these elements were followed by noting the amount of precipitate formed on adding ammonium hydroxide to each 4 ml fraction of eluant.

Fe^{III} and aluminum were only slightly adsorbed, being eluted in from 4 to 5 column volumes of elutriant. U^{VI} was strongly adsorbed and remained fixed on the resin even after 15 column volumes of elutriant had been collected.

Displacement of zirconium and niobium by U^{VI}, Fe^{III} *and aluminum*

Since U^{VI} was strongly adsorbed onto Dowex-1 from 0.3*M* hydrofluoric acid, vertical displacement of the zirconium and niobium on the column by U^{VI} would be expected. Such a displacement could significantly change the geometry of the counting system and result in variations in the counting rate which would be dependent on the quantity of uranium adsorbed.

Five solutions containing Zr^{95}–Nb^{95} tracer and also 0, 200 and 400 mg of uranium, 200 mg of iron, and 200 mg of aluminum, respectively, were converted to a 0.3*M* fluoride system and each solution was loaded onto columns of Dowex-1-X4, 100–200 mesh resin 7 mm in diameter by 100 mm in length. The columns were inverted and 1-cm portions of the resin bed were expelled into 10-ml tubes and counted. The distribution of zirconium and niobium on the columns was as shown in Figs. 4 and 5. Little or no displacement of the zirconium or niobium took place in the presence of Fe^{III} or aluminum. U^{VI}, however, caused significant displacement of these elements.

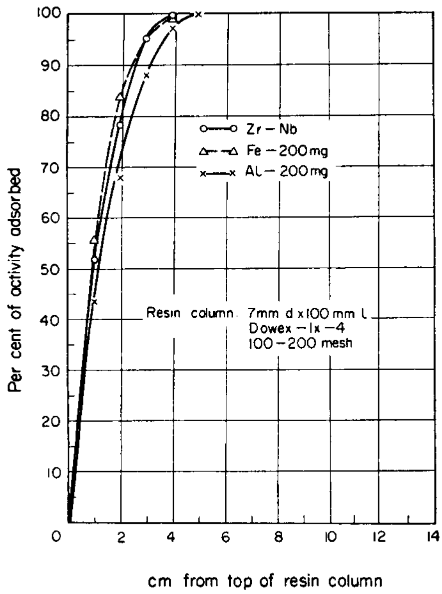

FIG. 4.—Vertical column displacement of zirconium and niobium by aluminum and/or Fe^{III}.

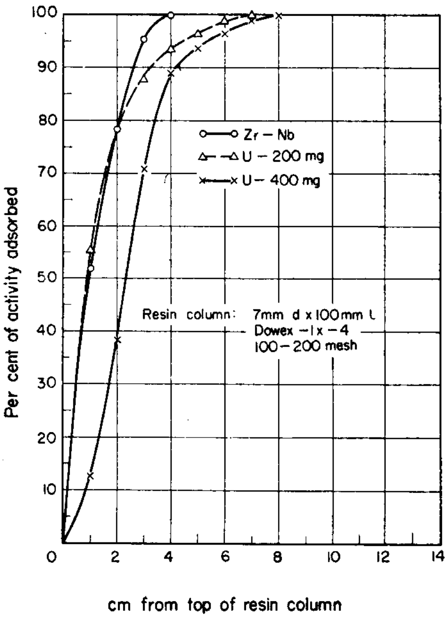

FIG. 5.—Vertical column displacement of zirconium and niobium by U^{VI}.

Counting rate variations due to the adsorption of U^{VI}

Since the displacement of the zirconium and niobium was significant in the presence of uranium, column studies were made to measure the variation in counting rate due to the adsorption of known quantities of uranium.

Solutions containing accurately measured aliquots of tracer and 0, 100, 200 and 400 mg of uranium were converted to a 0.3*M* fluoride system and were then loaded on

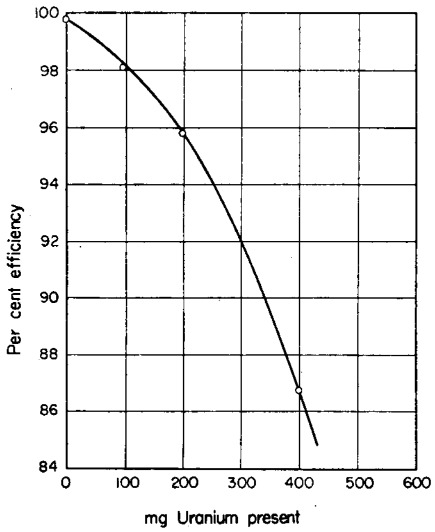

FIG. 6.—Zirconium-95 and Nb-95 counting efficiency due to vertical column displacement by uranium.

the columns. The columns were inverted and the resin was expelled into 10-ml tubes and counted. The counting rates were calculated as a percentage efficiency, based on the counting rate observed when the same quantity of tracer was counted in a volume of 1 ml. When no uranium was present, the counting rate of the tracer on the resin was essentially equal to 100 per cent of the standard. Adsorption of 200 mg and 400 mg of uranium on the column caused reductions in the counting rate of 4 and 13 per cent, respectively (Fig. 6). If the uranium in the sample is unknown, an estimate can be made by measuring the length of the yellow uranium adsorption band. A 2-cm band is equivalent to about 100 mg of uranium. When uranium was present on the columns in the preceding measurements, the 0.75-meV γ-counting rates for Zr^{95} $-Nb^{95}$ were corrected for the 0.75- and 1.0-meV gamma counts from UX_2. When the uranium solutions were converted to the fluoride system and loaded on the columns, the UX_1 appeared to be adsorbed on the resin in a manner similar to cerium. The UX_2 grew into equilibrium in a few minutes. When cerium carrier was present during the conversion of a sample to a fluoride system, the UX_1 was carried with the insoluble cerium fluoride and no UX_2 correction was required.

METHOD

A separation scheme was established based on the preceding data. The method consisted of adding zirconium, niobium and cerium carriers to the sample, precipitating with an excess of ammonium hydroxide and dissolving the zirconium and niobium with $0.3M$ hydrofluoric acid. (If uranium or iron is present, the dissolution of these colored precipitates indicates the complete dissolution of the zirconium and niobium.) The cerium fluoride was centrifuged out and the supernate was transferred to a column 7 mm in diameter and 100 mm in length of Dowex-1-X4, 100–200 mesh resin in the fluoride form. The cerium fluoride was washed with two 5-ml portions of $0.3M$ hydrofluoric acid and the wash solutions were transferred to the column. Complete removal of the zirconium and niobium from the cerium fluoride was verified by γ-energy analysis. The resin was then washed with 20 ml of $3M$ hydrofluoric acid, the column inverted and the resin expelled into a 10-ml tube. The resin was placed in a 3-in. NaI(Tl) well-type crystal and counted with a multichannel energy analyzer. Since the major portion of the zirconium and niobium was adsorbed near the top of the resin column, the expulsion of the resin from the inverted column into the tube placed the greater portion of the activity nearer the center of the well-type crystal. This resulted in maximum counting efficiency when measuring the activity on the resin.

RESULTS

Ru^{106}, Ce^{144} *and* Cs^{137} *decontamination*

Ru^{106}, Ce^{144} and Cs^{137} tracers were carried through the procedure (Appendix I) to measure the percentage of each activity remaining. Ru^{106} was reduced to 4.4 per cent of its initial activity. The activities of Cs^{137} and Ce^{144} were reduced to 0.1 per cent.

Zr^{95} *and* Nb^{95} *recovery*

A series of six synthetic samples containing 200 mg of uranium and a known quantity of Zr^{95} and Nb^{95} tracer was analyzed, using the procedure as described in Appendix I. The average recovery was 99.5 per cent with a standard deviation of 0.7 per cent.

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APPENDIX I

Procedure

(1) To a 50 ml Lusteroid tube add:
   (a) A Teflon-covered stirring bar.
   (b) A sample aliquot containing less than 400 mg of uranium.
   (c) $6M$ HNO_3, 1 ml.
   (d) Water to make the volume 10 ml.
   (e) Zirconium carrier, 1 mg.
   (f) Niobium carrier, 1 mg.
   (g) Cerium carrier, 20 mg.
(2) While stirring, add $6M$ ammonium hydroxide until an excess is present.
(3) Centrifuge and discard the supernate.
(4) Wash the precipitate with 5–10 ml of water.
(5) Centrifuge and discard the supernate.
(6) Dissolve the zirconium, niobium and other soluble precipitates in a minimum quantity of $0.3M$ hydrofluoric acid.
(7) Centrifuge and transfer the supernate to a prepared free-flow resin column (7 mm in diameter by 100 mm long) of Dowex-1-X4, 100–200 mesh in the fluoride form.
(8) Wash the precipitate with two 5-ml portions of $0.3M$ hydrofluoric acid and transfer the wash solutions to the resin column.
(9) Wash the column with 20 ml of $3M$ hydrofluoric acid.
(10) Invert the column and expel the resin into a 10-ml tube.
(11) Count the resin with a gamma scintillation spectrometer. Apply geometry corrections as required for the uranium present.

Talanta, 1960, Vol. 6, p. 273. Pergamon Press Ltd. Printed in Northern Ireland

THE SEPARATION AND RADIOACTIVE ASSAY OF FISSION PRODUCTS FROM SAMPLES OBTAINED FROM HIGH-TEMPERATURE PRESSURIZED-WATER LOOPS

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United Kingdom Atomic Energy Authority and the
Westinghouse Electric Corporation, Bettis Atomic Power Division,
Atomic Energy of Canada Ltd., Chalk River Project, Chalk River, Ontario, Canada

Summary—Two radiochemical separation procedures for the analysis of samples from the pressurized-water loops at Chalk River are presented.

A description is given of a typical loop and the associated sampling facilities, which include autoclaves for activity deposition and corrosion samples, hot and cold probes for filtering out insoluble materials in the loop water, and ion-exchange columns for use in determining soluble and insoluble activities in the loop water. A number of different types of samples are obtained from these facilities. The types of samples and the various methods of attack which are used to convert the samples to a form suitable for analysis are described.

In the first method, the separation of Ru, Ce, Ba, Sr, I, Te, Zr and Mo from samples such as loop water, crud (insoluble corrosion products), etch solutions from metal specimens, and ion-exchange resins is described. This method is applied to crud or resin samples after decomposition by an alkaline fusion, or to water or etch-solution samples after digestion with an $NaOH–Na_2CO_3$ solution. The attack is carried out in the presence of carriers.

An initial separation of the fission products is effected by boiling the alkaline carbonate solution from the liquid samples with HIO_4 or leaching the solidified melt from the fusion with water. Under these conditions, Ru, I and Mo are soluble, while the other elements are present as insoluble hydroxides, carbonates, or sulfates. The two fractions are separated into the individual components by normal chemical methods. The individual components are then purified by modified standard procedures which are described.

In the second method, the separation of fission gases from loop water is described. No chemical separation of the mixture of gases is carried out. The assay of the individual elements and nuclides is based on the careful choice of time intervals for the various steps in the initial separation and for counting the individual nuclides. Further separation is obtained by the use of differential γ-ray counting to select various nuclides for counting at set time intervals after sampling.

Fission products from the first separation were mounted on flat filter paper sources and counted by beta proportional counting, either directly or through absorbers. Details are given of the counter and the mathematical methods used to compute absolute disintegration rates.

The gases, as has been mentioned, were determined by differential gamma counting. A full description is given of the counting equipment and the sample containers. The theoretical and practical details relative to the energies counted and the time intervals between counts are given, together with the mathematical methods necessary for calculating the results.

Talanta, 1960, Vol. 6, p. 274. Pergamon Press Ltd. Printed in Northern Ireland

EVALUATION OF FLAME PHOTOMETRY FOR THE DETERMINATION OF ELEMENTS OF THE RARE-EARTH GROUP*†

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Summary—Because of the occurrence of several of the rare-earth elements and closely related elements as important constituents of the fission products from nuclear reactors, methods for the determination of these elements are essential in the evaluation of control and reprocessing procedures, as well as in the operation of reactors. A study was therefore made of the complex flame spectra of the rare-earth elements and the closely related elements, Y and Sc, for the purpose of evaluating, extending and improving flame photometric methods for the estimation of these elements. Flame photometric data were developed by the use of organic extracts of the chelates of the several elements. The areas in which flame photometry may be applied and limitations imposed by mutual interference are discussed elsewhere.†

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* Work performed under contract with the U.S. Atomic Energy Commission.

† This paper is not included in the proceedings because it was published in *Anal. Chim. Acta*, 1960, **22,** 315–27.

Talanta, 1960, Vol. 6, p. 275. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF THE DISTRIBUTION OF FISSION Xe IN IRRADIATED UO_2 FUEL ELEMENTS

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Summary—In the development of UO_2 fuel elements for power reactors, one of the important aspects to be considered is the physical behavior of the fission gas. The engineering concern is mainly that of pressure buildup inside the sheath, due to the release of fission gas from the oxide. Two analytical methods in use at Chalk River have contributed considerably to the investigation of the fate of the fission gas in experimental fuel elements: measurement of Xe released on puncturing the sheath of the fuel element and measurement of the radial distribution of Xe remaining in the UO_2. These two methods are described in this paper.

THE Zircaloy-clad UO_2 rod is punctured in an evacuated chamber inside a hot cell. All the gas is then pumped from the rod into a purification system containing a Ca furnace at 700°C which removes any N_2 or O_2. Xenon is separated from A, Kr and He by freezing it out at −195°C. It is possible to prepare fission-product Xe with a purity in excess of 99 per cent by this means. After purification, the Xe is expanded into a calibrated volume where the pressure is measured on a McLeod gage. The over-all accuracy of the method is 2 per cent.

Samples for the determination of the radial distribution of Xe remaining in the UO_2 normally weigh in the order of 20–200 mg. The weighed UO_2 fragment is frozen in a small quantity of HNO_3 in a stainless-steel reaction bomb. The bomb is then attached to a purification and measuring system and is evacuated to less than 1 μ, after which it is isolated from the remainder of the system and heated to 100°C to dissolve the UO_2 and release the fission gases. The $UO_2(NO_3)_2$ solution is then frozen at −80°C and the bomb is vented to the purification system. The reaction gases are removed by reacting them with Ca metal at 700°C. The fission gases are then pumped to a preliminary measuring system containing a second Ca furnace and a McLeod gage. At this point, the volume of total rare gases is measured. A separation of Xe from other rare gases is then made by absorbing the sample on a charcoal trap at −195°C and pumping on the trap at −80°C. The purified Xe is expanded into a calibrated volume where a final pressure measurement is made. The accuracy of the method is 10 per cent for samples with a Xe content equal to or greater than 0.02 ml at N.T.P. As the amount of gas falls to about 0.004 ml at N.T.P., the accuracy decreases to the order of 25 per cent.

Results to date show that the Xe released on puncturing the sheath has come from the central, high-temperature region of the fuel elements. There appears to be very little release of Xe from oxide which has not reached a temperature in excess of 1400°C.

Talanta, 1960, Vol. 6, p. 276. Pergamon Press Ltd. Printed in Northern Ireland

RADIOCHEMICAL ANALYSES THROUGH POLAROGRAPHIC METHODS—II

RAPID PROCEDURE FOR TECHNETIUM AND RUTHENIUM RADIONUCLIDES IN FISSION PRODUCTS*

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Summary—Techniques have been developed for using polarographic methods in the analysis of radioactive isotopes. These new techniques consist essentially of removing the radioactive isotope of interest from a sample solution by amalgamating it with Hg from a dropping Hg electrode at a given potential and then assaying this amalgam by a radioactivity measurement. This technique was applied in developing the following accurate and rapid procedure for the analysis of Tc^{99m} and $Ru^{103,106}$ in fission-product mixtures: (1) an aliquot is removed from a solution of fission products and evaporated to dryness; (2) the residue is dissolved in a supporting electrolyte of $1M$ sodium citrate–$0.1M$ NaOH and this solution is placed in the polarographic cell; (3) a potential of 1.55 V vs. the S.C.E. is applied. The Tc and Ru are selectively amalgamated with the dropping Hg. The Hg is then separated from the solution by falling through CCl_4 and assayed by gamma counting. The amalgam is recounted after decay of the Tc^{99m} to provide data for computing the separate Tc^{99m} and $Ru^{103,106}$ counts. Corrections were also made for decay of Tc^{99m} during the period of time from the start of mercury collection to the time that the count is made; variation in collection time of Hg drops; simultaneous growth (from Mo^{99}) and depletion ($\sim$0.07 per cent min^{-1}) of Tc^{99m} during the time of collection.

Test results for Mo by the polarographic method in which the daughter element, Tc^{99m}, is separated and counted, agree within 2 per cent with those obtained by the conventional method in which Mo^{99} is precipitated with α-benzoinoxime. The relative standard deviation based on forty-eight determinations by the former method was 0.8 per cent, whereas, for forty-four determinations by the latter method, the standard deviation was 1.8 per cent.

Good radiochemical purity is indicated for the polarographically separated Tc^{99m} and $Ru^{103,106}$ by half-life measurements, by gamma spectrometric analysis and by assaying the Hg collected as drops at 1.55 V vs. the S.C.E. from solutions containing known amounts of the most abundant fission product radionuclides. Decontamination factors of about 10^5 are obtained.

A single separation of Tc^{99m} (and $Ru^{103,106}$) by the polarographic method requires about 3 min. The rapidity of the entire assay procedure (including data reduction) may be estimated by the fact that 48 analyses noted above were completed in 1 day by two people. For comparison, about eight Mo^{99} or $Ru^{103,106}$ analyses can be made per day by one analyst, utilizing conventional methods. The aliquot size of the fission-product mixture needed for the present polarographic determination of Tc^{99m} (and $Ru^{103,106}$) is larger by about a factor of 10 than that required by conventional analytic methods. The Hg collected during a period of 3 min from a solution of a 3 day old fission-product sample of 10^{12} fissions will give approximately 15,000 d/min of Tc^{99m} and 300 d/min of Ru^{103}.

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* This article is published in full in *Analytical Chemistry*, June 1960.

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959

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1960 VOLUME 6

ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

Analysis of Reactor Fuels, Fission-Product Mixtures and Related Materials: Analytical Chemistry of Plutonium and the Transplutonic Elements

Third Conference
Gatlinburg, Tennessee
October 26–29, 1959

Sponsored by:
Oak Ridge National Laboratory
Oak Ridge, Tennessee
Operated by
Union Carbide Nuclear Company,
A Division of Union Carbide Corporation
for the
U.S. Atomic Energy Commission

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