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A SYSTEM OF METHODS FOR THE SPECTROCHEMICAL
ANALYSIS OF URANIUM-BASE MATERIALS

by

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1. INTRODUCTION

The production of uranium metal and compounds of very high purity involves a most searching analysis into the composition of the raw materials and of the intermediate and final products. This requires the determination of 60 or more chemical elements in a variety of materials on a routine basis where speed is an important consideration. The problem is complicated by the need for detecting small concentrations of certain deleterious impurities of the order of 0.1 ppm or less. Investigations at this Bureau early in 1942 revealed that, despite previous misgivings, the spectrograph would serve as an invaluable tool for the analysis of uranium-base materials. Further work at this and other laboratories has led to a successful combination of spectrographic and chemical procedures that has been applied in the analysis of thousands of samples of project materials. Fundamentally, the original structure of the methods serves well but gradual improvements and extensions have brought about a need for a more detailed description of the general system of analyses. This report presents the current spectrochemical methods applied to the analysis of uranium-base materials at the National Bureau of Standards. The report necessarily emphasizes the methods developed and used in this laboratory, but the work of others along similar lines has been indicated by references to analytical reports.

The first five sections of the report cover general principles, equipment, and the preparation of gallium oxide carrier and of standard samples. The remaining four sections describe the various steps in the analytical procedures. A decimal system of designations is employed for the divisions of the various sections to facilitate making cross references. The report is essentially a series of laboratory procedures, so arranged that sections may be removed for assignment of work among the chemical and spectrographic operators. In line with this purpose, the uranium-base materials to which the methods apply are referred to by their common names familiar to the operators. However, chemical formulae of the matrix materials are also given, when known, to avoid uncertainty in the meaning of the names. For those interested in the evaluation of the methods and of analytical results, Section 2 is recommended. Section 3 will be found useful in designing and equipping the laboratory, and also in establishing the general laboratory operations essential to the application of the analytical procedures of Sections 7 and 9. Literature citations are listed at the end of each main section.

*****

The chemical group of the project at this Bureau is responsible for the development and application of the procedures under Section 6 on Preliminary Preparation of Samples for Analysis and Section 8 on Chemical Concentration of the Less Volatile Elements. We are indebted to C.J. Rodden for his current revisions of these procedures and for his suggestions during the preparation of the full report. It is a pleasure to acknowledge the assistance of members of the spectrographic group in preparing the report, in particular Virginia C. Stewart for Sections 4 and 5, Mary Jo Adrian for Sections 7 and 9, and

J. Dudley Richards for Section 7.7-2.

2. SURVEY OF METHODS EMPLOYED

2.1. Choice of Methods

Uranium is characterized by exceedingly complex spectra derived from a multiplicity of electron configurations in both the neutral and ionized atoms. The ionization potential is low, probably near that of cesium, consequently it is difficult to separate the spectra arising from neutral and ionized atoms. The rich line spectrum is further confused by a heavy background attributed to unresolved, weak lines and to continuous radiation of solid particles, characteristic of the spectra of elements forming refractory oxides. As a result of these properties, the direct excitation of uranium materials by the common methods, employing the d.c. arc, the a.c. arc, and higher-energy, condenser discharges, produces highly complex spectra. Thus, little or no choice is offered for the simplification necessary to the observation of impurity lines at low impurity concentrations. The possibility of employing a spectrograph of very high dispersion, for example, 1 Å per mm or better, to resolve the thousands of lines and reduce the background is not a practicable solution for most laboratories in view of the space requirements for the equipment and the large number of photographic plates or films necessary to cover the spectral range for a variety of impurity elements. For the majority of analytical laboratories, the practical limitation of dispersion is represented by that available in the largest commercial instruments, for example, grating spectrographs having a dispersion of 5 Å per mm in the first order and 2.5 Å per mm in the second order. With an instrument of this type we have found it possible, by direct arcing of a uranium oxide sample, to determine calcium with a limit of detection of two parts per million. However, this is an exceptional case; for the majority of elements the dispersion is far from that necessary for the direct observation of impurities at the low concentrations desired in the analysis.

The alternative to direct observation of the spectrum is the separation of the impurities from the uranium matrix, followed by spectrographic determination. The system of methods to be described includes four concentrational methods. The first is a physical method, known as pyroelectric concentration, in which 33 volatile impurity elements may be separated from the uranium matrix by fractional distillation, and their arc spectra simultaneously recorded to permit spectrographic determination. The three remaining methods provide chemical separation of three groups of the more refractory elements, namely, the rare-earth concentrate, the zirconium-group concentrate and the platinum-group concentrate. The chemical concentrates are examined spectrographically for the refractory elements, the concentrations of which are reported in terms of the original sample. These methods, combined with direct determination of calcium in the analytical scheme, permit the determination of 63 chemical elements in uranium-base materials at concentrations in most cases of a few parts per million and extending in important cases to the order of 0.1 part per million.

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2.2. Pyroelectric Concentration Method

2.2-1. Development of the Method

It is a well-known observation to spectrographers that the constituents of a sample undergoing excitation for spectral study may distill at different rates depending on their volatilities. This is particularly true in excitation by the d.c. arc when the sample is contained in a cupped graphite electrode which acts much like a small furnace. The application of this phenomenon in separating constituents of different volatilities was described by Rubies (1) in 1934, and later extended by Rubies (2) and by Preuss (3) to various problems. The method, offering possibilities for the analysis of uranium-base materials, was investigated in our laboratory first in connection with the analysis of uranyl nitrate. Conversion of the nitrate to the refractory oxide U_3O_8 , followed by partial volatilization of 10 mg oxide charges in a d.c. arc, was found to be qualitatively useful in detecting volatile impurities in impure samples. However, the simple procedure was not capable of high accuracy and sensitivity. Further study of the problem led to an improved method (4) wherein a selected volatile material is added to the sample, its functions being to sweep out the impurities, and, at the same time, to stabilize the arc to permit more reproducible excitation of the impurity elements. Several likely volatile materials, or carriers, as they may be termed, were tried and gallium oxide was adopted. The method was first applied quantitatively to the determination of boron (5), for which improved sensitivity was obtained by an increase of the sample charge to 100 mg. Further improvements were realized in accuracy and sensitivity by modifying the exposure technique and adopting a two-piece anode in the electrode assembly (6). The method then provided for the determination of boron to a limit of 0.1 ppm, and included the determination of arsenic, cobalt, lithium, manganese, nickel, silver, and sodium. This method is essentially the basis of our present procedures, with minor changes incorporated to improve the sensitivity and accuracy for some elements, and with extensions to include the determination of a total of 33 elements. The application of photometric measurement improved the accuracy in the determination of several important elements. However, the simple photometric procedure did not suffice for the accurate determination of iron, magnesium, and manganese. An improved method was developed (7) in which the three elements are measured relative to an internal standard added to a portion of the sample.

The pyroelectric method was adopted by other laboratories engaged in the analysis of uranium-base materials, and various modifications have been reported in parallel investigations and extensions of procedures. A series of investigations at the Massachusetts Institute of Technology has been reported by Harrison. One of the first reports (8) described the substitution of silver chloride for the gallium oxide carrier, which has proved of considerable value in applications of the method, although contamination of other samples by

silver must be guarded against. The electrode advocated in this report was provided with a vent hole for escape of gases. Recently the use of a specially designed, two-piece electrode was reported (9). Other contributions of this laboratory, and procedures developed in producer laboratories, may be found by reference to a general index (10).

A considerable amount of work was carried out at the University of Chicago and at Iowa State University on the analysis of uranium-base materials and the extension of the method to the analysis of other refractory materials (11). A useful development reported by Corvin (12) is the forming of sample charges into pellets prior to application of the pyroelectric method. This procedure was incorporated in our method of determining boron in green salt. Section 7.7-2.

Investigations on the pyroelectric method at the Tennessee Eastman Corporation are of interest for the analysis of limited quantities of samples (13)

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2.2-2. Characteristics of the Method

It is of importance to examine the fundamental characteristics of the pyroelectric method with a view toward establishing its accuracy and limitations, especially when applied to the analysis of a variety of uranium-base materials. The choice of a carrier material is a prerequisite of the method. In general the carrier should have the following characteristics:

- (a) The carrier should not be composed of elements for which determinations are to be made.
- (b) The carrier should be readily available with high purity or be capable of preparation and purification by simple methods.
- (c) The carrier compound should be of intermediate volatility with respect to the elements determined.
- (d) The carrier elements should give simple spectra in order that interference with the spectra of the samples may be minimized.
- (e) The carrier compound should be stable, inert, non-hygroscopic, and easily incorporated in samples by grinding.

Gallium oxide meets these requirements well, particularly for the general scheme of analysis in which the determination of gallium by the pyroelectric method is not required. This element is separated as a member of the zirconium group of elements, Section 8.2, and is determined spectrographically by the procedure of Section 9.2.

The selection of the concentration at which the carrier is added is based upon the amount required to sweep out the impurities and to maintain a steady arc for a sufficient length of time to provide a reasonable exposure of the photographic plate. The upper limit on the amount of carrier is determined first, by the necessity of conserving the carrier material, and second, by the tendency of excessive amounts to carry particles of the uranium sample mechanically into the arc stream. The choice of a ratio of two parts of gallium oxide to 98 parts of uranium oxide has served satisfactorily.

The physical form of the carrier is of some importance in the weighing operations. The dense oxide obtained by ignition at 1200°C has been found preferable, since it may be weighed and transferred readily without loss. The carrier is incorporated in the sample charge by hand-grinding in a small mortar. This operation serves generally for mixing of the sample, although, for certain more highly segregated samples, a preliminary grinding of a larger portion of several grams of the sample is required. This additional grinding is particularly important for the determination of iron in oxide prepared from uranium metal samples.

A portion of 100 mg of the charge mixture is transferred to a cupped graphite electrode prior to arc excitation. The form of the electrode, the quantitative transfer of the sample charge, and the treatment of the charge before arcing all affect the results. The electrode combination shown in Figure 1 consists of a narrow ($1/8$ in.) cathode sharpened to a point and a two-piece anode made of, first, a cap piece ($1/4$ in.) having a deep cup in which the sample charge is placed; and, second, a supporting pedestal of narrow ($1/8$ in.) rod. The dimensions and preparation of the pieces are described in Section 3.3. This form of the cathode provides a hot spot almost immediately when the arc is struck, resulting in improved arc stability. The two-piece anode provides a more uniform and considerably reduced heat conduction from the cap piece, affording optimum regulation of the heating of the electrode charge. Prior to arcing the electrode, a vent hole is made in the charge to allow escape of vapors that otherwise might cause ejection of the charge into the arc stream.

The arc excitation of the samples is characterized by a cycle of burning that is quite reproducible for the purer uranium materials. The electrodes are mounted in the holder, with a 4 mm electrode gap, and a 10-ampere arc is struck. The arc burns somewhat erratically for about ten seconds, being supported mainly by volatilization of the electrode material. At the end of this period the arc changes in color from indigo to blue and runs quietly and steadily for approximately 25 seconds, changing at this point to the unsteady condition of the initial period. Studies by the moving plate technique have shown that the steady period of burning results from distillation of the carrier and the greater part of the volatile impurities into the arc stream. However, certain highly volatile impurities, such as mercury, cadmium, and boron, start to volatilize ahead of the steady period, and elements, such as aluminum and beryllium, forming refractory oxides may be observed to persist in the arc at the end of the steady period. Examination of the burned charges has shown that the end of the steady period of burning does not represent complete volatilization of even the more volatile elements. The incomplete volatilization of the impurities is a necessary result of the restriction that the temperature of the charge must be kept below the limit at which the charge fuses and uranium is evolved. The working temperature, in the neighborhood of 2000°C , is below the boiling point or decomposition temperature of many of the impurity oxides; their volatilization probably depends on their vapor pressures at the charge temperature. For most of the elements (gold is an exception), the volatility can be considered proportional to the boiling point of the oxide. The behavior of the impurities suggests a division into three groups; (1) oxides with boiling points below 1500°C , (2) oxides with boiling points around 2000°C , and (3) oxides with boiling points in the neighborhood of 3000°C . Impurities in the first group volatilize rapidly and nearly completely; those in the second group volatilize more slowly, resembling gallium oxide in behavior; those in the third group volatilize less completely and the degree of volatilization is more severely affected by changes in the heating of the electrode. The reproducibility of volatilization of the first two groups permits satisfactory determination of the respective elements by interpolation against standard samples handled in the same manner. For the third group, however, the addition of an internal

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FIGURE 1. ELECTRODE ASSEMBLY
SCALE 3 IN. = 1 IN.

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standard element has been found necessary for accurate results. The determination of iron, magnesium, and manganese, which are third-group elements, is now made (7) by photometric measurement relative to chromium added as an internal standard to samples and reference standards. Consideration of volatility is important in adjusting exposure times in the analytical procedures. For second and third-group elements a portion of the initial burning period of the arc may be omitted from the exposure without appreciable error; this is useful in some cases in reducing spectral background. For the first-group elements, which begin to volatilize almost immediately, the pre-arc period is omitted but the total exposure may be cut short if necessary to reduce background.

The above discussion of excitation characteristics assumed application to the purer grades of uranium-base materials. If the total impurity content of a sample exceeds 0.1 or 0.2 per cent, the steady burning period will be longer. In these cases the results may be affected by the high concentration of volatile material, including, for example, the sodium in a soda salt. Dilution of the impure sample by pure oxide (U_3O_8) serves to minimize these effects, and the diluted sample may be analyzed according to the basic procedures, the results being corrected by the dilution factor.

The additional assumption that the impurities are present as oxides, or compounds acting like oxides, in the samples prepared as uranium oxide for analysis appears to be generally justified. However, a potential source of error lies in the possibility that an impurity, usually volatile, may be encountered in a sample in a non-volatile form. Fortunately this possibility is remote for most of the uranium-base materials encountered in analysis; only one instance has been observed in which this condition was apparently the explanation for peculiar behavior. This was observed in the analysis of a sample of uranium carbide that had been ignited to the oxide. Chemical analysis of the sample revealed 100 ppm of molybdenum, but spectrographic analysis by the pyroelectric method showed no molybdenum, the apparent explanation being that the high stability of its carbide prevented formation of the more volatile oxide on ignition. It may be noted that, following the system of spectrographic analysis, molybdenum would be detected in the zirconium-group concentrate. Since other elements forming stable carbides may act similarly to molybdenum, further investigation of the matter would be desirable in applying the pyroelectric method to the analysis of uranium carbide.

The volatility of certain elements or compounds may result in losses on ignition of samples. Mercury is completely volatilized on ignition, and losses of 20 per cent of thallium have been observed from synthesized standards. Loss of boron of the order of 20 per cent may occur in the ignition of uranyl salts. Arsenic showed no appreciable loss under these conditions, and gold, added as chloride to standards, was not appreciably affected by ignition of the standards, contrary to expectations. The conversion of the green salt to black oxide by simple ignition in air may result in the loss of a number of volatile fluorides. Hydrolysis of the green salt by steam, followed by ignition (Section 6.7), retains As, Sb, and Mo, and probably other elements volatile as fluorides. However, boron and mercury are not retained by any method as yet devised for conversion of the green salt to oxide, and provision is made for determining these elements by spectrographic examination of the original green salt.

In any doubtful cases spectrographic comparison of ignited and un-ignited portions of synthesized standards should be made. The analytical procedures to be described in Section 7 include modifications designed to minimize errors from these various factors as far as possible at the present time.

2.2-3. Accuracy of Results

The accuracy of the determinations by the pyroelectric method depends upon matching the excitation behavior of the samples and properly prepared standards, and upon the precision of the spectrographic measurements. Increased precision is provided by photometric measurements, but this advantage is offset by the additional time and labor required, which would be excessive if applied to all determinations. A compromise has been adopted in which the more important determinations are made by photometric measurement and the remainder are made by visual comparison of the spectra of samples and of standards. The accuracy of determinations made for Ba, Cd, Si, Fe, Mg, and Mn by photometric measurement is estimated to be plus or minus ten per cent except for values at the extreme limits of the measurable range. Examples of the comparison of repeated results taken from a recent report (7) are shown in Table I.

Table I

Repeated Spectrographic Determinations, in ppm, Of Impurities in Uranium Metal Samples

Sample No.	Element	Observation					Mean
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	
M-150	Iron	28	32	30	28	27	29
	Manganese	7	7	8	9	7	8
M-152	Iron	30	33	30	28	30	30
	Magnesium	12	13	10	14	15	13
	Manganese	7	8	9	9	9	8
M-157	Iron	108	110	104	111	106	108
	Manganese	14	13	12	12	14	13
M-158	Iron	89	76	77	87	88	83
	Manganese	8	8	9	9	9	9
M-162	Iron	76	79	69	68	-	73
	Manganese	11	9	11	11	-	10
M-165	Iron	33	37	34	27	-	33
	Magnesium	35	33	30	36	-	33
	Manganese	10	8	8	9	-	9

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In view of the fact that the chemical determination of iron is considered quite reliable, it is of interest to compare routine results by the two methods on a typical set of uranium oxide samples as shown in Table II.

Table II

Determinations of Iron in Uranium Metal Samples by
Routine Spectrographic and Chemical Methods; Values in ppm

<u>Sample</u> <u>No.</u>	<u>Spec.</u>	<u>Chem.</u>	<u>Sample</u> <u>No.</u>	<u>Spec.</u>	<u>Chem.</u>
151	28	41	161	38	35
152	32	35	162	77	74
153	33	32	163	41	41
154	149	154	164	83	79
155	31	32	165	34	36
156	26	32	166	19	24
157	110	139	167	34	34
158	83	70	168	26	31
159	35	35	169	41	34
160	33	31	170	38	42

Repeated determinations of B, Cd, and Si, without an internal standard, show similar reproducibility. However, some uncertainty is involved at the present time in the determination of boron below 0.3 ppm, because of the difficulty of preparing or obtaining reliable standards in this concentration range, and, possibly, because of contamination of samples or electrodes (see the discussion under Section 3.7-1). Investigation of this problem is being continued.

The accuracy of results in general is shown by the number of significant figures and by qualifying designations given in the analytical report. In cases where visual estimates are made against proper standards, an approximate value is given, the figure being preceded by the letter "a". In rare cases, where the result is outside of the range of standards, the limit beyond which the concentration lies may be given, for example, "Pb, L1" indicating lead less than 1 ppm and "Si, G2000" indicating silicon greater than 2000 ppm. In reporting qualitative results the scale of designations given in Table III is employed.

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Table III

Designations for Qualitative Analysis

<u>Designation</u>	<u>Name</u>	<u>Concentration Range</u>
VS	Very Strong	10 to 100%
S	Strong	1 to 10
M	Moderate	0.1 to 1
W	Weak	0.01 to 0.1
VW	Very Weak	0.001 to 0.01
T	Trace	0.0001 to 0.001
FT	Faint Trace	Less than 0.0001

An additional consideration of accuracy is involved in the application of the pyroelectric method to the analysis of uranium-base materials other than the black oxide, U_3O_8 . These materials are converted to black oxide by ignition, and are analyzed by comparison with standards having a black-oxide matrix. The results should then be corrected by the conversion factor representing the change of matrix in order to report the correct concentrations in the original material. For several of the materials analyzed, the conversion factor may be ignored, but for other materials it may be significant, especially for the determinations made with highest spectrographic precision. The conversion factors for correction of results are given in Table IV. When these are significant, the correction is incorporated as a step in the analytical procedures of Section 7.

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Table 1V

Factors for Reduction of Results on Ignited Samples
to the Basis of the Original Sample

<u>Original Sample</u>	<u>Calculation</u>	<u>Factor</u>
Black Oxide	(not ignited)	1.00
Metal	$\frac{U_3O_8}{3U}$	1.18*
Brown Oxide	$\frac{U_3O_8}{3UO_2}$	1.04
Orange Oxide	$\frac{U_3O_8}{3UO_3}$	0.98
Peroxide	$\frac{U_3O_8}{3UO_4 \cdot 2H_2O}$	0.83*
Tetrafluoride	$\frac{U_3O_8}{3UF_4}$	0.89*
Hexafluoride	$\frac{U_3O_8}{3UF_6}$	0.80*
Soda Salt	(not ignited)	1.00
Carbide	$\frac{U_3O_8}{3UC_2}$	1.07
Acetate	$\frac{U_3O_8}{3UO_2(C_2H_3O_2)_2 \cdot 2H_2O}$	0.66* 398 017
Nitrate	$\frac{U_3O_8}{3UO_2(NO_3)_2 \cdot 6H_2O}$	0.56*

*These factors are significant; analytical results are multiplied by the factor to obtain determination in the original sample.

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2.3. Chemical Concentrates and their Analysis

2.3 -1. Rare-earth Group

The present procedure, Section 8.1, for chemical separation of the rare-earth group is based on that previously reported by Rodden (14). It involves a series of operations culminating in oxalate precipitation followed by ignition to obtain a mixture of oxides. The elements separated are Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th. In view of the small total concentration of rare earths commonly observed in uranium-base materials, a large sample, 25 to 100 g of the material, is employed. The concentrate usually obtained amounts to 5 to 10 mg, and is mainly yttria containing small amounts of rare earths and impurities of the common elements. When the uranium-base material is very pure or when the quantity of the sample is limited, the concentrate may amount to only a few tenths of a milligram or may be too small to weigh. The method when applied to the separation of known added amounts of rare earths showed a recovery of 80 to 90 per cent.

The spectrographic examination of the rare-earth concentrate was originally limited to qualitative analysis, and this suffices at the present time when only a few tenths of a milligram of a concentrate is obtained. A procedure (Section 9.1) has been developed in which the more important rare-earth elements are determined in the concentrate of 1 mg or more with an accuracy of plus or minus ten per cent. In view of variations in the matrix composition of the concentrates it was found necessary to add an internal standard element, with reference to which the impurity concentrations may be measured. The internal standard should, of course, behave similarly to the rare earths under the spectrographic excitation conditions, and should not be found present in the concentrates in appreciable amount. Consideration of the possibilities of several elements in the titanium and columbium groups led to the selection of titanium. It may be noted here that titanium and zirconium may be found in the rare-earth concentrate if the procedure for the separation is not carefully followed. The titanium is added to the rare earth concentrate by solution (Section 8.1-2) since attempts at preparing dry oxide mixtures were unsuccessful. The spectrographic procedure provides for d.c. arc excitation of a weighed portion of the concentrate (plus titanium) mixed with graphite, and the photometric measurement of lines of Eu, Gd, Dy, and Er relative to lines of Ti. The concentrations are determined by reference to an analytical curve obtained for synthesized standards treated in the same manner. Knowing the concentration of rare earths in the concentrate, the weight of the concentrate, and the weight of the uranium-base sample, the concentration of the rare earths may be reported in terms of the original sample. The results will tend to be low by the amount lost in the chemical separation.

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The question might be raised as to the value of carrying out the involved quantitative spectrographic procedure in view of the uncertainty of recovery of the rare earths. This procedure has been found worth while because of the spectroscopic variations encountered in excitation of the rare-earth oxides, which are highly refractory and consequently difficult to volatilize in arc excitation. The spectrogram obtained for the quantitative procedure permits qualitative analysis for the remaining rare earths and thorium. If desired, the methods could be extended to quantitative determination of all of the elements in the group.

If the amount of the concentrate is very small, the important rare earths are usually below the limits of spectrographic detection and the titanium addition is not required. In these cases, the qualitative determination of yttrium will provide useful information since the rare earths such as gadolinium occur roughly in the ratio of one part in fifty with respect to the yttrium.

The sensitivities of detection of important rare earths in the concentrate are given in Table V. The sensitivities calculated on the basis of the original sample are given in Table VII, Section 2.4-2.

Table V

Limits of Detection of Rare Earths in the Concentrate

<u>Element</u>	<u>Limit</u>	<u>Element</u>	<u>Limit</u>
Dysprosium	0.1%	Samarium	0.8%
Erbium	0.1	Terbium	0.25
Europium	0.05	Thulium	0.1
Gadolinium	0.1	Ytterbium	0.01
Holmium	0.1		

2.3-2. Zirconium Group

Precipitation by cupferron serves for the separation (15) of a number of elements, including a group of importance in the analysis of uranium-base materials. The procedure described in Section 8.2 is employed for concentration of Cb, Ga, Hf, Mo, Pd, Ta, Ti, V, W, and Zr. In view of the low concentrations of these elements, a gathering agent is added to the sample solution to ensure recovery of the impurities. Bismuth was chosen for this purpose because of its simple spectrum and ease of volatilization in arc excitation. The insoluble material in the uranium sample, which may contain considerable amounts of the refractory group of elements, is collected with the precipitate of cupferrides. The mixture is ignited to oxide and submitted for spectrographic analysis.

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The spectrographic procedure, Section 9.2, involves the addition of more bismuth as the oxide to provide a sample composed mainly of bismuth oxide and containing the refractory elements as impurities. This material volatilizes readily from a graphite electrode in a d.c. arc, sweeping the refractory impurities into the arc stream. In view of the possibility of losses in the chemical separation, synthesized standards are carried through the chemical procedure before being applied as reference standards in the analysis of samples. The spectrographic determinations are made by visual comparison of the spectra of the samples and standards, the results being reported as estimates. Molybdenum and vanadium, included in the concentrate, are also determined by the pyroelectric method, the two procedures providing check results

2.3-3. Platinum Group

Reduction by hydrochloric acid and zinc serves for separation of the noble metals from solution (15). This principle is applied in the analysis of uranium-base materials (Section 8.3) to concentrate Ru, Rh, Pd, Ir, and Pt, using gold as a gathering agent. Osmium is volatilized in the procedure, but may be collected and determined colorimetrically if desired. The portion of the sample insoluble in the solution prepared for reduction is collected with the gold precipitate, and the mixture is subjected to spectrographic examination. In view of possible incomplete precipitation, standard samples containing added amounts of the platinum metals are carried through the same procedure.

The spectrographic analysis (Section 9.3) is made by volatilizing a small portion of the sample completely in a d.c. arc. A shallow electrode is employed to avoid incomplete volatilization of the platinum metals, all of which have high boiling points. The analysis is complicated by rather complex spectra derived from impurities from the insoluble portion of the original sample. This disadvantage combined with the poor spectral sensitivities of the platinum metals leaves much to be desired in the method. The sensitivity of detection of iridium (100 ppm) is the poorest of all of the elements determined in the general analytical scheme. Palladium is determined with higher sensitivity in the zirconium-group concentrate, and its determination by the latter method is preferred. The sensitivities of the elements determined by the method are given in Table 7, Section 2.4-2.

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2.4. Summary

2.4-1. Analytical System

The analytical methods discussed in the foregoing sections provide an analytical system for specific application to the determination of 63 elements in uranium-base materials. In addition the methods, with minor modifications, will apply to the analysis of metals similar to uranium and to compounds of these metals. The pyroelectric method, in particular, is general in scope and may be employed in the analysis of many substances when appropriate standard samples are available (4, 11). In our laboratory this method has been applied to the analysis of samples with bases of thorium, beryllium, and magnesium, and for the determination of boron in rare-earth mixtures. The analytical system for the analysis of uranium-base materials is conveniently represented by the schematic outline of Table 6. The elements of the periodic system not included in the scheme are mostly gases or metalloids not readily determined by spectrographic analysis, radioactive elements for which more sensitive methods are available, or rare elements for which spectra have not been well described. However, a few elements such as strontium, tellurium, and rhenium probably could be incorporated in the system by modification of procedures of Sections 7 and 9 if desired. The elements not included at present are listed below, with remarks on the possibility of including them in the system.

- (a) Elements that exhibit poor spectral sensitivity except by special methods that may involve time-consuming operations, such as use of vacuum technique: H, He, Ne, Ar, Kr, Xe, Rn, F, Cl, Br, I, C, S, O, N.
- (b) Elements for which spectra are not known: Atomic Numbers 43, 61, 84, 85, 87, and 91.

The predicted properties of elements 43, 84, and 87 should permit determination of the two elements by the pyroelectric method. Element 61 should exhibit the general properties of the rare-earth group and be capable of determination by procedure 9.1. Element 85 should resemble the halogens and would fall among the elements determined with difficulty; Group (a). Element 91 probably would be partially precipitated with the zirconium group.

- (c) Elements that may be lost in preparation of the sample for spectrographic analysis: Os (Re, Se, and Te).

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Table 6. Scheme for the analysis of uranium-base materials (See Note 1)

Material	Preliminary (2) Preparation	Final Preparation	Resulting Material	Spectrographic Operation	Electrode Charge	Photography	Elements Determined (3) Visual Comparison Photometric Meas.
1. U Metal	Ignite			I. General Run Pyroelectric Conc. Method (P.C.)	100 mg in deep cup (9/32 in.)	2200-3500 A E SA No.1 plate Pre-arc 5 sec Exposure 40 sec	Ag, Al, As, Au, Be, — B(2), Si Bi, Co, Cr, Cu, Ge In, Mo, Na, Ni, P, Fe, Mg, Mn (relative Pb, Sb, Sn, Ti, V, to Cr) (5) Zn
2. Brown Oxide UO ₂				II. Cadmium Run P.C. Method	100 mg in deep cup (9/32 in.)	2200-2935 A (2nd order) E SA No.1 plate No pre-arc Exposure 20 sec	Hg (2), <u>As</u> — Cd (4)
3. Orange Oxide UO ₃				III. Lithium Run P.C. Method	100 mg in deep cup (9/32 in.)	5700-7000 A E II-F plate Expose as for General Run	Ba, Li, <u>Na</u>
4. Peroxide UO ₄ ·2H ₂ O				IV. Potassium Run P.C. Method	100 mg in deep cup (9/32 in.)	7450-8750 A E I-N plate Expose as for General Run	K, Rb, Cs
5. Black Oxide U ₃ O ₈	Dilute 1:10 with U ₃ O ₈	Add 2% Ga ₂ O ₃ carrier	U ₃ O ₈ plus 2% Ga ₂ O ₃	V. Calcium Run Complete Burning Method (C.B.)	10 mg in shallow cup (1/32 in.)	3700-5000 A E SA No.1 plate Complete burning Exposure 30 sec	Ca
6. Soda Salt Na ₂ O·xUO ₃							
7. Green Salt UF ₄	Hydrolyze and ignite						
8. Hexafluoride UF ₆							
CHEMICAL SEPARATION							
9. Rare Earth Concentrate	Add 1% Ti inter- nal standard	Dilute 1:6 with graphite	R.E. oxides plus 1% Ti, in graphite	VI. Rare Earth Run C.B. Method	3 mg in shallow cup (1/32 in.)	2800-4100 A E SA No.1 plate Complete burning Exposure 40 sec	Sc, Y, La, Ce, Pr, Eu, Gd, Dy, Er Nd, Sm, Tb, Ho, (relative to Ti) Tm, Yb, Lu, Th
10. Refractory Concentrate		Add 100 mg Bi ₂ O ₃	Bi ₂ O ₃ matrix plus refractory elements	VII. Refractory Run C.B. Method	10 mg in shallow cup (1/32 in.)	2200-3500 A E SA No.1 plate Complete burning Exposure 60 sec	Cb, Ga, Hf, Mo, Pd Ta, Ti, <u>V</u> , W, Zr
11. Platinum Concentrate		(Graphite is added later to the electrode charge)	Au matrix plus Pt metals	VIII. Platinum Run C.B. Method	5 mg Au, add 2 mg graphite, in shal- low cup (1/32 in.)	2200-3500 A E SA No.1 plate Complete burning Exposure 100 sec	Ru, Rh, Pd, Ir, Pt (6)

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- Notes:
- (1) Numbers in parentheses in the scheme refer to the following notes. For complete details refer to the analytical procedures (sections 6, 7, 8, 9).
  - (2) Most of the materials are converted by ignition to a common base, U₃O₈. Since ignition results in loss of Hg, a portion of the original sample may be examined for this element (usually UO₂ and UO₄ samples); also, boron is determined on a portion of the original green salt.
  - (3) As, Na, Mo, V, and Pd may be determined alternatively by two of the spectrographic operations as discussed in detailed instruction; the most sensitive test is indicated by underlining the chemical symbol.
  - (4) As-rich samples are treated to remove As to permit determination of Cd (usually UO₄ and U₃O₈ samples).
  - (5) For determination of Fe, Mg, and Mn in pure materials, Ga₂O₃ containing 1% Cr as Cr₂O₃ is added to provide Cr internal standard.
  - (6) Os is not determined spectrographically.

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Osmium is lost as the volatile oxide in the preparation of the platinum-group concentrate. Rhenium forms volatile oxides but may be determined in un-ignited samples such as black oxide, although the spectral sensitivity is poor. Selenium and tellurium are somewhat volatile, particularly under acid conditions. However, un-ignited samples could be examined by the pyroelectric method for these two elements in the region of 2000 to 2400 Å, using a plate specially sensitized for the ultra-violet region. A method devised for the determination of the two elements in bismuth oxide was found to be sensitive to 10 ppm Te and 100 ppm Se.

- (d) Elements that may be included in the system of analysis in addition to those of group (c): Ra, Ac, and Sr.

Radium and actinium may be observed by more sensitive electroscopic methods. However, radium probably could be determined in a manner similar to that of procedure 7.1-4 for barium, and actinium would be obtained in the rare earth concentrate. Strontium should be capable of determination by modification of the method for calcium; Procedure 7.1-6. However, both of the sensitive lines, Sr 4077.71 and Sr 4215.52 Å, are confused by uranium lines, and recourse to other sensitive strontium lines would require a separate spectrogram.

2.4-2 Limits of Detection

The limits of detection of the elements and the methods of determination are given in Table 7. The limits are those observed in routine analysis, and do not necessarily represent the ultimate that may be obtained under the most favorable conditions. The limits in each case refer to the amount in parts per million detectable in the original sample. For the rare earth concentrate, a typical example was assumed in which a concentrate weighing 1 mg is obtained from a 25 g portion of the original sample. The limits of detection for Dy, Er, Eu, Gd, Ho, Tb, Tm, Yb, and Sm in the original sample were then calculated from the data on sensitivities for the determination of rare earths in the concentrate given in Section 2.3-1. The sensitivities for the remaining rare earths and thorium are estimated.

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As the elements Mo, Pd, and V may be determined by two procedures, the limits of detection are given for both, with the less satisfactory method indicated by parentheses.

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Table 7. Present Lower Limit of Routine Spectrographic Determination of Impurities in Uranium Metal and Compounds

Element	Method					Element	Method				
	1	2	3	4	5		1	2	3	4	5
Ag	0.05					Mo	1		(1)		
Al	5					Na	0.5				
As	5					Nd					10.5
Au	0.3					Ni	2				
B	0.1					Os					
Ba	10					P	50				
Be	0.1					Pb	1				
Bi	0.5					Pd			0.5	(5)	
C						Pr					
Ca		2				Pt				1	10.5
Cb			3			Ra					
Cd	0.07					Rb	1				
Ce					10.1	Re					
Co	1					Rh				20	
Cr	3					Ru				5	
Cs	8					Sb	10				
Cu	0.3					Sc					10.1
Dy					0.04	Si	3				
Er					0.04	Sm					0.3
Eu					0.02	Sn	1				
Fe	1					Sr					
Ga			1			Ta			40		
Gd					0.04	Tb					1.0
Ge	0.5					Te					1.
Hf			10			Th					
Hg	10					Ti			3		
Ho					0.04	Tl	3				
In	0.5					Tm					0.04
Ir				100		U					
K	2					V	(5)		1		
La					10.1	W			40		
Li	0.1					Y					10.1
Lu					10.5	Yb					0.004
Mg	0.5					Zn	20				
Mn	1					Zr			1		

Method

1. Pyroelectric Concentration Method on Oxide
2. Direct Examination of the Oxide
3. Examination of Refractory Concentrate in Bi_2O_3
4. Examination of Platinum Metal Concentrate in Gold
5. Examination of Concentrate of Rare Earth Oxides

Note: (1) Sensitivity values are given in parts per million of the original sample.

(2) Values in parentheses indicate determinations not usually made in the general scheme by the method involved.

(3) Sensitivities for rare earths are based on a concentrate of 1 mg from 25 g sample.

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3. LABORATORY EQUIPMENT AND GENERAL OPERATIONS

The equipment employed in the analytical methods is described in the following sections. Instruments commercially available are listed with the manufacturer's name and other pertinent information; instruments especially designed or modified for this work are described more fully with details on the application. It is to be understood that the equipment listed is that employed in our laboratory and in many cases its equivalent may be available commercially or may be constructed to accomplish the same purposes.

3.1 Chemical Laboratory

The chemical operations are carried out in two chemical laboratories, the first in the chemical section of the project and the second in conjunction with the spectrographic laboratory. The first laboratory carries out the preliminary preparation of routine samples and the preparation of the rare-earth, refractory, and platinum metal concentrates. This laboratory is equipped with the usual facilities for general chemical work including chemical benches, with water, gas, air, and suction, chemical hoods, steam baths, muffle furnaces (max. 1000°C), drying ovens (max. 250°C) and chemical balances, one of which should be accurate to 0.1 mg. Cleanliness and care are necessary to the operations carried out, particularly in the preliminary preparation of samples where dust and fumes from other operations must be avoided. As an example of the precautions that are necessary, cadmium-plated ring stands must be excluded from the neighborhood of the work. The ignition of pure samples should be carried out in a furnace reserved for the purpose and contamination from the furnace walls prevented by use of a silica liner. The reagents employed should be checked for interfering impurities. All test samples are handled in clean glass vials with plastic screw-caps lined with paper coated with a plastic such as vinylite. Many of the operations require platinum or quartz dishes and crucibles as specified in the detailed chemical procedures of Sections 6 and 8 of this report.

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The second chemical laboratory is located in a section of the spectrographic laboratory and is equipped similarly to the first. It is reserved for chemical operations closely related to the spectrographic procedures, and it will be discussed as a part of the spectrographic laboratory.

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3.2. Spectrographic Laboratory

This laboratory, originally employed for a variety of spectrographic problems, was refitted and its operations reserved exclusively for spectrographic research and analysis on the uranium project. Two requirements are met in the plan of the laboratory (Figure 2), first, adequate space and facilities for a personnel of twelve; and second, proper subdivision to minimize both the interferences among various operations and the ~~over~~^{ever}-present danger of contamination of samples. The latter problem is particularly serious in view of the large number of elements determined, the low level of concentrations involved, and the variety of materials handled, principally magnesium, thorium, beryllium, lime, and dolomite in addition to the uranium-base materials.

The floor of the laboratory is concrete, covered with waxed asphalt tile. Ventilation and exhaust of fumes are provided by a large exhaust fan with conduit leading from the chemical laboratory, from the smaller rooms, and from various points where fumes or dust are evolved, such as the electrode holders and tool grinder. Air entering the laboratory by way of the building ventilating system is carried through spun-glass filters. The small chemical laboratory is closed off from the remainder of the section by a door normally closed; adequate ventilation of this room is obtained by the exhaust system, intake of air being provided through spun-glass filters mounted in the wall separating the chemical and spectrographic laboratories. This arrangement prevents diffusion of chemical vapors into the spectrograph room and also provides clean air for the chemical laboratory. The small chemical laboratory serves for the preparation of spectrographic standard samples, the preparation of gallium oxide, and other special chemical operations closely related to the spectrographic procedures.

Electrodes are machined in the tool room, which is kept free of any operations on samples. The central preparation room is reserved for the grinding and weighing of uranium-base samples and concentrates prior to spectrographic examination, while materials of other types are handled in a part of the office section. The visual and photometric examinations of spectrograms are made in the photometer room, which is separated from other laboratory activities that tend to be distracting. The general operations carried out in the laboratory are described in Sections 3.3 to 3.7.

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FIGURE 2. FLOOR PLAN OF SPECTROGRAPHIC LABORATORY

SCALE $\frac{1}{8}$ IN. = 1 FT.

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3.3. Preparation of Electrodes

A three-piece electrode combination is employed for each procedure throughout the system of analysis. The number of pieces to be machined has been reduced to a minimum of four; the dimensions of these electrode pieces and of important tools are given in Figures 3A and 3B. Two anode cap pieces are required, piece A containing a deep cup for holding the sample in the pyroelectric method, and piece B having a shallow cup for direct arcing in the determination of calcium and for the analysis of concentrates. The anode cap in each case is mounted on a pedestal (D) through a taper fit, and the assembly is completed by the cathode (C). The anode cap pieces are machined on the motor driven cutter shown in Figure 4, equipped with two drilling tools and a cut-off saw. The cathode pieces are cut with the pencil sharpener shown at the right of Figure 4. This is modified to provide a bearing at the left end of the shaft and a stainless steel guide extending between the cutters to ensure a symmetrical cone on the cathode. The cathode pieces are marked to proper length on a razor edge mounted on the block shown behind the pencil sharpener, and then are broken by hand. The electrodes are cut from high-purity graphite rods, 1/4-inch and 1/8-inch in diameter, 12-inches long (National Carbon Co., Special Spectroscopic Graphite Electrodes, ash less than 0.001 per cent). Sample pieces of electrode are tested for purity, especially for freedom from boron, prior to use.

Procedure:-----Prepare the motor-driven cutter for operation by inserting the proper anode-cup drilling tool in the drilling assembly at the right, and insert in the assembly at the left the tool for cutting the tapered mounting hole. Set the guide on the cut-off saw assembly to cut sections 5/8-inch long. Place boxes under the machine frame to catch waste graphite, which is subsequently added to a storage bottle. Open the cellophane wrapping of the 1/4-inch electrode rod at one end, being careful at this point and in the following operations not to touch the electrode rods with the hands. If at any time the cut pieces are touched or are dropped they must be discarded. Hold the graphite rod at the end covered by the cellophane and insert the opened end into the guide at the right. Push the rod in until it rides against the shank of the drilling tool. Remove the rod and insert it in the guide in the cut-off saw and raise the lever to cut the electrode, the cut piece falling into a box provided. Repeat this operation until the 12-inch rod has been consumed. Cut a pedestal hole in each anode piece by placing the piece in the cutter guide at the left, using tweezers and pushing the piece in, and using clean filter paper in holding the rod. Remove the piece, shake out the loose graphite, and place the electrode in a box labelled to indicate the wall depth of the cup.

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Prepare for cutting the cathodes by opening the cellophane on one end of the 1/8-inch rod, being careful not to touch the bare rod at any time.

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B. ANODE CAP $\frac{1}{32}$ " CUP

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FIGURE 3A. ELECTRODE SHAPES

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FIGURE 3B. ELECTRODE TOOLS

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FIGURE 4. ELECTRODE CUTTERS

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Insert the rod and machine it to a point in the pencil sharpener. Remove the rod, mark it on the razor edge to the length indicated by the guide, and, holding the pointed end of the rod with filter paper, break the rod at the mark. Place the piece in a box labelled "cathode". Repeat this operation until the section of rod is shortened to two cathode lengths. After the point is cut on one end of this section, reverse the rod and cut the point on the remaining end before breaking the rod.

Fashion the pedestal pieces from cathodes by inserting the cathode in the pedestal-forming tool (Figure 3B) and removing the protruding tip. Place the pedestals in a box reserved for the purpose. Keep all electrode boxes in a clean place with the cover closed prior to use.

3.4. Preparation of Sample Charges

The equipment employed in grinding, weighing, and handling in the preparation of electrode charges is listed below.

- (a) Mortars and pestles: Mullite, for hand-grinding, Catalog No. 12-948, sizes 75 mm and 120 mm outside diameters; Fisher Scientific Company. Mortars and pestles are ground and polished prior to use.
- (b) Cleaning supplies: Paper, lens tissue, according to Federal Specification No. UU-P-313A, dated July 30, 1943, 1000 sheet package; Scott Paper Company. Bleached cheesecloth.
- (c) High-range balance: Analytical beam balance, capacity 200 g preferably equipped with magnetic damping device. Pan: Bent sheet aluminum.
- (d) Medium-range balance: Double-hook precision balance, scale range 0 to 250 mg, Catalog No. 2429; with single-lip powder loading pans, sheet aluminum, type M-20663-1 and pan compensating weight; Roller Smith Company. (Note: Pan and weight are trimmed to 400 mg each and the pan is fitted with an off-center hole prior to use.)
- (e) Low-range balance: Double-hook precision balance, scale range 0 to 50 mg, Catalog No. 2409; with round, shallow weighing pans, type SS-24386-2 and pan compensating weight; Roller Smith Company. (Note: Pan and weight are trimmed to 100 mg each and the pan is fitted with an off-center hole prior to use.)

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- (f) Spatulas: Hayman micro spatulas, stainless steel, Catalog Nos. 9007-c and 9007-s; Arthur H. Thomas Company. ✓
- (g) Vials: (1) Glass vials, 60 by 28 mm, capacity 17 ml, with black, plastic screw-caps having cork plug plus vinylite lining.
(2) Same, except size 45 by 15 mm, capacity 5 ml.
- (h) Forceps: (1) Cover glass type, with flat, bent blades, 105 mm long, Catalog No. 5555; Arthur H. Thomas Co. (For handling balance pans). (2) Cover glass type, with thin, straight blades, 115 mm long, Catalog No. 5556. (Prior to use the jaws are bent to grasp 1/4-inch electrodes).
- (i) Electrode blocks: Bakelite, 6 x 1-3/4 x 1/2 inches, drilled with 16 holes to take 1/4-inch electrodes, holes numbered 1 to 16 and blocks labelled with letters for identification.
- (j) Covers for electrode blocks: Bell shields, cellulose acetate, height 3 inches, diameter 8 inches, Catalog No. A-5-540; Burrell Technical Supply Company.
- (k) Storage cabinet: Desiccator cabinet, Catalog No. 12690; Central Scientific Company.

Samples are ground in the mortars for time intervals depending on the size and type of sample, varying from 5 to 10 minutes for small amounts up to 1-1/2 hours for 50 g portions of standard samples. The specific times for grinding given in the analytical procedures were determined by trial grindings checked by spectrographic analysis of parts of the mixtures. Separate mortars and pestles are employed for samples of different matrices when contamination by the matrix may be serious. For example, the mortar employed for grinding the uranium-base samples with gallium oxide should not be used for grinding the zirconium-group concentrate, because of danger of contaminating the latter with gallium. The mortars are cleaned between applications to samples of the same type and purity by rinsing with distilled water and drying with the special non-fraying paper (b). When the samples to be ground differ in type and purity, for example, pure black oxide as compared with crude oxide, the mortars and pestles are cleaned with nitric acid, rinsed, and then dried with paper. The ground portions of samples are placed in clean vials. ✓

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The weighings of quantities of samples larger than 250 mg, as for addition of carrier (Procedures 7.1-1 and 7.1-2), are made on balance (c). The 50 and 100 mg electrode charges of uranium-base samples are weighed on balance

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(d) in the pan reserved for the purpose. A second pan is used for 100 mg quantities of bismuth oxide for procedure 9.2. The charges are weighed to a tolerance of plus or minus two per cent and are transferred as demonstrated in Figure 5. The pan is removed from the balance using the forceps (h) with flat, bent blades, and is placed over the electrode, which is held in an electrode block (i) with the hole in the pan in line with the electrode cup. The pan is tilted and is tapped gently so that the charge flows through the hole and into the cup. The pan is removed and any dust remaining on the pan is blown off. The pan must be kept clean and bright by occasional polishing with fine polishing paper. Quantities of samples amounting to 50 mg or less are weighed on the small balance (e). These include portions of gallium oxide carrier for Procedures 7.1-1 and 7.1-2, and charges of the concentrates for the procedures of Section 9. One pan is reserved for weighing gallium oxide for Procedures 7.1-1 and 7.1-2 and uranium oxide charges for determination of calcium, Procedure 7.1-6, and another pan is reserved for weighing charges of concentrates in the procedures of Section 9. If other materials such as beryllium oxide are to be weighed on the same balance, a separate pan should be used in each case. The electrode block is protected by a cover (j) between operations, and when the weighings have been completed the electrode block is placed in the storage cabinet (k).

3.5 Spectrography

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The spectrographic assembly (Figure 6) consists of three essential sections; first, the grating spectrograph; second, the optical system for illuminating the spectrograph; and third, the excitation unit. The assembly provides for d.c. arc excitation of samples in a water-cooled electrode holder, projection of the image of the arc by means of a quartz lens through a step sector and the slit of the spectrograph to form an image on the grating, and formation of the spectrum at the plate holder. An accessory lens and screen are provided at the opposite end of the optical bench for observation of the arc image and adjustment of the position of the electrodes. The step sector provides, for each burning of the arc, a set of 2 to 5 exposures, the magnitude of the exposures being determined by the ratio of the step openings in the sector. This is a well-known system for obtaining a spectrum in which the spectral lines of different intensities may be observed at optimum densities on the photographic plate. It is particularly useful in the determination of the large number of elements required for the methods described in this report. The spectrograph, an Eagle mounting consisting of the simple system of slit, concave grating, and plateholder, has various controls for rotating the grating to obtain different spectral regions at the 10-inch plate holder and for focussing to obtain sharp images. This mounting of the grating is astigmatic, so that

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FIGURE 5. TRANSFER OF ELECTRODE CHARGES

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FIGURE 6. SPECTROGRAPHIC ASSEMBLY

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the vertical edges, represented by the slit, and the horizontal edges, represented by the periphery of the step sector disk, must necessarily be at different positions in order that the images of the two edges be well-defined on the photographic plate. The secondary focus point, at which the step sector is placed, varies with the spectral region photographed, thus requiring the re-setting of the sector, electrode stand, and accessory projection lens at different points on the optical bench. This adjustment of the system is not a serious disadvantage once the proper positions have been determined and recorded. A list of parts included in the system is given below, with notes on modifications or special features not provided by the manufacturer.

- (a) Spectrograph: Eagle-mounting, 3-meter, grating spectrograph, with 25 and 50 micron fixed slits; Baird Associates. The instrument is mounted on tables furnished by the manufacturer. (The adjustable diaphragm at the grating is replaced by a series of interchangeable, heavy-paper diaphragms in which slot-like openings are provided for control of light intensity.)
- (b) Optical bench: Cenco demonstration bench, Catalog No. 85800, Central Scientific Company; consisting of a rigid steel channel with graduated centimeter scale 125 mm long, and hinged carriages for mounting optical devices. (Adjustable set screws may be required in the hinge face of the carriages for accurate positioning of the vertical supporting tube.)
- (c) Step sector: Sector mounting with motor and sector disc, 3 inches diameter having 5 steps cut in the ratio of 2; Baird Associates (Figure 7). The sector frame is fitted with a mask consisting of two metal leaves adjustable vertically in front of the sector face to permit choice of any combination of successive steps of the sector disc as required by the methods of analysis. A crystal quartz lens ($f_D 44$ cm) is mounted on the reverse side of the sector in a manner permitting vertical and horizontal adjustment.
- (d) Electrode holder: This holder, Figure 8, designed and built in our shop (1) is now built by the Jarrell Ash Co., Boston, Mass. It is a fully enclosed, precision mounting of two water-cooled electrode clamps, each with vertical adjustment; the whole being adjustable horizontally at right angles to the optical axis by a screw and in the direction of the optical axis by movement along the optical bench. A safety circuit is provided to open the power circuit to the electrode clamps when the door is opened. The water-cooling system for the electrode clamps consists of a reservoir, a 5-gallon bottle, connected by tubing through a rotary pump (Catalog No. 72-820; Burrell Technical Supply Co.) to the clamps.

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FIGURE 7. STEP SECTOR

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FIGURE 8. ELECTRODE HOLDER

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- (e) Projection lens and screen: A glass lens, 6 cm diameter, f equals 6 inches, is mounted in a carriage to permit setting at different positions on the optical bench. A metal plate with a paper face for marking outlines of electrodes provides a convenient screen for observing the position of electrodes and the behavior of the arc during an exposure.
- (f) Excitation unit: A full-wave rectifier unit converts 220 volt a.c. to 250 volt d.c., maximum 15 amperes, for operation of the arc. H.W. Dietert Co., Detroit, Michigan; Catalog No.2000.
- (g) Electrical switches: Switches with indicating pilot lamps are mounted under the optical bench as shown in Figure 6. From left to right, the switches control (1) shutter, (2) electrode illuminating lamp, (3) sector, (4) water-cooling pump, and (5) master power for the other switches and the spectrograph controls.
- (h) Timer: Electrical clock with a sweep second hand and a large dial, type II; Warren Telechron Company.

Procedure for Alignment of the Optics:----- Level the spectrograph and adjust the optical bench approximately in position under a line extending from the grating through the slit. Place the electrode holder on the bench and insert the electrodes. Adjust the holder laterally so that the electrodes are centered exactly on a perpendicular line midway between the rails on the bench. Set the spectrograph for the visible region of the spectrum, remove the slit, and adjust the plate mask to a 2 mm separation. Place a ribbon filament lamp at the plate-holder opening and observe the light beam emerging from the spectrograph. This beam serves to define the optical axis over the optical bench. Orient and level the bench so that when the electrode holder is moved along the bench the electrode gap remains centered on the beam. Now place the sector on the bench at the stigmatic position for the spectral region selected for use. Adjust the sector vertically until the sector opening is centered on the optical path. Calculate the distance of the electrodes from the sector lens such that a sharp image of the electrodes will be formed on the grating. (This distance is obtained from the formula $1/p = 1/f - 1/q$; where p is the distance of the source from the lens, f is the focal length of the lens for the average wave length of the region to be photographed, and q is the distance from the lens to the grating.) Set the electrode holder at the calculated position, and adjust the sector lens so that the images of the electrodes are observed to fall symmetrically on the grating face. Set the screen in position at the end of the optical bench, and mount the glass projection lens on the optical axis in a position to form a sharp image of the electrodes on the screen. Mark the outline of the electrode image on the screen for future reference.

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For each setting of the spectrograph (Sections 7 and 9) having an appreciably different stigmatic position, repeat the procedure to obtain appropriate settings of the optical accessories. The setting for the infra-red region will require mounting an auxiliary screen beyond the end of the optical bench. Make a record in tabular form of all settings.

Note 1. The zero of the optical-bench scale is not centered under the slit and furthermore the index marks on the optical accessories do not necessarily center under the optical part involved. The settings of these parts given in the detailed procedures of Sections 7 and 9 therefore will not apply directly to other equipment. If the distances from the slit of the spectrograph to the working parts are desired the following corrections should be applied.

Distance desired, from slit to:	Correction to be added to scale settings: cm
Face of sector	10.0
Center of sector lens	11.5
Center of electrodes	22.7
Center of projection lens	18.4
First screen	19.0
Second screen	36.5

Note 2. The position of the electrode stand for most uniform illumination of slit and sector combination should be adjusted critically after the general alignment of the optics has been established. Remove the sector disk from its shaft, place the slit on the spectrograph and make a series of 3 or 4 exposures with the electrode holder at various distances at and near the calculated setting. Examine the line images on a photometer to determine the setting at which the spectral lines show optimum uniformity of density from top to bottom.

3.6. Photography

The dark room for processing the plates is equipped with an electrical refrigerator for storing II-F and I-N plates, a sink with hot, cold, and ice water, and a bench on which is mounted the following equipment:

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- (a) Developing machine for plates, with constant temperature bath and rocking device; Catalog No. 2300 P, ARL-Dietert Company.
- (b) Plate washer; Catalog No. 2326, ARL-Dietert Company.
- (c) Plate dryer; Catalog No. 2351, ARL-Dietert Company.
- (d) Electrical interval timer clock, 110 volts a.c., with interval setting 1 to 120 minutes and sweep-second hand; Catalog No. A-22480, Burrell Technical Supply Company. (Prior to use the sweep-second hand was coated with phosphorescent paint.)
- (e) Safe lights: Wratten Series 1.
- (f) Supplies:

Photographic plates 4 x 10 in.; Eastman Kodak Company.

- 1. Spectrum Analysis No. 1
- 2. Spectroscopic Type II-F
- 3. Spectroscopic Type I-N

Developer: Eastman D-19
Stop bath: Eastman SB-5, double strength
Fixing bath: Eastman F-5
Sponge: Vis.cose No. 4

The plates are processed according to the schedule of Table VIII.

Table VIII

Photographic Processing Schedule

<u>Step</u>	<u>Spectrum Analysis No.1</u>	<u>Types II-F and I-N</u>
1. Safe light	On	Off
2. Development	Two minutes	Four minutes
3. Stop bath	Fifteen seconds	Fifteen seconds
4. Fixing	One minute	Bathe two minutes after clearing
5. Washing*	One minute	Ten minutes
6. Drying	2-1/2 minutes with No.3 heat on dryer	2-1/2 min. with No. 1 heat on dryer

* After a plate has been washed it is rubbed lightly with the wet sponge, the sponge is squeezed dry, and the plate is wiped with the sponge to remove all drops of water before it is dried. The dry plate is labelled in ink with the plate number and is stored in the plate envelope. Care must be exercised to avoid scratches or abrasions in handling the plate since these seriously affect the photometric measurements.

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3.7. Photometry

Spectrograms are examined in a room set aside for this work where the operators may make visual inspection of plates and photometric measurements under conditions of quiet and freedom from interruptions. The following equipment is employed:

- (a) Comparator-Densitometer, with power controlled by an Electronic Voltage Regulator; Catalog No. 2255 PE, ARL-Dietert Company.
- (b) Calculating Board, for converting photometric measurements to line intensities by a plate calibration curve.
- (c) Viewing box. Size 20 x 30 in., with a flashed opal-glass cover and fluorescent lamps; Baird Associates.

Note: The intensity of illumination provided by the lamps in the viewer as received is too high and is not uniform. This condition may be modified by mounting a piece of pot-opal (milk) glass between the lamps and the flashed-opal glass. With this modification the viewer then provides a more uniform field of illumination with an optimum intensity level and with a minimum of heat. These factors are important to the comfort of the operator in the almost continuous observing work required by the analytical procedures.

The subject of photographic photometry has been discussed in the general literature. The use of the step sector has been treated by Strock (2), and specific applications similar to those of this report have been described by Scribner (3). Two types of photometric procedures are involved in our system of analyses. The first, termed the external standard method, is applied to the determination of B, Cd, and Si. The second, termed the internal standard method, is applied to the determination of Fe, Mg, Mn, Dy, Er, Eu, and Gd. A typical example of each method will be described, namely, for the determination of boron and of iron. The spectrograms, prepared according to the procedures of Sections 7 and 9, are measured on the photometer as soon as possible to minimize errors from scratches or abrasions of the emulsion. After the photometric measurements have been completed, the plate is examined visually on the viewing box for estimation of the concentrations of the remaining elements as required.

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3.7-1. External Standard Method: Determination of Boron

This method involves (a) measuring the intensity of a boron line in the spectra of a graded series of standards; (b) plotting these intensities against concentration of boron to obtain an analytical curve; (c) measuring the intensity of the boron line in the spectra of samples and of selected standards on the same plate; (d) determining the correction necessary to bring the boron intensities for the standards to the analytical curve; (e) applying this correction to the boron intensities for the samples; and (f) reading from the analytical curve the concentrations of boron corresponding to the corrected intensity values.

The first two operations, resulting in an analytical curve, are required only in setting up the original procedure or, subsequently, if the procedure is modified or if improved standards are introduced. The spectra of the standard samples for boron, Section 5.2-6 are photographed according to Procedure 7.1-2 (which provides for the determination of iron, magnesium, and manganese with the same set of standards). The exposures are made under conditions kept as nearly constant as possible. Eight exposures with the step sector (5 steps) may be made on one plate, providing for duplicate runs for each of the four standards in set 5.2-6. The densitometer is adjusted for use by allowing a two hour warm-up period, adjusting the lamp to obtain a uniform field, and making other operations as described by the manufacturer (4). Before measurements are begun, a table is prepared with blank spaces for entering observations for the five sector steps for each spectrum (3); for convenience the table is mimeographed.

Procedure:-----Place the standard plate in the densitometer, adjusting it so that the spectra move parallel to the edge of the projection screen as the plate carriage is moved. With the scanning head out, adjust the galvanometer scale to zero (dark reading). Move the scanning head into contact with the plate at a clear, unexposed portion of the emulsion, and adjust the galvanometer scale to 100 (transmittancy 100 per cent). Remove the scanning head, and move the plate carriage to bring the boron line 2497.73 into position for scanning. Choose a step of the line image having medium transmittancy, move the scanning head into place and scan the line image by slow hand-operation of the control. (In view of the narrow spectral line images measured, it is important that the scanning slit and spectrum line be accurately parallel and that the image be scanned slowly and uniformly.) For the boron line in each standard, record measurements on two steps of the line; when possible measurements falling within 20 to 80 per cent transmittancy are preferred. Measure additional steps for two of the line images to provide for plate calibration.

Establish the plate calibration curve as follows. Plot the transmittancies of the steps of a calibration line against log relative intensity value for the step of the sector (i.e. 0.300, 0.600, etc. where the sector step ratio is 2). Plot the points for the second line so that the central points are in line. Draw a smooth curve through the points. Read from this curve the log I values corresponding to all of the measured transmittancies.

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To each of these recorded log I values, add the log I increment necessary to reduce the values to log I for the strongest step. Measure the remaining plates of the standards in the same manner but use the same plate calibration curve if inspection shows no shift.

Establish the analytical curve (Figure 9) by plotting the log I values for each standard against log concentration of boron, using semi-log paper on which the concentration of boron is read on the log scale. The multiple determinations for each standard should agree within plus or minus ten per cent. In Figure 9, the mean of the plotted values for each standard is represented by a small circle, and the spread of the values is indicated by the vertical line through the circle.

For the analysis of samples by procedure 7.1-1, the spectrogram will include samples and two of the boron standards used in establishing the analytical curve. Measure the transmittancy of each of the boron lines and reduce the values to log I for the strongest steps as described above. Usually it is necessary to draw only the straight-line portion of the calibration curve (20 to 80 per cent transmittancy). Observe the average log I correction necessary to bring the two standards on the analytical curve, and correct the log I values for the samples accordingly. Apply the corrected log I values to the analytical curve to obtain the concentration of boron. Average the results on duplicate exposures of the samples.

Note: Determination of boron below 0.25 ppm.

The additional standard at 0.15 ppm was added to the analytical curve by the preparation of a separate set of boron standards. In view of the fact that uranium oxide free of boron could not be obtained, the residual amount was determined by the method of successive approximations (5). This involves (a) assuming values for the residual boron in the base material, (b) adding this correction to the values of boron in the synthesized standards, and (c) plotting an analytical curve for each set of data. The value of the residual boron giving a linear curve is adopted. Correction for background in the spectrum was made when appreciable. The results of these operations have been carried as far as possible at the present time. Further improvement awaits receipt of highly-refined base material free of boron, and comparison with carefully devised and controlled chemical analysis. It is estimated that the spectroscopic results below 0.2 ppm are uncertain to plus or minus 0.05 ppm with respect to the true content. The relative values between 0.1 and 0.25, representing the mean of duplicate runs, are believed to be good to plus or minus 0.02 ppm.

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FIGURE 9
ANALYTICAL CURVE FOR BORON

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3.7-2. Internal Standard Method: Determination of Iron

This method follows the preceding method closely except that the intensity of the impurity line, iron, is measured relative to that of an internal standard, chromium. Chromium was selected since its volatilization was observed to be affected similarly to that of iron. The log I values for Fe 2599.40 and Cr 2762.59 are determined and the log ratio $I(\text{Fe})/I(\text{Cr})$ is obtained by subtraction. The log I ratio is then applied in the same manner as that for log I in the case of boron, including correction by two standards photographed with the samples. The analytical curve is shown in Figure 10.

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FIGURE 10
ANALYTICAL CURVE FOR IRON

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4. PREPARATION OF GALLIUM OXIDE

4.1. Requirements

The gallium oxide employed as a carrier in the pyroelectric method should be of high purity but not necessarily free of all impurities. It is important that the concentrations of the volatile impurities be reduced below the level of interference with the determinations to be made. For the analysis of uranium-base materials, the gallium oxide constitutes two per cent of the electrode charge, which results in a dilution of 50 to 1 for the carrier impurities as far as their effects in the determinations are concerned. This means that spectrographic traces of elements such as manganese may be tolerated in the gallium oxide, but for elements such as boron and cadmium, determined at very low concentrations in uranium materials, it is safest to follow the rule that no traces be observed in the carrier on spectrographic examination.

Gallium metal of high purity may be prepared by methods described by Hoffman (1,2). However, many of the operations involved in these procedures may be avoided for our purposes, depending on the purity of the gallium available as a starting material. Tests of gallium metal and gallium oxide supplied by A.D. Mackay, New York, showed the metal to be purer, the nature of the impurities usually permitting simple chemical manipulation to reduce their magnitude to insignificant amounts. The metal from this source may contain troublesome amounts of In, Pb, Sn, and Zn. The first three of these elements may be removed by virtue of their positions in the electromotive series relative to gallium, since on incomplete solution of the gallium in acid, the elements below gallium in the series remain largely in the undissolved globule. However, zinc and other elements above gallium in the series will go into solution. If objectionable amounts of these elements should be found by spectrographic examination of the metal, the gallium solution is further purified by ether extraction as described by Hoffman (1) and by Bubes (3). After purification the gallium is converted to sulfate, and, if desired, an internal standard element for spectrographic application is added. The gallium sulfate is dried, converted to oxide over a flame, and finally ignited in a furnace at 1200°C. The high-temperature ignition produces a dense oxide which possesses desirable characteristics for spectrographic application. The product is usually contaminated by small amounts of platinum metals derived from the platinum dish; however, this contamination is insignificant for the intended use. The results of qualitative spectrographic tests of portions of the gallium material removed at various steps in the purification are shown in Table 9. The first column gives a test of a recent stock metal free of zinc; the second column, that of the undissolved globule of metal showing an accumulation of impurities; and the third column, the analysis of the final gallium oxide product of the simple purification without ether extraction. Columns 4 and 5 show analyses of sample taken from the ether layer and the acid layer, respectively, following the ether extraction of the solution of an earlier lot of gallium containing zinc. The results show the tendency of a number of impurities, including zinc, to concentrate in the water layer. The steps in the purification given in the following sections result in an over-all yield of about 90 per cent.

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NBS Form 82 Table 9. Spectrographic analyses in the preparation of gallium oxide.
NBS Test No. IV-1/Tp

TABLE OF RESULTS

Element	Sample					Element	Sample				
	1	2	3	4	5		1	2	3	4	5
Ag	T	VW	T	FT	FT	Mo	-	-	-	-	-
Al	-	-	-	FT	T	Na	-	-	-	FT	VW
As	-	-	-	-	-	Nd	-	-	-	-	-
Au	-	-	-	-	-	Ni	-	-	-	-	-
B	-	-	-	-	-	Os	-	-	-	-	-
Ba	-	-	-	-	-	P	-	-	-	-	-
Be	-	-	-	-	-	Pb	VW	W	-	FT	W
Bi	-	-	-	-	-	Pd	-	-	-	-	-
C	-	-	-	-	-	Pr	-	-	-	-	-
Ca	FT	FT	FT	FT	W	Pt	-	-	T	VW	W
Cb	-	-	-	-	-	Ra	-	-	-	-	-
Cd	-	-	-	-	-	Rb	-	-	-	-	-
Ce	-	-	-	-	-	Re	-	-	-	-	-
Co	-	-	-	-	-	Rh	-	-	T	W	T
Cr	-	-	-	-	FT	Ru	-	-	T	-	-
Cs	-	-	-	-	-	Sb	-	-	-	-	-
Cu	VW	W	FT?	T	W	Sc	-	-	-	-	-
Dy	-	-	-	-	-	Si	T	T	T	FT?	VW
Er	-	-	-	-	-	Sm	-	-	-	-	-
Eu	-	-	-	-	-	Sn	T	VW	-	T?	W
Fe	FT	FT	FT	-	T	Sr	-	-	-	-	-
Ga	VS	VS	VS	VS	VS	Ta	-	-	-	-	-
Gd	-	-	-	-	-	Tb	-	-	-	-	-
Ge	-	-	-	-	-	Te	-	-	-	-	-
Hf	-	-	-	-	-	Th	-	-	-	-	-
Hg	-	-	-	-	-	Ti	-	-	-	-	-
Ho	-	-	-	-	-	Tl	-	-	-	-	-
In	VW	W	-	-	W	Tm	-	-	-	-	-
Ir	-	-	T	VW	VW	U	-	-	-	-	-
K	-	-	-	-	T	V	-	-	-	-	-
La	-	-	-	-	-	W	-	-	-	-	-
Li	-	-	-	-	-	Y	-	-	-	-	-
Lu	-	-	-	-	-	Yb	-	-	-	-	-
Mg	FT	FT	FT	T	VW	Zn	-	-	-	FT?	M
Mn	-	-	-	-	FT	Zr	-	-	-	-	-

No.	IV-1 Lab. No.	Label of Sample
1	13050B	Gallium metal, original stock, Ga lot 3-6-45
2	13050B	Gallium metal, undissolved globule, Ga lot 3-6-45
3	14497	Gallium oxide, final product from Ga lot 3-6-45
4	9519	Gallium oxide, from ether layer, Ga lot 3-14-14
5	9520	Gallium oxide, from acid layer, Ga lot 3-14-14

Qualitative scale: VS, 10-100%; S, 1-10%; M, 0.1-1%; W, 0.01-0.1%; VW, 0.001-0.01%; T and FT, less than 0.001%.

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4.2. Preparation of Gallium Chloride Solution

Weigh accurately 10 to 12 g of gallium metal of highest commercial purity, place the metal in a 250 ml quartz flask, and add 100 ml 1:1 hydrochloric acid (purified by distillation). When the reaction slows down, add an additional quantity of 25 to 50 ml of the acid in two or three portions, making a record of the additions. Place a small quartz crucible containing water on the mouth of the flask to act as a loose-fitting cover, and heat the flask on a hot plate until 90 to 95 per cent of the metal is dissolved, leaving a globule the size of a small pea (this operation may require several days). Chill the remaining metal and solution in ice water, and pour the solution into a platinum dish. Wash the flask and globule of metal with distilled water, and add the washings to the main solution. Dry the globule of metal, weigh it to determine by difference the weight of metal dissolved, and set the globule aside as scrap to be re-worked after a sufficient quantity has been collected. If the original metal was found by spectrographic test to contain significant amounts of zinc or other active metals, further purification is necessary by ether extraction as described in Section 4.3; otherwise proceed to Section 4.4.

4.3. Ether Extraction of Gallium Chloride

Adjust the acid concentration of the chloride solution to slightly greater than 1:1 hydrochloric acid, transfer it to a separatory funnel immersed in a beaker of cold water, and add a total of 250 ml of absolute ether (A.C.S.) in small amounts, mixing the liquids gently on each addition. Remove the funnel from the bath, shake the contents, and allow the funnel to stand until distinct liquid layers are formed. Draw off, but do not discard, the acid layer. Wash the ether solution in the funnel by seven successive additions of 10 ml 1:1 hydrochloric acid, adding the washings to the acid layer. Transfer the ether solution to a quartz beaker and evaporate the ether by suction, without heating, through a funnel inverted above the solution as shown in Figure 11. (This arrangement avoids the creeping of the solution over the edge of the beaker, which, in the usual procedure of evaporation, would result in serious loss of gallium chloride.) After removal of the ether, the gallium chloride is dissolved in water and returned to the platinum dish.

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FIGURE II. SYSTEM FOR EVAPORATING
ETHER SOLUTION

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4.4. Conversion of the Gallium Chloride to Oxide

To the gallium chloride solution resulting from operation 4.2 or 4.3, add 30 to 40 ml of sulfuric acid (2:1), 5 ml in excess of the calculated quantity to convert the gallium chloride to sulfate. Evaporate the solution on a hot plate, using suction through a funnel similar to the arrangement shown in Figure 11, until fumes of sulfuric acid appear. (At this point the addition of an internal standard for spectrographic application may be made according to the procedure given in Section 4.5)

Heat the dish slowly on a hot plate to remove the excess acid; then heat over a Meker burner, beginning with low heat and gradually increasing the heat until fumes of sulfuric acid are reduced to an insignificant amount. Complete the conversion to oxide by heating the dish in a muffle furnace at 1100 to 1200°C for two hours. Break up the gallium oxide in the dish, transfer the loose material to a polished agate mortar, and grind it to a powder. (A portion of the sample sticking to the wall of the dish is placed with the scrap). Place the powder in a clean, screw-cap vial; label the vial with the lot number and date. Test each lot for purity by qualitative spectrographic analysis, comparing it with an established standard sample having the required purity.

4.5. Preparation of Gallium Oxide Containing an Internal Standard: Chromium

For this preparation the procedure for obtaining pure gallium oxide is followed through paragraph one of section 4.4. After the gallium has been converted to sulfate and the hydrochloric acid removed by evaporation, the dish is allowed to cool, the sulfate is redissolved, and a calculated volume of chromic acid solution is added to give the desired concentration of chromium in the gallium oxide.

Calculate the quantity of gallium in the dish, accounting for losses in the undissolved globule in Section 4.2 and in the acid layer from the ether separation, Section 4.3, if the latter procedure was applied. (The loss in the ether extraction may be determined by conversion of an aliquot of the acid solution to oxide as described in Section 4.4.) Add to the gallium sulfate solution a quantity of standardized chromium solution (chromic acid) such that

$$W_{Cr} = W_{Ga} \times 0.0134*$$

where W_{Cr} is the weight of chromium to be added, and W_{Ga} is the weight of gallium in the solution. Mix the solutions well and convert to oxide as described in Section 4.4.

- * The proportion of Cr:Ga is derived as follows:
The desired addition of chromium is one per cent of the gallium oxide.

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$$W_{Cr} = W_{Ga} \times Ga_2O_3 / 2Ga \times 0.01$$

or

$$W_{Cr} = W_{Ga} \times 0.0134$$

When the ignited carrier, $Ga_2O_3-Cr_2O_3$, is added to uranium oxide in the proportion of two parts carrier to 98 parts uranium oxide, the chromium concentration in the mixture will be equivalent to that obtained with a sample of uranium oxide containing 200 ppm Cr mixed with pure gallium oxide carrier in the same proportions.

Literature Cited

- (1) J.I. Hoffman.
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J. Research National Bureau of Standards, 13, 665-672 (1934).
- (2) J.I. Hoffman and B.F. Scribner.
Purification of Gallium by Fractional Crystallization of the Metal.
J. Research National Bureau of Standards, 15, 205-209 (1935).
- (3) I.S. Bubes.
Purification and Testing of Gallium Oxide for Spectrographic Use.
Project Report CC-1831 (A-2656) (1944).

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5. PREPARATION OF STANDARD SAMPLES

5.1. Requirements for Standards

The accuracy of spectrographic analysis depends primarily on the reliability of the comparison of unknown samples with standards; properly prepared standards, therefore, are essential to the success of the methods. The factors involved in obtaining reliable standards, especially for application in the pyroelectric method, may be listed as follows.

1. The standards should match the unknown samples as closely as possible in chemical form and density.
2. The concentrations of the added elements, varied in a graded series, should not result in an excessive accumulation of total impurity in any standard. (The limit may be set at a factor of three times the average total impurity for the samples to be analyzed.)
3. Provision must be made, in adding constituents and in final mixing, to obtain standards sufficiently uniform in composition to provide representative portions of the size employed in the analytical procedure.
4. The composition of the prepared standard must be accurately known, taking into account the possibility of errors in preparing standard solutions, in adding the solutions, in losses by igniting the mixture, and in correcting for impurities present in the matrix.
5. Reliance on a single preparation of standards should be avoided; the standards should be checked for accuracy by independent duplicate preparations and by chemical analysis in important cases.

The selection of a material having the required purity to serve as a matrix for standards may be difficult. Usually the purest uranium-base materials contain small amounts of B, Si, Fe, Mg, Ag, and Cu, and the standards prepared for these elements may require correction either by chemical analysis or by the spectrographic method of successive approximations (Section 3.7-1). The routine testing of samples of high-purity uranium materials may uncover a sample in which a particular element is very low, possibly below the limit of spectrographic detection. This material may then serve as a base for a special set of standards prepared in small amounts for determinations at low concentrations of the element in question.

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The quantities of the standards conveniently prepared in the laboratory, taking into account the amount of base-material available, usually do not exceed 50 g for each standard sample, and, for rare earth standards, may be as small as 0.5 g. The sizes of these samples permit hand-grinding with a mortar and pestle. Grinding by an automatic grinding machine with a mortar has been employed in the past but, at present, machine grinding is rarely employed in view of the attention required during the grinding operation and the objectionable contamination of the samples by the mortar material. However, in one instance (Section 5.2-6), a much larger quantity of a set of uranium oxide standards was prepared by the chemical section for distribution among the project laboratories. In this case the preparations were mixed in a porcelain ball mill but the resulting contamination by silicon was unimportant for the proposed use of the standards. ✓

The addition by small amounts of solutions of the elements to the dry matrix of the standards has been found satisfactory. In cases where the addition of several portions of solutions would result in excessive wetting of the matrix with the tendency to loss on the sides of the dish, the mixture is dried between additions. In rare cases where the addition of a constituent in solution would require an excessive volume of liquid, the element may be added as a dry compound. This procedure requires considerable care to ensure a homogeneous mixture. Very hard compounds should be avoided and, prior to addition, the material should be powdered to pass a 325-mesh sieve. When contamination by the sieve may be serious, the fineness of the ground material may be tested by sieving a small representative portion, which is discarded. The purity required for the materials to be added to the standard matrix is not a critical problem for a single element added. However, when a number of elements are added to the same set of standards, precautions must be taken to avoid the accumulation of certain common impurities. This is most important when an element such as lithium, in a low range of concentrations in the standards, may be found as a common impurity among several elements added in higher concentration ranges to the same set of standards.

The chemical combination of the element added is important in minimizing losses on ignition and in obtaining, as a final result, a standard that matches the samples in composition and in behavior under the conditions of analysis. The addition of a compound that converts to the oxide on drying and ignition is usually preferred. However in certain cases, such as silicon added in solution, it is necessary to employ an alkaline salt. The amount of the alkali element added in this way often satisfies the requirement for its concentration in the standards; excessive concentrations of alkalis are to be avoided.

The standard samples in current use in our laboratory are described in the following sections. The ranges of composition, in general, were chosen to meet specific problems in the analysis of the production samples of uranium materials as described in the detailed analytical procedures of Sections 7 and 9 of this report.

5.2. Uranium-base Standards

The base materials employed for these standards are usually derived from uranium metal, dioxide, or trioxide samples found by spectrographic test to be of suitable purity. The base material is ignited at 800 to 900°C to the common form, uranium oxide, prior to preparation of the standards.

5.2-1. General Standards for 24 Elements in Uranium Oxide

The compositions of this set of standards, as given in Table X, provide a graded series of concentrations for 24 of the 27 elements observed in one setting of the spectrograph, 2200 to 3550 Å. The ranges of concentrations permit application to several purity grades of uranium materials. Standard solutions are prepared for the elements to be added by dissolving an oxide or pure non-halide salt in water or by dissolving the element to provide a nitrate solution free of excess acid. The concentration of the standard solution is adjusted to a value such that the volume to be added to the standard of highest concentration does not result in excessive wetting of the matrix. The standard solutions listed in Table XI were prepared from pure metals or pure compounds available in our laboratory. For each of the standard samples prepared, 50 g of the selected uranium oxide matrix material were weighed and transferred to a clean platinum dish. The volumes of the standard solutions required to give the desired concentration of the element in the matrix were calculated, and the solutions were added by pipette. The desired result in adding the solutions is that the solution be absorbed by the matrix without loss on the walls of the dish; therefore the mixture is dried in an oven at 110°C at the necessary intervals. The standard solutions were diluted in the ratio of 1:10 when the added volume would otherwise be too small for accurate addition. After addition of the solutions, the dishes were placed in an oven to dry the mixtures thoroughly, and then were placed in a cold muffle furnace where they were heated to 900°C for three hours. The ignited material was transferred from the dish to a polished agate mortar, ground and mixed for one hour, and finally placed in a clean glass vial.

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Table X

Compositions of General Standards
Uranium Oxide Base.

<u>Element</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>X</u> (Blank)
	5 ppm	2 ppm	1 ppm	0.5 ppm	0.2 ppm	0.1 ppm	0.05 ppm	-
Ag	500	200	100	50	20	10	5	-
Al	500	200	100	50	20	10	5	-
As	500	200	100	50	20	10	5	-
B *	5	2	1	0.5	0.2	0.1	-	-
Be	5	2	1	0.5	0.2	0.1	0.05	-
Bi	50	20	10	5	2	1	0.5	-
Co	50	20	10	5	2	1	-	-
Cr	50	20	10	5	2	1	-	-
Cu	50	20	10	5	2	1	0.5	-
Fe	500	200	100	50	20	10	5	-
Ge	50	20	10	5	2	1	0.5	-
In	5	2	1	0.5	0.2	0.1	-	-
Mg	500	200	100	50	20	10	5	-
Mn	500	200	100	50	20	10	5	-
Mo	500	200	100	50	20	10	5	-
Na**	660	330	165	82.5	33	16.5	8.2	-
Ni	50	20	10	5	2	1	-	-
P	500	200	100	50	20	10	-	-
Pb	50	20	10	5	2	1	-	-
Sb	50	20	10	5	2	1	-	-
Si	500	200	100	50	20	10	5	-
Sn	50	20	10	5	2	1	0.5	-
V	500	200	100	50	20	10	5	-
Zn	500	200	100	50	20	10	5	-

* Losses of boron up to 20 per cent in this preparation are indicated on comparison with the chemically analyzed special standards 4.2-6.

** Figures for Na are the totals of Na added as salts of other elements.

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Table XI

Standard Solutions for the General Standards

<u>Element</u>	<u>Conc.</u> <u>mg/ml</u>	<u>Source</u>	<u>Solution</u>	<u>Element</u>	<u>Conc.</u> <u>mg/ml</u>	<u>Source</u>	<u>Solution</u>
Ag	0.1	Ag	Nitric acid	As	10.0	As ₂ O ₃	Nitric acid
Cu	10.0	Cu	Nitric acid	B	1.0	Na ₂ B ₄ O ₇ ·10H ₂ O	Water
In	1.0	In	Nitric acid	Be	1.0	BeSO ₄ ·4H ₂ O	Water
Mg	10.0	Mg	Nitric acid	Cr	10.0	K ₂ CrO ₄	Water
Mn	20.0	Mn	Nitric acid	Ge	1.0	GeO ₂	Water
Ni	1.0	Ni	Nitric acid	Mo	10.0	MoO ₃ ·NH ₃	Water
Pb	10.0	Pb	Nitric acid	P	10.0	KH ₂ PO ₄	Water
Zn	20.0	Zn	Nitric acid	Sb	10.0	K(SbO)C ₄ H ₄ O ₆	Water
Fe	5.0	Fe	Nitric acid	Si	10.0	Na ₂ SiO ₃ ·9H ₂ O	Water
Bi	5.0	Bi	Nitric acid	Sn	10.0	Na ₂ SnO ₃ ·3H ₂ O	Water
Co	5.0	Co	Nitric acid	V	5.0	NH ₄ VO ₃	Water
Al	10.0	Al(NO ₃) ₃ ·9H ₂ O	Water				

5.2-2. Standards for Cadmium in Uranium Oxide

A set of standards (Table XII) was prepared for the determination of cadmium, which requires a separate spectrographic exposure for optimum sensitivity as described in Section 7.1-3.

Table XII

Standards for Cadmium in Uranium Oxide

<u>Element</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>X</u>
Cd	1 ppm	0.5 ppm	0.3 ppm	0.2 ppm	0.15 ppm	0.10 ppm	Blank U ₃ O ₈

A standard solution of cadmium nitrate (Cd 0.1 mg/ml) was prepared, and the procedure described in the preceding section was employed in preparing the standards, except that the quantity of each of the standards was reduced to 25 g.

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5.2-3 Standards for Ba, Ca, Na, Li, and Sr in Uranium Oxide

These standards with uranium oxide matrix are employed for the determination of Ba, Na, and Li by Procedure 7.1-4 and for the determination of calcium by Procedure 7.1-6. Strontium is not determined at the present time. The compositions are given in Table XIII

Table XIII

Standards for Na, Li, Ca, Ba, and Sr in U₃O₈

Element	A-1	A	B	C	D	E	F	X Blank
Na	500 ppm	100 ppm	50 ppm	20 ppm	10 ppm	5 ppm	2 ppm	U ₃ O ₈
Li	25	5	2.5	1	0.5	0.25	0.1	--
Ca	500	100	50	20	10	5	2	--
Ba	-	500	250	100	50	25	10	--
Sr	-	500	250	100	50	25	10	--

Nitrate solutions of the oxides or carbonates were prepared and the procedure of Section 5.2-1 was followed, with the exceptions that the quantity for each standard was 25 g, and dry salts were added to obtain the concentration of 500 ppm for Ba and Sr in A.

5.2-4. Standards for K, Rb, and Cs in Uranium Oxide

This set of standards was prepared for the determination of K, Rb, and Cs by procedure 7.1-5 and has the compositions listed in Table XIV.

Table XIV

Standards for K, Rb, and Cs in U₃O₈

Element	A	B	C	D	E	F	X
K	500 ppm	100 ppm	50 ppm	20 ppm	5 ppm	2 ppm	Blank U ₃ O ₈
Rb	100	20	10	4	1	0.4	
Cs	200	40	20	8	2	0.8	

Nitrate solutions of the elements were prepared with the following concentrations.

K	10 mg/ml	398	062
Rb	2 mg/ml		
Cs	2 mg/ml		

The calculated volumes of the solutions were added to a 25 g portion of pure uranium oxide for each standard sample, following the procedure given in Section 5.2-1.

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5.2-5. Standards for Au, Hg, and Tl in Uranium Oxide

These standards were prepared without ignition, which would result in losses of the added elements by volatilization. The standards are applied in the analysis of un-ignited samples in the general procedure 7.1. The compositions are given in Table XV.

Table XV

Standards for Au, Hg, and Tl in Uranium Oxide

<u>Element</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>X</u>
Au	20 ppm	10 ppm	5 ppm	2 ppm	1 ppm	Blank U ₃ O ₈
Hg	200	100	50	20	10	
Tl	20	10	5	2	1	

Standard solutions were prepared as follows:

<u>Element</u>	<u>Conc.</u> <u>mg/ml</u>	<u>Source</u>	<u>Solution</u>
Au	1.0	AuCl ₃	Water
Hg	10.0	Hg(NO ₃) ₂	Water
Tl	1.0	TlSO ₄	Water

Calculated volumes of the solutions were added to 25 g portions of the matrix following the procedure 5.2-1 except that the mixtures were dried at 100°C and the ignition was omitted.

5.2-6. Special Standards for B, Fe, Mg, and Mn in Black Oxide (U₃O₈)

These standards were prepared in large quantities by the NBS chemical section for distribution among the project laboratories. The concentration values, Table XVI, represent the results of extensive chemical and spectrographic tests (1).

Table XVI

Special Standards for B, Fe, Mg, and Mn in Black Oxide (U₃O₈)

<u>Element</u>	<u>1393 D</u>	<u>1393 E</u>	<u>1393 F</u>	<u>1393 G</u>
Boron	0.25 ppm	0.62 ppm	0.92 ppm	1.44 ppm
Iron	17	41	91	187
Magnesium	10	24	48	96
Manganese	5	10	24	48

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The standards were prepared by adding solutions to a U_3O_8 matrix, igniting the mixtures, and finally grinding the mixture in a porcelain ball mill.

5.2-7. Standards for Hg and Tl in Peroxide ($UO_4 \cdot 2H_2O$)

This set of standards, Table XVII, was prepared for the determination of the elements that are subject to loss on ignition. The standards are applied in the analysis of original samples of uranium peroxide.

Table XVII

Standards for Hg and Tl in Uranium Peroxide ($UO_4 \cdot 2H_2O$)

<u>Element</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>X</u>
Hg	100 ppm	50 ppm	20 ppm	10 ppm	Blank $UO_4 \cdot 2H_2O$
Tl	100	50	20	10	

A sample of uranium peroxide free of Hg and Tl was selected, and a 10 g portion was weighed out into a platinum dish for each standard. Standard solutions were prepared as follows:

<u>Element</u>	<u>Conc.</u> <u>mg/ml</u>	<u>Source</u>	<u>Solution</u>
Hg	10.0	$Hg(NO_3)_2$	Water
Tl	10.0	Tl_2SO_4	Water

Calculated volumes of the solutions were added to provide the required concentration in each standard. The mixtures were dried at $100^\circ C$ and then ground in an agate mortar.

5.2-8. Standards for B and Hg in Green Salt (UF_4)

This set of standards, Table XVIII, was prepared for the determination of boron and mercury by examination of the original green salt using the procedure of Section 7.7-2.

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Table XVIII

Standards for B and Hg in Green Salt (UF₄)

<u>Element</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>X</u>
B	10 ppm	5 ppm	2 ppm	1 ppm	0.5 ppm	0.2 ppm	Blank UF ₄
Hg	100	50	20	10	5	2	

The standards were prepared by adding portions of solutions of borax and mercuric chloride to weighed portions of green salt. The additions were made according to Procedure 5.2-1, except that the mixtures were dried over calcium chloride under reduced pressure.

5.3. Rare-earth Standards

This set of standards provides for the determination of the important rare-earths Dy, Er, Eu, Gd, and Sm in rare-earth concentrates according to Procedure 9.1. Similar sets of standards are employed as reference samples for the qualitative estimation of the other rare-earth elements and thorium. The matrix chosen for this set of standards represents that of the typical rare-earth concentrate, although it was later found not necessary to match the matrix closely. The compositions of the standards as they were prepared are given in Table XIX. For application in analysis the concentrations of the oxides were converted to those for the elements, Table XX.

Table XIX

Rare Earth Standards

<u>Constituent</u>	<u>A-2</u>	<u>A-1</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>X</u>
Dy ₂ O ₃	16%	8.0%	4.0%	2.0%	1.0%	0.50%	0.25%	Blank
Gd ₂ O ₃	-	4.0	2.0	1.0	0.5	0.25	0.12	
Eu ₂ O ₃	-	-	2.0	1.0	0.5	0.25	0.12	
Er ₂ O ₃	-	-	4.0	2.0	1.0	0.50	0.25	
Sm ₂ O ₃	-	-	2.0	1.0	0.5	0.25	0.12	

Matrix:

Y ₂ O ₃	-	70%	Al ₂ O ₃	-	5%
U ₃ O ₈	-	10%	CaO	-	5%
SiO ₂	-	10%			

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Table XX

Rare-Earth Standards; Concentration as Elements

<u>Constituent</u>	<u>A-2</u>	<u>A-1</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>X</u>
Dy	13.9%	6.97%	3.48%	1.74%	0.87%	0.44%	0.22%	Blank
Gd	-	3.47	1.73	0.87	0.43	0.22	0.11	
Eu	-	-	1.73	0.86	0.43	0.22	0.11	
Er	-	-	3.50	1.75	0.87	0.44	0.22	
Sm	-	-	1.77	0.88	0.44	0.22	0.11	

The matrix mixture was prepared by grinding each oxide separately and then grinding the weighed quantities together. The five rare-earth oxides were ground separately, and weighed quantities were then ground into the required weight of matrix to prepare 1 g of standard A-2, 1 g of A-1, and 2 g of A. A 1 g portion of standard A was then mixed with 1 g of the matrix to obtain standard B, and similar successive dilutions were made to obtain standards C, D, and E. Each mixture was ground 45 minutes in a polished agate mortar.

5.4. Zirconium-Group Standards

A set of seven standards and a blank was prepared by adding measured amounts of solutions of the desired constituents to aliquots of pure uranium oxide dissolved in nitric acid. The mixed standard solutions were carried through Procedure 8.2 for separation of the zirconium group of elements. The resulting concentrates, which involve losses that might be encountered in the chemical separations of the impurities from analytical samples, are employed as standards for the spectrographic procedure 9.2. The compositions represented by the standards are given in Table XXI.

Table XXI

Standards for the Zirconium Group; the Values Represent
Concentrations for Each Element in the Original
Uranium Sample

<u>Element</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>X</u>
Cb, Ga, Hf,) Ti, V, W & Zr) Mo, Pd, Ta)	160 ppm	80 ppm	40 ppm	20 ppm	10 ppm	5 ppm	3 ppm	Blank

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5.5. Platinum Group Standards

A set of five standards and blank were prepared by adding measured amounts of solutions of the desired constituents to aliquots of pure uranium oxide dissolved in mixed acids (See Section 8.3). The mixed solutions were carried through procedure 8.3 for separation of the platinum group of elements (except Os). The resulting concentrates, which involve losses by the chemical procedure, are employed as standards for the spectrographic procedure 9.3. The compositions represented by the standards are given in Table XXII.

Table XXII

Standards for the Platinum Group; the Values
Represent Concentration of each Element in the Original Uranium
Sample

<u>Element</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>X</u>
Ru, Rh, Pd, Ir, Pt	160 ppm	80 ppm	40 ppm	20 ppm	10 ppm	Blank

Literature Cited

- (1) Project Report No. A-1028, Section 2A (1944).

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6. PRELIMINARY PREPARATION OF SAMPLES FOR SPECTROGRAPHIC ANALYSIS

The preparation of samples to be submitted for spectrographic analysis involves preliminary sampling and, in certain cases, chemical treatment. The types of operations that may be applied to samples are as follows:

- (a) Mixing the sample and setting aside a representative portion;
- (b) Ignition to the black oxide (U_3O_8);
- (c) Removal of arsenic followed by ignition to the black oxide; (Arsenic is removed because of interference of a strong spectral line of arsenic with the most sensitive cadmium line.)
- (d) Hydrolysis (of the fluorides) followed by ignition to the black oxide.

The operations applied to the various uranium-base materials are described under the type of material in the following sections. Considerable care must be exercised in avoiding contamination of the samples; it is advisable to reserve a clean section of the chemical laboratory exclusively for this work.

6.1. Black Oxide (U_3O_8)

Original Sample:-----Transfer a representative portion of three to four g of original black oxide to a clean vial.

Arsenic-free Sample:-----Samples in which arsenic is expected to be higher than 50 ppm, or in which arsenic has been found by spectrographic test to be higher than this amount, are treated to remove arsenic as follows. Place three to four g of the black oxide in a 25 ml porcelain evaporating dish and add 10 ml concentrated nitric acid. Dissolve the oxide and evaporate the solution to dryness on an electric hot plate. Volatilize all nitric acid by heating the dish in a muffle furnace at 325°C for about 30 minutes. Remove the dish from the furnace and while the dish is still warm add 10 ml of concentrated HBr. Evaporate to dryness on the hot plate and volatilize all HBr from the sample. Cool and treat again with HBr. If the arsenic is very high in the sample, repeat the HBr treatment four more times. While the dish is warm add 10 ml of concentrated nitric acid. Evaporate the solution to dryness and heat it over a Meker burner. Complete the ignition by heating the dish in a clean muffle furnace at 900°C for 30 minutes.

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Note:---Do not ignite this product in the furnace used to decompose the first nitrate since contamination may result from arsenic present in the atmosphere of the furnace.) Grind the sample to a fine powder in an agate mortar, transfer the powder to a small, clean vial, and label the vial "As-free".

6.2. Uranium Metal (U)

Ignited Sample:-----The metal is usually obtained in the form of small blocks (Note 1). Break the metal into small pieces and place the pieces in a silica dish, which should be in good condition (Note 2). Transfer the dish to a muffle furnace and ignite the sample overnight at 600 to 800°C. Grind the resulting oxide to a fine powder in an agate mortar, mixing the powder thoroughly. Place three to four g in a small clean vial.

Note 1. Uranium metal in the form of powder may be highly pyrophoric, and considerable care must be exercised in handling it. Small amounts of the powder can be ignited in a silica dish in the open, although some of the sample may be scattered. Chemical determinations of boron in the metal and in the ignited oxide have shown good agreement, indicating negligible loss of boron. However, solution of the metal in nitric acid followed by ignition to oxide showed a tendency toward lower results for boron (1).

Note 2. No appreciable increase of silicon content of the sample has been observed as a result of the use of the silica dish.

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6.3. Brown Oxide (UO_2)

Ignited Sample:-----Ignite three to four g of the original brown oxide sample in a silica dish in a muffle furnace at 600 to 800°C overnight. Place the sample in a clean vial labelled "Burnt".

6.4. Orange Oxide (UO_3)

Ignited Sample:-----Ignite three to four g of the original orange oxide sample in a silica dish in a muffle furnace at 900°C for 30 minutes. Remove the dish, stir the contents with a platinum spatula, and return the dish to the furnace for 30 minutes. Place the ignited sample in a clean vial labelled "Burnt".

Arsenic-Free Sample:-----Treat three to four g to remove arsenic according to the procedure for black oxide (Section 6.1). (Note: Removal of arsenic from the orange oxide is seldom required.)

6.5. Peroxide ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$)

Original Sample:-----Transfer a three to four g portion of the original peroxide to a clean vial; label the vial "Original".

Ignited Sample:-----Place three to four g of the finely powdered peroxide in a 25 ml porcelain evaporating dish and heat the sample over a Meker burner, stirring occasionally with a platinum spatula, until the sample has turned black. Transfer the dish to a muffle furnace and ignite the sample at 900°C for 30 minutes. Remove the dish from the furnace, allow it to cool and mix it well. Place the sample in a clean vial labelled "Burnt".

Arsenic-Free Sample:-----Treat three to four g of the sample to remove arsenic according to the procedure for the black oxide (Section 6.1).

6.6. Soda Salt ($\text{Na}_2\text{O} \cdot x\text{UO}_3$)

Original Sample:-----Transfer a three to four g representative portion to a clean vial.

6.7. Green Salt (UF_4)

Original Sample:-----Transfer a two or three g portion of the original green salt to a clean vial labelled "Original".

Hydrolyzed and Ignited Sample (See Note 1):-----Set up a system of water-boiler, preheater furnace, and a hydrolysis tube also in a furnace, the apparatus being similar to that described by Clive, Tevebaugh and Warf (2).

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Place two g of green salt in a platinum boat and insert it in the cold hydrolysis tube with the furnace at room temperature. Pass steam, pre-heated to 400°C, through the hydrolysis tube for five minutes. Now with steam passing through the tube, heat the tube slowly for 15 minutes. At the end of this period turn on the full heat of the furnace and heat to 800 to 900°C. When the furnace has reached this temperature, disconnect the steam generator and continue heating the tube at 800 to 900°C for 15 minutes. Remove the boat and transfer the sample to a clean vial labelled "Hyd.-Burnt".

Note 1. Conversion of the green salt to oxide by this procedure is preferred to simple ignition in air in view of loss of volatile fluorides, especially MoF₆, by the latter procedure. (A more detailed description of the procedure is in preparation.) The ignition of green salt by either method results in loss of boron. In an attempt to retain boron a method was applied (3) in which the sample was treated with ammonium hydroxide and hydrogen peroxide (30%). This method also failed to retain boron and, in addition, objectionable amounts of impurities notably sodium and phosphate were introduced by the hydrogen peroxide. Another method (4), for the chemical determination of boron was applied but the boron was so low that the results were inconclusive. Boron and mercury are now determined spectrographically on a portion of the original sample according to the procedure of Section 7.7-2.

6.8. Hexafluoride (UF₆)

A portion of the hexafluoride is distilled into a platinum tube, hydrolyzed with nitric acid, evaporated to dryness, and ignited to uranium oxide.

The following apparatus is required:

1.2
Platinum tube, ~~12~~ cm diameter by 24 cm long
Two-way pyrex stopcock
de Khotinsky cement
Cenco-Megavac pump
Copper tubing
One hundred ml platinum dish
Muffle furnace

Procedure:-----Connect the cylinder of UF₆ to the platinum tube as shown in Figure 12. With the cylinder valve closed, evacuate the system, and heat the cylinder to 150-200°C. Immerse the platinum tube in liquid air and open the cylinder valve. After the sample has distilled over, detach the platinum tube from the system, and, while it is still immersed in the liquid air, fill it with distilled water. Transfer the contents of the tube to a 100 ml

FIGURE 12

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platinum dish, washing the tube with 5 per cent nitric acid. Evaporate the solution to dryness, ignite the residue to uranium oxide in a muffle furnace at 900°C for one hour, and transfer the resulting uranium oxide to a clean vial.

Note: This procedure is not entirely satisfactory for conversion of the hexafluoride to oxide because of contamination by the copper and pyrex tubing. If an all-platinum system could be obtained the conversion should be satisfactory. The sample obtained by the present procedure serves for spectrographic qualitative examination for impurities other than copper and those present in pyrex glass.

6.9. Miscellaneous Materials

Uranium Carbide (UC_2):-----Place a three to four g representative portion of the carbide in a weighed platinum dish, and ignite in a muffle furnace at 800 to 900°C to constant weight.

Uranyl Nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$):-----Place a five g portion of the nitrate in a platinum dish and heat the dish at about 350°C to decompose most of the nitrate. Heat the dish to red heat over a Meker burner and ignite the sample in a muffle furnace at 800 to 900°C for one hour.

Uranyl Acetate ($UO_2C_2H_3O_2$) $\cdot 2.2H_2O$):-----Treat the sample by the procedure for ignition of the nitrate.

Literature Cited

- (1) J.A. Scherrer and C.J. Rodden.
Determination of Small Amounts of Boron.
Report No. A-133 (1941).
- (2) D. Cline, R. Tevebaugh, and J. Warf.
Hydrolytic Analysis of Heavy Metal Fluorides.
Report No. CC-1981 (1944).
- (3) C.J. Rodden.
Conversion of UF_4 to U_3O_8 .
Report A-182K (1942).
- (4) L.A. Haddock.
Some collated analytical investigations on uranium.
Report B-109, Section 2 (a), Boron (1942).

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7. SPECTROGRAPHIC DETERMINATION OF THE VOLATILE ELEMENTS

The determination of 33 volatile elements by the pyroelectric method and the determination of calcium by the complete-burning method are described in this set of procedures under the headings of the materials analyzed. The basic procedures are given in detail in Section 7.1 for the analysis of black oxide (U_3O_8). The analytical methods for other uranium-base materials, Sections 7.2 to 7.9, generally follow the basic procedures, but modifications are incorporated as required by the chemical form or degree of purity of the sample. The procedures involve the use of the equipment and the general laboratory practice given in Section 3 of this report but, with minor changes, the procedures may be adapted to other equipment having similar functions.

7.1. Analysis of Black Oxide (U_3O_8)

The basic methods to be described in Sections 7.1-1 to 7.1-6 have been applied to the analysis of black oxide of various degrees of purity. It is convenient in applying the procedures to divide the samples into three classes as follows.

<u>Class</u>	<u>Total Impurity</u>	<u>Examples</u>
A. High-Purity Oxide	Less than 0.1 per cent	"Pure Black"
B. Moderate-Purity Oxide	Between 0.1 and 1.0 per cent	"F-29"; "Crude Black"
C. Impure Oxide	Greater than 1 per cent	"Shotgun samples"

The class of the material to be analyzed is usually known in advance or is readily identified by application of procedure 7.1-1. Class A samples are analyzed by the basic methods, procedures 7.1-1 to 7.1-6, without change. For samples of classes B and C, the increased impurity content requires modification of the basic procedures. Class B samples may show a longer steady-burning period in the pyroelectric procedure than do purer samples. In these cases the exposure is terminated at 60 seconds after the arc is started. Also, for Class B samples, cadmium is usually determined on a sample from which interfering arsenic has been removed (the "As-free" sample), and procedure 7.1-2 for the accurate determination of iron, magnesium, and manganese is omitted. Class C samples, containing large amounts of impurities, are diluted 1:10 or 1:100 with pure U_3O_8 , and the mixture is treated as a Class B sample, the results being reported with appropriate correction for dilution. The dilution of samples involves a loss of sensitivity by the dilution factor, but this is of little importance.

The procedures are designed for the systematic determination of 34 elements. If the determinations are limited to only a few of these elements, the quantities of materials and steps in the procedure should be adjusted accordingly.

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7.1-1. Determination of 26 Elements by the General Run

The procedure provides for the determination of the following elements in Class A, high-purity black oxide by the pyroelectric method,

^{AG}₂₆, Al, As, Au, B, Be, Bi, Co, Cr, Cu, Fe, Ge, In, Mg, Mn, Mo, (Na), Ni, P, Pb, Sb, Si, Sn, Tl, V, and Zn.

Photometric measurements are made for determination of B and Si relative to measurements of standards; the remaining elements are determined by visual comparison of the spectra of sample and standards. Eight sector exposures are photographed on one plate, providing usually for the spectra of four samples and four standards. The typical plate will include two general standards such as 5.2-1 C and E, and two special standards, such as 5.2-6 C and D, the latter being employed only for correction in the determination of B, and for estimation of iron, magnesium, and manganese. The samples and standards to be entered on a plate are listed on the plate envelope, which forms a reference record throughout the procedure. A duplicate plate is prepared in the same manner.

Procedure:-----Enter the serial number and identity of the sample in the sample record book, and mark the number on the sample vial. Grind the sample (3 to 5 g) for ten minutes in a clean, mullite mortar. Weigh 1225 mg of the U₃O₈, add 25 mg of Ga₂O₃, and grind the mixture for seven minutes. Place the mixture in a clean vial labelled with the serial number followed by an "a" to indicate that Ga₂O₃ has been added. Treat portions of standard samples 5.2-1, 5.2-5, and 5.2-6 in the same manner except that 4.90 g of the standard are mixed with 0.10 g of Ga₂O₃. (Prior to the analysis of samples, prepare and photograph a reference plate for each set of standards following the conditions to be described for the routine analysis.)

Transfer to an electrode block eight electrodes with 9/32-inch cup (the electrodes are described in Section 3.3), protecting the block and electrodes with a cover as far as possible during the succeeding operations. Mark the block identifying letter on the plate envelope. For each of the samples and standards listed on the plate envelope, weigh 100 mg of the "a" mixture and transfer it completely to the electrode in the block, in proper sequence from numbers 1 to eight on the block. Transfer the block to the storage cabinet at the spectrograph.

Prepare the spectrograph for operation as follows.

Spectrograph: Baird.
Setting: 2.4 (2200 to 3550 A)
Cassette: 979.2
Rotation: 997.9
Position: 499.7

Electrode stand: 38.8 cm (Note: The positions of the optical parts on the bench are given throughout the procedures as scale settings. For the actual distances of the parts from the slit see Section 3.5.)

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Auxiliary lens: 62.3 cm
Screen: 125 cm
Filter: None
Slit: 25 micron (Examine slit and clean if necessary)
Line Mask: Full open
Grating aperture: 1 inch mask (unless indicated otherwise
on the plate envelope)
Sector: Steps 2 to 6, where 6 is 360°. Set sector
at 1.5 cm on the bench.
Upper electrode: 1/8-inch pointed cathode
Lower electrode: Sample electrode set firmly on the pedestal
which is a 1/8-inch tapered rod extending
1/2-inch above the electrode clamp. Replace
the pedestal after it has become burned near
the top; the pedestal may be used for one or
more plates depending on the type of ex-
posures made.
Electrode gap: 4 mm, adjusted by projection of the shadow
image of the electrodes on the scale at the
screen.
Excitation: Adjust rectifier d.c. current to 14 amp with
electrode clamps short-circuited; current
during operation of the arc will be approxi-
mately 10 amp.
Pre-arc: Five seconds.
Exposure: Continued to five seconds after end of quiet
period (total exposure about 35 sec).
Plate: Eastman S.A. No. 1; 4 x 10 inches
Racking: Begin at 30; rack 10 after each exposure
Inspection: Check above settings immediately before start-
ing exposures; turn on water pump and step
sector.
Venting electrode charge: Remove the electrode block from the
cabinet, and, for each electrode, tap to dis-
tribute the charge evenly. Insert the cleaned
vent-forming tool (Section 3.3) with slight
pressure to push the tool through the charge
to the floor of the cup, rotate the tool, and
then withdraw it carefully. If the hole in
the charge is rough, or if loose material is
present, repeat to obtain a smooth vent in the
charge. Cover the block.
Spectrogram record: Enter the briefed spectrogram description
and date in the record book, and record the
spectrogram serial number on the plate
envelope.

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Exposure cycle: Wipe off the electrode clamps, insert the electrodes, and adjust them to the proper position. With the shutter closed, start the arc by short-circuiting the electrodes by a clean, second grade graphite rod, observing the time of start. After five seconds open the shutter. Adjust the upper electrode to maintain the 4 mm gap distance continuously throughout the exposure. Close the shutter five seconds after the arc has become unsteady, and record on the plate envelope the time elapsed from the start of the arc (1) to the beginning of the quiet period of burning, (2) to the end of the quiet period, and (3) to the end of the exposure (e.g., 10-35-40 seconds). Rack the plate, remove the lower electrode, dump the charge into the scrap container, and discard both electrodes. Repeat the exposure cycle for the next sample. After the eight exposures have been made, rack the plate back to zero, remove the plateholder, and transfer it to the darkroom.

Development: Develop the plate according to the standard procedure for the S.A. No. 1 Plate (Section 3.6). Carry out the same procedure of exposures for the duplicate plate.

Examination of the plate: Make photometric measurements for determination of boron and silicon as follows. Measure B 2497.73 in the spectra of the samples and of standards 5.2-6 C and D, and reduce the measurements to concentrations of boron according to the external standard method described in Section 3.7-1. In a similar manner, measure Si 2506.90 in the spectra of the samples and of standards 5.2-1 C and E, and reduce the measurements to concentrations of silicon. After the photometric measurements have been completed, place the plate on a viewing box (Section 3.7) for visual examination for the lines listed in Table XXIII. If gold and thallium are present, estimate their concentrations by comparing the spectra of the samples with those on the reference plate of standards 5.2-5. For the remainder of the elements listed in Table XXIII, estimate the

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concentrations by comparing the spectra with those on the reference plate of standards 5.2-1. Correct the visual estimations, if necessary, by checking the results obtained for standards photographed with the samples. Examine the duplicate plate by the same procedure and average the two determinations for each element.

Note: The estimation of iron, magnesium, and manganese by this procedure may be omitted if improved determinations of the three elements are to be made by Procedure 7.1-2.

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Table XXIIISpectral Observations for the General Region 2200-3550 A

Element	Wavelength A	Intensity (MIT)		Remarks
		Arc	Spark	
Ag	3280.68 3382.89	2000R 1000R	1000R 700R	Absence of Ag is unlikely.
Al	3082.16 3092.71	800 1000	800 1000	Both lines are used to determine Al; absence is unlikely. Caution: Mg 3092.99 must not be mistaken for Al 3092.71.
As	2349.84 2780.20	250R 75R	18 75	Background lines must not be mistaken for As.
Au	2427.95 2675.95	400R 250R	100 100	The physical intensity of 2427.95 is higher than that of 2675.95 but because of its position in a less sensitive portion of the plate the first line appears weaker than the second. Presence of Au is unlikely in pure samples; if detected, check for contamination. Both lines should be present to report Au.
B	2497.73 2496.78	500 300	400 300	2497.73 is measured photometrically. Fe present in concentration less than 1% does not interfere with B.
Be	2348.61 3130.42 3131.07	2000R 200 200	50 200 150	Presence of Be unlikely; if detected, check for contamination.
Bi	3067.72 2897.98	3000hR 500WR	2000wh 500WR	Caution: Fe 3067.24 must not be mistaken for Bi.
Co	3453.51 2424.93	3000R 250R	200 -	Co 3453.51 is very sensitive and easily distinguished above background.
Cr	2843.25 2835.63 2762.59	125 100 40	400r 400r 100	Cr 2843.25 and 2762.59 are measured photometrically in Procedure 7.1-2. Caution: Background lines must not be mistaken for Cr.
Cu	3247.54 3273.96	5000R 3000R	2000R 1500R	Absence unlikely. Both lines are used.
Fe	2599.40 2788.11 3020.64 3021.07	1000 150 1000R 700R	1000h 150 600r 300r	When Fe runs high, 2788.11 is used for visual estimation. Fe 3020.64 and 3021.07 form a doublet, the absence of which is unlikely. (Fe 2599.40 is measured photometrically in Procedure 7.1-2.)

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Table XXIII (Continued)

Element	Wavelength A	Intensity (MIT)		Remarks
		Arc	Spark	
Ge	2754.59	30	20	Ge is rarely found.
	2651.18	40	20	
	2651.58	30	20	
In	3256.09	1500R	600R	Mo at 100 ppm interferes with In 3256.08. Caution: Ge 3039.06 in the standards must not be mistaken for In 3039.36.
	3039.36	1000R	500R	
Mg	2795.53	150	300	When Mg is high use the Mg quintuplet: 2776.69, 2778.29, 2779.83, 2781.42 and 2782.97 for visual estimation. (Mg 2802.70 is measured photometrically in Procedure 7.1-2).
	2802.70	150	300	
	2776.69	30	20	
	2778.29	25	20	
	2779.83	40	50	
	2781.42	20	8	
	2782.97	15	15	
Mn	2794.82	1000R	5	Check all 3 lines before reporting Mn. (Mn 2798.27 is measured photometrically in Procedure 7.1-2).
	2798.27	800R	80	
	2801.06	600R	60	
Mo	3132.59	1000R	300R	
	3170.35	1000R	25r	
	3193.97	1000r	50r	
Na	3302.32	600R	300R	This doublet appears only if the concentration of Na is above 100 ppm. Note strong Zn interference with Na 3302.99. See Procedure 7.1-4 for a more sensitive test for Na.
	3302.99	300R	150R	
Ni	3050.82	1000R	-	3050.82 is in a clear portion with no danger of confusion.
	3002.49	1000R	100	
P	2553.28	80	20	Usually detected only in crude blacks and other impure samples.
	2554.93	60	20	
Pb	2833.07	500R	80R	
	2802.00	250Rh	100h	
Sb	2598.06	200	100	Caution: Fe 2598.37 must not be mistaken for Sb 2598.06. Sb 2877.92 is usually unsatisfactory because of its position near Ga 2874.24.
	2877.92	250W	150	

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Table XXIII (Continued)

Element	Wavelength A	Intensity (MIT)		Remarks
		Arc	Spark	
Si	2506.90	300	200	Si 2506.90 is measured photometrically. 2881.58 is too strong to be generally useful.
	2881.58	500	400	
	2514.33	300	200	
	2516.12	500	500	
	2519.21	300	300	
	2524.12	400	400	
	2528.52	400	500	
Sn	3262.33	400h	300h	Little danger of Fe interference with either line.
	2863.33	300R	300R	
Tl	2767.87	400R	300R	
V	3183.41	200R	100R	This group of 3 lines must be definite to report V.
	3183.98	500R	400R	
	3185.40	500R	400R	
Zn	3345.02	800	300	Background is heavy but 3345.02 can be distinguished above it with care.
	3282.33	500R	300	

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7.1-2. Improved Determination of Fe, Mg, and Mn using an Internal Standard

If Cr is found to be negligible (less than 20 ppm) by Procedure 7.1-1, and improved determinations of Fe, Mg, and Mn are desired, as for Class A black oxide, separate runs are made following Procedure 7.1-1 except that the carrier employed is $\text{Ga}_2\text{O}_3\text{-Cr}_2\text{O}_3$ (1% Cr), hereinafter called Ga-Cr carrier. The plate envelope is marked to provide for eight exposures, including standards 5.2-6 C and D mixed with the Ga-Cr carrier.

Procedure:-----Weigh ¹³⁵~~735~~ mg of the pre-ground black oxide sample, add 15 mg of Ga-Cr carrier, and grind the mixture for seven minutes. Place the mixture in a clean, glass vial and label the vial with the sample serial number followed by a "k" to indicate that the special carrier has been added. Treat portions of standard samples 5.2-6 in the same manner except that 4.90 g of the standard are mixed with 0.10 g of Ga-Cr carrier. Prepare an electrode block holding eight electrodes with 9/32-inch cup, protecting the block with a cover as much as possible between the successive operations. Mark the block identifying letter on the plate envelope. For each of the samples and standards listed on the plate envelope, weigh 100 mg of the "k" mixture and transfer completely to the electrode in the block in proper sequence from number one to eight on the block. Move the block to the storage cabinet at the spectrograph. Photograph the plate of exposures exactly according to Procedure 7.1-1 and, after inspection of the first plate, run the duplicate plate.

Examination of the Plate:-----Make photometric measurements of the selected Fe, Mg, and Mn lines and Cr internal-standard lines according to the general procedure described in Section 3.7-2. Full stepped images are also measured to establish the calibration curve. The transmittancies of the selected analytical lines are reduced to log I values, and the log intensity ratios for the analytical line pairs are calculated. The lines employed in the determination are given in Table XXIV.

Table XXIV

Analytical Line Pairs for Determination of Fe, Mg, and Mn

<u>Wave Lengths</u>		<u>Index Value (1), ppm</u>
FeII 2599.40	CrII 2762.59	63
MgII 2802.70	CrII 2843.25	12
MnI 2798.27	CrII 2843.25 (2)	40

Note 1. The index value in the Table is the concentration of the element for which the intensity ratio of the pair of lines is unity.

Note 2. Although this line-pair involves a MnI line and a CrII line, it was found experimentally to be preferable to other line-pairs available in this wave length region for the determination of low concentrations of manganese.

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Measure the duplicate plate in the same manner, and average the two determinations for each element. If, as occasionally happens, the duplicate results show a deviation of more than 10 per cent from the mean, repeat the procedure to obtain a set of two additional exposures, and average all results.

7.1-3. Determination of Cd and Hg

This procedure is designed primarily for the determination of Cd by the pyroelectric method, using the increased dispersion of the second order and adjusting the exposure time to obtain maximum sensitivity. In view of the high volatility of the cadmium the pre-arc period of Procedure 7.1-1 is omitted and the exposure is cut short to avoid excessive spectral background. These exposure conditions serve equally well for the determination of the highly volatile element, mercury, included in the procedure. Since Cd and Hg are generally very low or not detected, only two sector steps are employed, thus permitting 16 exposures to be photographed on the plate. The plate envelope is marked to include two 5.2-2 Cd standards such as E and X, and 7 samples in duplicate.

Procedure:-----For Grade A black oxide, in which As is low, either of the sample-carrier mixtures "a" or "k", prepared in Procedures 7.1-1 or 7.1-2, may be employed in the analysis. (For Grade B or Grade C black oxide, or in general when As is greater than 50 ppm, an "As-free" sample is obtained (Section 6.1), and tested for Cd. Weigh 490 mg of this sample, add to it 10 mg of gallium oxide and grind the mixture for four minutes). Prepare portions of the 5.2-5 Hg standards for use by mixing 4.90 g of the standard with 0.10 g of gallium oxide. (Prior to the analysis of samples, prepare and photograph a reference plate for each of the standard sets 5.2-2 and 5.2-5, following the observing conditions to be described for routine analysis.)

Prepare an electrode block holding 16 electrodes with 9/32-inch cup, protecting the block with a cover as much as possible between the successive operations. Mark the block identifying letter on the plate envelope. For each of the samples and standards listed on the plate envelope, weigh 100 mg of the "a" (or "k") mixture and transfer completely to the electrode in the block in proper sequence from numbers 1 to 16 on the block. Move the block to the storage cabinet at the spectrograph.

Prepare the spectrograph for operation as follows:

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Spectrograph: Baird
Setting: 6.3 (2200 to 2935 Å)
Cassette: 966.2
Rotation: 994.0
Position: 493.5
Electrode Stand: 38.8 cm
Auxiliary lens: 62.3 cm
Screen: 125 cm
Filter: None
Slit: 25 microns (examine slit and clean it if necessary)
Line mask: Full open
Grating aperture: 1-1/4 inch mask (unless indicated otherwise on the plate envelope)
Sector: Step 5 and 6 (180° and 360°). Set sector at 1.5 cm on the bench.
Upper electrode: As for procedure 7.1-1.
Lower electrode: As for procedure 7.1-1.
Electrode gap: As for procedure 7.1-1.
Excitation: As for procedure 7.1-1.
Pre-arc: None.
Exposure: Ended 15 seconds after Ga starts burning, making the total time about 25 seconds.
Plate: Eastman S.A. No. 1; 4 x 10 in.
Racking: Begin at 30; rack 5 after each exposure.
Inspection: Check the above conditions immediately before starting exposures; turn on water pump and step sector.
Venting electrode charge: See Procedure 7.1-1.
Spectrogram record: See Procedure 7.1-1.
Exposure cycle: Wipe off the electrode clamps, insert the electrodes, adjust them to the proper position. With the shutter open, start the arc by short-circuiting the electrodes by a clean, second grade graphite rod. Observe the time of start and the time at which arc becomes steady. At 15 seconds after the steady period begins stop the exposure. Record on the plate envelope the time elapsed from the start of the arc (1) to the beginning of the quiet period of burning, and (2) to the end of the exposure (e.g., 10-25 seconds). Rack the plate, remove the lower electrode, dump the charge into the scrap container, and discard the electrodes. Repeat the exposure cycle for the next sample. After the exposures have been finished, rack the plate back to zero, remove the plateholder, and transfer it to the darkroom.

Development: Develop the plate according to the standard procedure for the S.A. No. 1 Plate (Section 3.6).

Examination of the plate: For each sample exposure, examine the spectrum first for As 2349.84 Å*. If this line is present considerable care must be exercised in observing Cd 2288.02 because of possible interference by As 2288.12. If the As does not exceed 50 ppm, the Cd line will be resolved. When Cd is found present, make photometric measurement of the line in the samples and standards according to the general procedure of Section 3.7-1. Measure a stepped line image for plate calibration, plot the plate calibration curve, and convert the photometric measurements to log I values. Correct the log I values for the Cd line in the samples by the correction necessary to bring the log I values for the standards to the proper position on the analytical curve established for Cd. Read the concentration of Cd from the analytical curve.

Examine the duplicate plate in the same manner and average the two determinations for Cd in each sample.

When determination of Hg is desired, examine the spectra for the presence of Hg 2536.52 Å, and, if it is found, estimate the concentration by visual comparison with the plate on which standards 5.2-5 have been photographed by the procedure employed for the samples.

* If the sample examined is the original (not treated for removal of arsenic), this procedure provides a more sensitive test for arsenic than that of Section 7.1-1

7.1-4. Determination of Ba, Li, and Na.

This procedure provides for the determination of Ba, Li, and Na by the pyroelectric method, the exposures being made in the region of the most sensitive Li and Na lines, 5700 to 7000 Å. Eight sector exposures are photographed on one plate, providing usually for the spectra of six samples and two standards such as 5.2-3 E and X. A duplicate plate is prepared in the same manner.

Procedure:-----Either of the sample-carrier mixtures "a" or "k" prepared in Procedure 7.1-1 or 7.1-2 may be employed in the analysis. Prepare mixtures of the 5.2-3 standards with gallium oxide carrier, using 4.90 g of the standard mixed with 0.10 g of gallium oxide. (Prior to the analysis of samples, prepare and photograph a reference plate for the set of standards 5.2-3, following the observing conditions to be described for the routine analysis.) Prepare an electrode block holding eight electrodes with

9/32-inch cup, protecting the block with a cover as far as possible during the successive operations. Mark the block identifying letter on the plate envelope. For each of the samples and standards listed on the plate envelope, weigh 100 mg of the "a" (or "k") mixture and transfer it completely to the electrode in the block in proper sequence from numbers one to eight on the block. Transfer the block to the storage cabinet at the spectrograph.

Prepare the spectrograph and carry out the exposure operations as follows:

Spectrograph: Baird 7000 Å
 Setting: 8.4 (5700 to 7000 Å)
 Cassette: 959.5
 Rotation: 991.9
 Position: 488.0
 Electrode stand: 51.3 cm
 Auxiliary lens: 77.0 cm
 Screen: 125 cm
 Filter: 4500 Å (Corning Noviol B, G-38) set about 19 cm on the bench.
 Slit: 25 microns (Examine slit and clean it if necessary)
 Line mask: Full open
 Grating aperture: 3/4-inch mask (Unless indicated otherwise on the plate envelope)
 Sector: Steps 2 to 6, where 6 is 360°. Set sector at 14.3 cm on the bench.
 Upper electrode: As for Procedure 7.1-1
 Lower electrode: As for Procedure 7.1-1
 Electrode gap: As for Procedure 7.1-1
 Excitation: As for Procedure 7.1-1
 Pre-arc: None
 Exposure: Continued to 5 seconds after end of quiet period (total exposure about 40 seconds)
 Plate: Eastman II-F; 4 x 10 in.
 Racking: Begin at 30; rack 10 after each exposure.
 Inspection: Check the above settings immediately before starting exposures; turn on water pump and sector.
 Venting electrode charge: As for Procedure 7.1-1.
 Spectrogram Record: As for Procedure 7.1-1.
 Exposure cycle: Wipe off the electrode clamps; insert the electrodes; adjust them to the proper position. With the shutter open, start the arc by short-circuiting the electrodes by a clean, second grade graphite rod, observing the time of start. Adjust the upper electrode to maintain the 4 mm gap distance continuously throughout the exposure. Stop the arc 5 seconds after it has become unsteady and record on the plate envelope the time elapsed from the start of the arc (1) to the

beginning of the quiet period of burning (2) to the end of the quiet period, and (3) to the end of the exposure (e.g. 10-35-40 seconds).

Rack the plate, remove the lower electrode, dump the charge into the scrap container, and discard both electrodes. Repeat the exposure cycle for the next sample. After the eight exposures have been made, rack the plate back to zero, remove the plateholder, and transfer it to the darkroom.

Development: Develop the plate according to the standard procedure for the II-F plate (Section 3.6). Carry out the same procedure for the duplicate plate.

Examination of the plate: Examine the plate for the presence of the selected lines of Ba, Li, and Na, listed in Table XXV. Estimate the concentrations in the samples by visual comparison with the plate of 5.2-3 standards previously photographed. Correct the visual estimations, if necessary, by checking the results obtained for the standards photographed on the analytical plate.

Table XXV

Spectral Observations for Ba, Li, and Na

<u>Element</u>	<u>Wavelength(A)</u>	<u>Remarks</u>
Ba	6141.72	
Li	6707.84	
Na	5895.92	For low Na concentrations
	5889.95	For low Na concentrations
	6154.23	For high Na concentrations
	6160.76	For high Na concentrations

Examine the duplicate plate in the same manner, and average the two estimations for each element.

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7.1-5. Determination of K, Rb, and Cs

This procedure provides for the determination of K, Rb, and Cs by the pyroelectric method, the exposure being made in the region of the most sensitive lines of these elements, 7450-8750 Å. The procedure is identical with that of 7.1-4 except for the region of spectrum photographed, the photographic plate, the slit, and the standards used. Eight-sectored exposures are photographed on one plate, providing usually for the spectra of six samples and two standards such as 5.2-4 F and C. A duplicate plate is prepared in the same manner.

Procedure:-----Either of the sample-carrier mixtures "a" or "k" prepared in Procedures 7.1-1 or 7.1-2 may be employed in the analysis. The 5.2-4 standards are prepared by mixing 4.90 g of the standard with 0.10 g of gallium oxide. (Prior to the analysis of the samples, prepare a reference plate for the 5.2-4 standards following the observing conditions to be described for the routine analysis.) Prepare a block of eight electrodes with 100 mg charges as for Procedure 7.1-4.

Adjust the spectrograph and carry out the exposure operations as follows:

Spectrograph:	Baird
Setting:	11.5 (7450 to 8750 Å)
Cassette:	950.0
Rotation:	988.8
Position:	476.5
Electrode stand:	69.2
Auxiliary lens:	95.0
Screen:	Auxiliary screen at 142.5
Filter:	4500 Å (Corning Noviol B, G-38)
Slit:	50 micron (Examine slit and clean it if necessary.)
Line mask:	Full open
Grating aperture:	1 inch mask (unless indicated otherwise on the plate envelope)
Sector:	Steps 2 to 6 (where 6 is 360°). Set sector at 30.4 on the optical bench.
Upper electrode:	As for Procedure 7.1-1
Lower electrode:	As for Procedure 7.1-1
Electrode gap:	As for Procedure 7.1-1
Excitation conditions:	As for Procedure 7.1-1
Pre-arc:	None
Exposure:	Continued to five seconds after end of quiet period (total exposure about 40 seconds).
Plate:	Eastman I-N; 4 x 10 in.
Racking:	Begin at 30; rack 10 after each exposure.
Inspection:	Check the above settings immediately before starting exposures; turn on water pump and sector.

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Venting electrode charge: As for Procedure 7.1-1.
Spectrogram record: As for Procedure 7.1-1.
Exposure cycle: As for Procedure 7.1-4.
Development: Develop the plate according to the standard procedure for the I-N plate (Section 3.6).
Carry out the same procedure for the duplicate plate.
Examination of the Plate: Examine the plate for the selected lines of K, Rb, and Cs listed in Table XXVI.

Table XXVI

Spectral Observations for K, Rb, and Cs

<u>Element</u>	<u>Wave length (A)</u>
K	7664.91 7698.98
Rb	7800.23
Cs	8521.10

If the element is present, estimate its concentration by visual comparison with a plate of standards 5.2-4 previously photographed. Correct the visual estimations, if necessary, by checking the results obtained for the standards photographed on the analytical plate. Examine the duplicate plate in the same manner and average the two estimations for each element.

7.1-6. Determination of Ca

This procedure provides for the determination of Ca by the complete-burning method in which a small charge of the sample is volatilized completely into the arc, and the spectrum is photographed in the region of the sensitive Ca line 3933.67 A. The two smallest steps of the sector are used, permitting 16 exposures on a plate. The plate envelope is marked to provide exposures of two standards such as 5.2-3 D and X, and exposures of the samples in duplicate for a maximum of seven samples.

Procedure:-----Either of the sample-carrier mixtures "a" or "k" prepared in Procedures 7.1-1 or 7.1-2 may be used. Mixtures of standards 5.2-3 containing 2 per cent gallium oxide, prepared for Procedure 7.1-4 are employed. Prior to the analysis of samples, prepare and photograph a reference plate for the 5.2-3 standards following the observing conditions to be described for the routine analysis. Prepare an electrode block holding 16 electrodes with 1/32-inch cup, protecting the block with a cover as far as possible during the successive operations. Mark the block identifying letter on the plate envelope. For each of the samples and standards listed on the plate envelope,

weigh 10 mg of the "a" (or "k") mixture of the sample, and transfer completely to the electrode in the block, in proper sequence from block numbers 1 to 16. Transfer the block to the storage cabinet at the spectrograph.

Prepare the spectrograph and carry out the exposure operations as follows:

Spectrograph:	Baird 5000 A
Setting:	5.0 (3700-500A)
Cassette:	970.6
Rotation:	995.3
Position:	496.1
Electrode stand:	38.8 cm
Auxiliary lens:	62.3 cm
Screen:	125 cm
Filter:	None
Slit:	25 microns (examine slit and clean it if necessary)
Line mask:	Full open
Grating aperture:	3/8-inch mask (unless indicated otherwise on the plate envelope, i.e., mask 1/8-inch for black oxide grades B and C).
Sector:	Steps 1 and 2 (smallest steps). Set sector at 1.5 cm on the bench.
Upper electrode:	1/8-inch pointed cathode.
Lower electrode:	Sample electrode (1/32-inch cup) set firmly on the pedestal, which is a 1/8-inch tapered rod extending 1/2-inch above the electrode clamp.
Electrode gap:	4 mm, determined by the projection of the shadow image of the electrodes on the scale at the screen.
Excitation:	As for Procedure 7.1-1.
Pre-arc:	None
Exposure:	30 seconds
Plate:	Eastman S.A. No. 1; 4 x 10 in.
Racking:	Begin at 30; rack 5 after each exposure.
Inspection:	Check above settings immediately before starting exposures; turn on water pump and sector.
Treatment of electrode charge:	The addition of a vent hole is not required. Tap electrode to spread charge evenly over base of cup.
Spectrogram record:	Enter the briefed spectrogram description and date in the record book, and record the spectrogram serial number on the plate envelope.

Exposure cycle: Wipe off the electrode clamps, insert the electrodes, and adjust them to the proper position. With the shutter open, start the arc by short-circuiting the electrodes by a clean, second-grade graphite rod, observing the time of start. Adjust the electrodes to maintain the 4 mm electrode gap distance continuously throughout the exposure. Stop the exposure at the end of 30 seconds. Rack the plate, discard the electrodes, and repeat the exposure cycle for the next sample. After the set of exposures has been completed, rack the plate back to zero and transfer it to the darkroom.

Development: Develop the plate according to procedure for the SA No. 1 plate (Section 3.6). Inspect the plate for defects.

Examination of the plate: Examine the plate for the presence of Ca 3933.67A. If Ca is present, estimate its concentration in the samples by visual comparison with a plate of 5.2-3 standards previously photographed by this procedure. Correct the visual estimations, if necessary, by checking the results obtained for the standards photographed on the analytical plate. Average the results for the duplicate exposures.

7.2. Analysis of Metal (U)

The sample is obtained as the oxide (U_3O_8) by ignition of the metal (Section 6.2). Analyze the oxide by the procedures of Section 7.1 for black oxide, omitting the determination of Hg. Correct the results on the oxide to the basis of metal matrix by multiplying by the factor 1.18 ($U_3O_8/3U$).

7.3. Analysis of Brown Oxide (UO_2)

The sample is obtained as the oxide (U_3O_8) by ignition (Section 6.3). Analyze the ignited sample by the procedures of Section 7.1 for black oxide, omitting the determination of Hg. Report the results as determined, the correction for difference in matrix being negligible.

7.4. Analysis of Orange Oxide (UO_3)

Two samples are received, an ignited oxide (U_3O_8) and an "As-free" oxide (U_3O_8). Analyze the ignited oxide by Procedures 7.1-1, 7.1-2, 7.1-4, 7.1-5, and 7.1-6. Determine Cd by Procedure 7.1-3 on the "As-free" sample, and omit the determination of Hg. Report the results as determined, the correction for matrix being negligible.

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7.5. Analysis of Peroxide ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$)

Three samples are received, an "Original", a "Burnt" and an "As-free" (Section 6.4). Examine the "Original" for Hg and Tl by Procedure 7.1-1 with the following modifications: Begin the exposure when the arc is started (omitting the pre-arc period), and employ a 50 mg charge of samples and of the peroxide standards 5.2-7.

Analyze the "Burnt" sample according to Procedures 7.1-1, 7.1-4, 7.1-5, and 7.1-6. If accurate determination of Fe, Mg, and Mn is desired, and if the concentrations are in the measurable range, determine these elements by Procedure 7.1-2. Determine Cd by Procedure 7.1-3 on the "Burnt" sample except when As interferes, in which case examine the "As-free" sample. Correct the results on the ignited samples to the basis of the peroxide matrix by multiplying by the factor 0.83 ($\text{U}_3\text{O}_8/3\text{UO}_4 \cdot 2\text{H}_2\text{O}$).

7.6. Analysis of Soda Salt ($\text{Na}_2\text{O} \cdot x\text{UO}_3$)

An "Original" sample is received. The sample is diluted 1:10 with pure oxide (U_3O_8) and the mixture is analyzed according to the procedures of Section 7.1 for black oxide as follows: Dilute the sample and add the carrier simultaneously by mixing 137 mg of sample, 1235 mg of pure U_3O_8 , and 28 mg Ga_2O_3 . Apply Procedures 7.1-1, 7.1-3, 7.1-4, 7.1-5, and 7.1-6. Determine B and Si by photometric measurement and the other elements by qualitative estimation. Correct the results on the diluted mixture to the basis of the original soda salt by multiplying by 10.

7.7. Analysis of Green Salt (UF_4)

7.7-1. General Analysis of Green Salt (UF_4)

Two samples are obtained, a portion of the original green salt ("Original") and a portion converted to oxide ("Burnt") by hydrolysis and ignition according to Procedure 6.7. Analyze the "Burnt" sample by the procedure for black oxide, Section 7.1, omitting determination of boron and mercury. Correct the results to the basis of the original green salt by multiplying by the factor 0.89 ($\text{U}_3\text{O}_8/3\text{UF}_4$).

7.7-2. Determination of B and Hg in Green Salt (UF_4)

This procedure is designed for the determination of elements lost in the conversion of the green salt to oxide. The original green salt is examined by a method based on the general pyroelectric concentration procedure, modified to obtain slower heating and a lower temperature in the electrode charge. This results in a partial separation of the boron and mercury from the uranium tetrafluoride in arcing the sample and thus provides a means for determining these more volatile elements. Gallium oxide, added to the sample charge, assists in

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stabilizing the arc but its action is much less effective as a carrier here as compared to the behavior in the analysis of black oxide. The electrode charge is pressed into a pellet which provides more uniform and reproducible volatilization.

Procedure:-----Weigh 490 mg of green salt, add to it 10 mg gallium oxide, and grind the mixture for five minutes in a mullite mortar. Place the mixture in a vial labelled with the sample serial number followed by an "a" to indicate that gallium oxide has been added. Treat portions of standard samples 5.2-8 in the same manner. Prepare an electrode block holding eight boron-free electrodes with 9/32-inch cup (Section 3.3); protect the block with a cover as much as possible between successive operations. Prepare the pellet press* for operation by cleaning all parts with borax-free soap and water. For each of the samples and standards, totalling eight for a plate, first transfer an electrode to the recess in the pellet press and then weigh 50 mg of the "a" mixture, transfer the charge to the press, form the pellet with moderate pressure, and then force it out of the die and into the electrode. Return the loaded electrode to the block. Between operations on successive samples, wipe the parts of the press with lens paper.

Prepare the spectrograph for operation as described in Section 7.1-1 for general analysis of black oxide, but with the following exceptions:

Grating aperture:	No mask (full open).
Excitation:	Adjust rectifier d.c. current to 7 amps with the electrodes short-circuited. The current flowing during operation of the arc will be approximately 5 amps.
Pre-arc:	None.
Exposure:	Make from moment of striking the arc to the point at which the steady, brilliant, white light of uranium is observed in the arc (exposure time about 15 seconds).
Plate:	Eastman 33.
Racking:	Begin at 30, rack 10 after each exposure.
Exposure cycle:	Wipe off the electrode clamps and insert the upper electrode. Before inserting the lower electrode make sure the pellet is lying horizontally and centered in the cup. The pellet can be moved to the proper position by tapping the side of the electrode gently. Adjust the electrode gap to 4 mm and maintain this gap during the exposure.

* The pellet press employed in this procedure was designed and built at the University of Chicago Metallurgical Laboratory, and was loaned to us through the courtesy of Dr. Mark Fred. With this press, a charge of 50 mg of green salt is formed into a pellet having a diameter of 1/8 inch and a thickness of 1/16 inch.

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With the spectrograph shutter open, start the arc by short-circuiting the electrodes by a clean first grade (boron-free) graphite rod and observe the time of start. When the arc changes in appearance to the steady, white light emitted by uranium, turn off the arc and record the time of exposure. Rack the plate, remove, and discard the electrodes. (The charge remaining in the electrode may be recovered if desired.) Repeat the exposure cycle for the remaining samples, rack the plateholder to zero, remove the plateholder, and transfer it to the dark room.

Development:

Develop the plate according to the standard procedure for the Eastman ~~33~~ ^{II-F} plate (Section 3.6).

Examination of the plate:

Make photometric measurements of B 2497.73 for samples and standards, and reduce the measurements for the samples to concentrations of boron, correcting by the standards according to the procedure described for determination of boron in black oxide (Section 3.7-1). The analytical curve used in this case is established with Standards 5.2-8. Average the results of duplicate determinations.

Examine the plate visually for the presence of Hg 2536.52, and, if it is present, estimate the concentration by comparison with a reference plate of Standards 5.2-8.

7.8. Analysis of Hexafluoride (UF_6)

A sample resulting from hydrolysis and ignition to oxide (U_3O_8) (Section 6.8) is obtained. Apply procedure 7.1-1 and report qualitative ranges for the elements included in this procedure. (Note: The sample is contaminated by impurities derived from the copper and glass tubing employed in preparation of the samples. See the note following Section 6.8.)

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7.9. Analysis of Miscellaneous Materials

Uranium Carbide (UC₂)

An ignited sample is obtained (Section 6.9). Apply the procedures for the black oxide, omitting determination of Hg and Mo. Molybdenum apparently forms a stable carbide that is not oxidized in preparation of the sample; this element may be determined in the zirconium-group concentrate (Section 9.2). Other elements forming refractory carbides may be affected similarly; the limitations of the methods for application to the carbide have not been investigated extensively.

Uranyl Salts:-----An ignited sample is obtained (Section 6.9). Apply the procedures for the black oxide, omitting the determination of Hg. Correct the results on the ignited oxide to the basis of the original salt matrix by multiplying by the appropriate factor as follows:

<u>Salt</u>	<u>Factor</u>	<u>Multiply Results by</u>
Nitrate	$U_3O_8/3UO_2(NO_3)_2 \cdot 6H_2O$	0.66
Acetate	$U_3O_8/3UO_2(C_2H_3O_2)_2 \cdot 2H_2O$	0.56

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8. CHEMICAL CONCENTRATION OF THE LESS VOLATILE ELEMENTS

The principles on which the separations of the concentrates are based are discussed in Section 2 of this report. The detailed laboratory procedures are given in the following sections.

8.1. Preparation of the Rare-Earth Group Concentrate

This preparation involves two procedures; the first, Section 8.1-1, resulting in the separation of the rare earths as oxides; and the second, Section 8.1-2, the addition of an internal standard of titanium to the concentrate prior to spectrographic examination.

8.1-1. Chemical Separation

Dissolve the sample in 1:1 nitric acid, using 15 ml for each 10 g of sample. Evaporate to crystals on a steambath. Cool and dissolve in ether, 100 ml being required for each 50 g of sample. Transfer the ethereal solution to a separatory funnel and wash the residue in the beaker with ether, adding the washings to the solution in the funnel. Extract with three 5 ml portions of water, catching the water layers in the original beaker.

Wash down the sides of the beaker, boil off any residual ether (on a steambath), add 20 ml concentrated hydrochloric acid and boil for several minutes. Cool and dilute to 200 ml.

Dissolve 30 g of Na_2O_2 in 400 ml of water, or dissolve 30 g of NaOH in 400 ml of water and add 40 ml of 30% H_2O_2 . Add some filter pulp. Pour the sample slowly and with moderate stirring into the cold alkali solution. Filter through a Buchner funnel using rapid, hardened paper (Whatman #54) covered by a thin mat of filter pulp. Wash with 0.5% NaOH.

Dissolve the precipitate through the filter using 1:1 hydrochloric acid. (A suction-type bell jar is convenient for this operation.) Neutralize the solution with ammonia, and add an excess of 10 ml of concentrated ammonia per 100 ml of solution. Digest warm for 10 minutes, cool, and filter through medium paper (Whatman #40). Wash with 5:95 ammonia. Dissolve the precipitate with 1:1 hydrochloric acid. (If much calcium is present, as indicated by the formation of a precipitate upon addition of ^{ammonium} ammonium oxalate to the filtrate from the ammonia precipitation, the precipitation should be repeated one or more times.)

Evaporate the acid solution to dryness and bake to dehydrate silica. Dissolve the residue in 50 to 100 ml of 1% H_2SO_4 , and bubble a gentle stream of H_2S through the solution for 10 minutes. Allow to stand for one-half hour

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and filter through tight paper (Whatman #42). Wash with water.

Evaporate the solution to approximately one-half its original volume, add a few drops (1/2 ml) of hydrogen peroxide and boil. Cool, neutralize the solution with ammonia, and add 10% excess. Digest, cool, and filter through medium paper. Dissolve the precipitate through the filter paper with 1:1 hydrochloric acid. Evaporate to dryness on a steam bath.

Dissolve the residues in 5 ml saturated oxalic acid solution and 20 ml water, and digest at 60°C for ten minutes. Allow to cool and stand overnight. Filter through a small, tight paper and ignite at 1000°C for 15 minutes in a weighed crucible. Cool and weigh to 0.1 mg.

Note 1: The ether extraction may be omitted on samples weighing 20 g or less, the nitric acid solution being diluted and partially neutralized with NaOH solution, and added directly to the alkaline peroxide solution.

Note 2: Large amounts of iron, which interfere in the alkaline peroxide separation, may be removed by extraction of FeCl_3 with ether. To the nitric acid solution obtained from the ether extraction add 50 ml of concentrated hydrochloric acid, and evaporate the solution to syrupy consistency. Take up this syrup in a minimum amount of hydrochloric acid (sp.gr. 1.10-1.15) and transfer to a separatory funnel. Add a volume of ether at least equal to the volume of hydrochloric acid solution. Draw off the hydrochloric acid layer and wash the ether twice with 5-10 ml of hydrochloric acid (sp.gr. 1.10-1.15). Combine the hydrochloric acid layers and evaporate to a low volume to remove residual ether and most of the acid. Dilute to about 200 ml and proceed with the alkaline peroxide precipitation.

8.1-2. Addition of the Internal Standard: Titanium

To prepare the rare-earth concentrate for spectrography, dissolve the precipitate in nitric acid (2 ml 1:1 nitric acid for 10 mg of concentrate). Add a measured volume of standardized Ti solution* such that Ti is one per cent of the weight of the concentrate. Evaporate the solution on a steam bath to a volume of 0.5 ml, add 2 or 3 small circles of soft filter paper (cut with a No. 10 cork borer) and evaporate to dryness. Ignite the concentrate over a Meker burner slowly to avoid spattering, and transfer the resulting oxide mixture to a glass vial.

* Ti solution: Prepare a solution of 0.1 mg Ti/ml by dissolving NBS standard sample of TiO_2 , No. 154, in H_2SO_4 as described on the provisional certificate.

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8.2. Preparation of the Zirconium Group Concentrate

A cupferron precipitation is made to obtain a concentrate of the insoluble cupferrides of Cb, Ga, Hf, Mo, Pd, Ta, Ti, V, W, and Zr. The concentrate is regularly prepared for samples of metal, black oxide, brown oxide, peroxide, and soda salts, but the procedure may be applied to other uranium-base materials when desired. The ignited concentrate is submitted for spectrographic examination by procedure 9.2.

Procedure:-----Weigh a 5.000 g sample, place it in a 250 ml beaker and add enough nitric acid (1:1) to dissolve the sample (20 ml is sufficient). After all of the acid-soluble material is in solution, heat the beaker on a hot plate until fumes of NO_2 are driven off, and evaporate the solution to dryness. Bake the sample in an oven at 350°C for 30 minutes to decompose all of the nitrate. Allow the beaker to cool, and add 50 ml of 10% H_2SO_4 . Cover the beaker and heat it on a steam bath to dissolve the oxide. While the solution is still hot, add a slight excess of 0.1 N KMnO_4 solution (add 2 drops after the pink color has developed). Cool the solution to 5°C with ice.

Transfer the cold solution to a separatory funnel and add a quantity of bismuth solution * containing 5.00 mg of Bi. Precipitate the cupferrides by adding from 2 to 10 ml of 8% cupferron solution. Shake the mixture well and extract the cupferrides with about 25 ml of chloroform. Separate the chloroform layer, catching it in a No. 42 filter paper (18.5 cm) folded into a No. 4 crucible. When fitting the filter paper in the crucible, dampen the paper slightly with water to hold it in place. Repeat the extraction several times with additional quantities of chloroform until all the cupferrides are removed. Usually some precipitate remains at the chloroform-water interface after extraction. Wash this precipitate out with a little of the solution into a small No. 42 filter paper (9cm), and then wash it with hot, dilute H_2SO_4 (1%) until all the uranium is removed**. Wash the precipitate once with water and set the filter paper aside.

Place the large crucible containing the chloroform solution under a hood at room temperature to permit evaporation of the chloroform from the extending filter paper. Keep the filter paper damp by adding a small amount of water in the bottom of the crucible. When all of the chloroform has evaporated place this filter paper and the paper containing the insoluble material from the interface into a small No. 1 crucible. Transfer the crucible to a cold furnace set for a maximum of 350°C and heat gradually to the maximum temperature. (When decomposing the cupferron and cupferrides, care must be taken that the papers are heated very gently at first.) Transfer the ignited precipitate to a small vial for spectrographic analysis.

* Prepare a solution of bismuth containing 1 mg Bi/ml, as follows: Dissolve 1.115 g Bi_2O_3 (1.000 g Bi) in 200 ml 1:1 H_2SO_4 and dilute to one liter.

** Care must be taken throughout the procedure to avoid contamination of the product with uranium.

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8.3. Preparation of the Platinum-Group Concentrate

The platinum metals Ru, Rh, Pd, Ir, and Pt are separated by reduction with zinc and hydrochloric acid, using gold as a gathering agent. The elements are determined by spectrographic examination of the gold precipitate according to Section 9.3. The chemical separation is as follows:

Procedure:-----Weigh a portion of uranium-base samples equivalent to 3.75 g of U_3O_8 , place it in a beaker, and add 30 ml 1:1 hydrochloric acid and 2 ml nitric acid (sp.gr. 1.42). Cover the beaker and heat it on a steam bath until the sample is dissolved; remove the cover and evaporate the solution to dryness. Cool the beaker, wash down the walls with water, and add 5 to 7 ml of H_2SO_4 (sp.gr. 1.84). Add a quantity of gold solution* equivalent to 15 mg of gold. Dilute the solution to 125 ml and add enough 20 mesh metallic zinc (1 to 2 g) to reduce the gold completely to metal. (The solution turns green.) Allow the solution to stand several hours or overnight. Filter the solution through a No. 42 filter paper (9 cm) and wash the precipitate thoroughly with hot 2% hydrochloric acid to remove the zinc. Burn off the paper in a porcelain crucible and ignite at $500^{\circ}C$. Place the ignition product, Au and Pt metals except Os **, in a clean vial for spectrographic analysis.

* Gold Solution: - Dissolve 2.500 g Au metal in a solution made up of 3 ml HNO_3 , 18 ml HCl and 9 ml H_2O . Evaporate the solution to a paste on a steambath, add 10 ml HCl, and evaporate again. Repeat this operation three times and, if gold precipitates, add a few crystals of sodium chlorate to redissolve the gold. Finally add 10 ml of HCl to the paste and dilute the solution to 250 ml in a volumetric flask. This solution contains 10 mg Au per ml.

** This method is not applicable to the determination of osmium in uranium metal, but a chemical method for its determination has been described (1). The separation of iridium is also not very satisfactory because of incomplete reduction of this element by zinc. For this reason it is necessary to carry standard samples through the procedure in the same manner as the substance being analyzed.

Literature Cited

- (1) J.P. Williams and C.J. Rodden.
Method Used to Determine Small Amounts of Osmium in Metal.
Project Report CC-1706, Section 13 (1944).

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9. SPECTROGRAPHIC ANALYSIS OF THE CONCENTRATES

This section covers procedures for the analysis of three concentrates of less-volatile constituents separated from uranium-base materials by the chemical procedures of Section 8.

9.1. Determination of the Rare Earths and Thorium

This procedure provides for the examination of the rare-earth concentrate for two groups of elements listed in Table XXVII. The first group consists of rarer elements of importance in the analysis of uranium-base materials, and the second group includes common elements of interest in checking the completeness of the chemical separations. The four underlined elements of the first group are determined by photometric measurement relative to titanium internal standard, and the remaining elements are estimated by visual inspection of the spectrogram.

Table XXVII

Elements Determined in Examination of the Rare Earth Concentrate

Group 1. Rarer elements: Sc, Y, La, Ce, Pr, Nd, Sm, Eu,
Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Th.

Group 2. Common elements: Al, Ca, Cu, Mg, Pb, Si, Sr, and U.

The rare-earth concentrate may be separated from various uranium-base materials, but the concentrate obtained from very pure samples such as uranium metal, brown oxide (UO_2), and green salt (UF_4), if weighing less than 0.4 mg, is not examined spectrographically. The usual weight of concentrate submitted for spectrographic analysis varies from 0.4 to 40 mg, with the majority weighing approximately 5 mg. The sample is obtained with the internal standard of titanium added at a concentration of one per cent according to procedure 8.1-2. The spectrographic analysis consists briefly of the following operations. A portion of the concentrate is mixed with graphite, transferred to a graphite electrode and burned in a d.c. arc. The spectrum is photographed using the step sector and spectrographic assembly described in Section 3, and the spectrum is compared with the spectra of standard samples for the determinations. Eight sector exposures may be photographed on the same plate providing for the spectra of six samples and two standards such as 5.3 A and B. Duplicate exposures are made for each sample when the quantity of concentrate permits. Detailed instructions are as follows:

Procedure:-----Label the sample vial with a laboratory serial number which is used to identify the sample in the records throughout the procedure. Set up an electrode block containing eight graphite electrodes with 1/32-inch cup (Section 3.3). For each sample, weigh a 0.5 mg portion on the 50 mg

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balance as accurately as possible, and to the sample in the pan add 2.5 mg of *325 mesh* graphite powder. Mix the materials on the pan and transfer the mixture to an electrode. Prepare each charge of samples and standards in the same manner, and transfer the electrode block to the storage cabinet at the spectrograph. Prepare and operate the spectrograph as follows:

Spectrograph:	Baird
Setting:	3.5 (2800 to 4100 A)
Cassette:	975.4
Rotation:	996.8
Position:	498.5
Electrode stand:	38.8 cm
Auxiliary lens:	62.3 cm
Screen:	125 cm
Filter:	None
Slit:	25 micron (Examine slit and clean it if necessary)
Line Mask:	Full open.
Grating aperture:	3/8-inch mask (unless indicated otherwise on the plate envelope).
Sector:	Step 1 to 5, where 5 is 180°C. Set sector at 1.5 cm on the bench.
Upper electrode:	1/8-inch pointed cathode.
Lower electrode:	Anode, containing sample, set firmly on the pedestal, which is a tapered 1/8-inch rod extending 1/2 inch above the electrode clamp.
Electrode gap:	4 mm, adjusted by projection of the shadow image of the electrodes on the screen.
Excitation:	Adjust rectifier d.c. current to 14 amp with the electrode clamps short circuited; the current during operation of the arc will be approximately 10 amp.
Pre-arc:	None.
Exposure:	40 seconds
Plate:	Eastman S.A. No. 1; 4 x 10 inch.
Racking:	Begin at 28 and rack 10 after each exposure.
Inspection:	Check the above settings immediately before starting the exposures; start the water pump and sector.
Spectrogram record:	Enter the briefed spectrogram description and date in the record book. Record the spectrogram serial number on the plate envelope.
Exposure cycle:	Wipe off the electrode clamps, insert the electrodes and adjust them to the proper position. With the shutter <u>open</u> start the arc by short-circuiting the electrodes with a clean, second-grade graphite rod, observing the time of start. After 40 seconds shut off the arc.

(The arc will burn somewhat erratically, the color changing as more or less of the rare earth is being volatilized. At the end of 40 seconds only a thin film of residue should be observed in the electrode.) Rack the plate and discard the electrodes. Repeat the procedure for the remaining exposures and rack the plate holder back to zero. Remove the plateholder and transfer it to the dark room.

Development: Develop the plate according to the standard procedure for the S.A. No. 1 plate (Section 3.6).
Examination of the plate: Following the typical procedure given in Section 3.7 make photometric measurements of the lines in Table XXVIII, calibrate the plate, and reduce the measurements to log intensity ratios of the line pairs.

Table XXVIII

Analytical Line Pairs

<u>Impurity line</u> <u>A</u>	<u>Internal Standard Line</u> <u>A</u>	<u>Remarks</u>
Dy 3407.80	Ti 3361.22	
Er 3264.78	Ti 3361.22	The line given as Y 3264.78 in the MIT tables is probably Er 3264.78; Y does not interfere. Avoid confusing this line with a background line separated 0.05 mm.
Eu 3971.99	Ti 3361.22	
Gd 3422.47	Ti 3361.22	

Determine the correction necessary to fit the standards to the analytical curve established for the standards (log intensity ratio versus per cent of rare earth). Apply the correction to the log intensity ratios for the impurities in the samples, and read the impurity concentrations from the analytical curves. Report the mean of duplicate determinations in each case.

Examine the plate on a viewing box for the presence of the selected lines of the elements listed in Table XXIX. For the elements found present estimate the concentrations by comparison of the spectra of the samples and of standards previously photographed. Report the concentrations according to the qualitative scale given in Table III, Section 2.2-3. Care is required to avoid errors in the identification of lines in the rather complex spectra involved.

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Table XXIX

Spectral Observations for the Qualitative Analysis of
Rare Earth Concentrates

Element	Wave Length	Intensity (MIT)		Remarks
	A	Arc	Spark	
Al	3961.53	3000	2000	Al has always been found present; it is included in the matrix of standards.
	3092.71	1000	1000	
Ca	3933.67	600R	600R	Ca has always been found present; it is included in the matrix of standards.
	3968.47	500R	500R	
Ce	4012.39	60	20	Ce is seldom found present; the line 4040.76 may be confused with background.
	4040.76	70	5	
Cn	3247.54	5000R	2000R	
Ho	3416.46	30	40	
	3398.98	40	60	
La	3988.52	1000	800	
	3265.67	300	200	
Lu	2911.39	100	300	
	2900.30	50	150	
Mg	2852.13	300R	100R	
Nd	3951.15	40	30	Nd may be found present if Ce is strong. Fe interferes at both lines but Fe is never present when rare earths are very strong.
	3963.11	30	25	
Pb	2833.07	500R	80R	
Pr	4008.71	150	50	Pr may be present if Ce is strong.
Sc	3353.73	50	60	
	3613.84	40	70	
Si	2981.58	500	400	Present in matrix of standards.
Sm	3634.27	100	25	This line exhibits poor sensitivity (0.8% Sm) but apparently is the best available on the plate.
Sr	4077.71	400r	500W	Avoid mistaking Y 4077.27 for the Sr line.
Tb	3324.40	70	50	
Th	2870.41	18	20	
	4019.14	8	8	
Tm	3131.26	400	500	
	3151.04	200	200	

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Table XXIX (Continued)

Ele- ment	Wave Length A	Intensity (MIT) arc	Spark	Remarks
U	3932.03	35	50	Useful for identification when U is strong.
Y	3242.28	60	100	Y rarely absent in concentrates.
	3200.27	30	40	
	3216.68	40	70	Faint Dy coincident
Yb	3289.37	500R	1000R	This very sensitive Yb line is usually found present.

9.2. Determination of the Zirconium-Group Elements

This procedure provides for the spectrographic examination of the zirconium group concentrate, prepared according to Procedure 8.2. The elements included in the examination are Cb, Ga, Hf, Mo, Pd, Ta, Ti, V, W, and Zr. The results are obtained as concentrations of the elements in the original uranium-base sample. The concentrates are regularly prepared from samples of uranium metal, black oxide (U_3O_8), brown oxide (UO_2), peroxide ($UO_4 \cdot 2H_2O$), and soda salts ($Na_2O \cdot xUO_3$). The concentrates range in weight from 5 to 20 mg except for very impure samples. If the concentrate exceeds 20 mg, the sensitivity of the method is affected and the standards of Section 5.4 do not apply strictly, but qualitative comparisons may be made. Sixteen exposures, not sector, are made on one plate, usually omitting standards. The concentrations of the impurities are estimated by comparing the spectra of samples and of standards photographed on a separate plate reserved for the purpose. The equipment used is described in Section 3 of this report.

Procedure:-----Prepare the samples for analysis as follows, using balance pan, spatula, and mortar reserved for the purpose. For each sample weigh 100 mg of bismuth oxide (Bi_2O_3) on the 250 mg balance, and add this oxide to the sample vial. Grind each mixture in a small mortar until the materials are well blended (3 to 5 minutes). Set up an electrode block containing 16 electrodes with 1/32-inch cups, for eight sample charges in duplicate. For each sample charge, weigh 10 mg of the charge mixture on the 50 mg balance and transfer the charge to the electrode. Protect the block of electrodes as far as possible with a cover. Prepare the spectrograph for operation in setting 2.4 as described in Section 7.1-1 with the following exceptions:

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Step sector:

Mask the sector to expose steps 5 and 6, where 6 is 360°C. The sector disk is turned by hand until the openings for steps 5 and 6 on the optical path are clear. Allow the sector disk to stand stationary in this position during the exposures. Set the sector at 1.5cm on the bench.

Grating aperture:

1/8-inch mask.

Pre-arc:

None.

Exposure time:

60 seconds.

Racking:

Begin at 30, rack 5 after each exposure.

Examination of the plate: Examine the plate for the lines of the 10 elements listed in Table XXX. Estimate concentrations by visual comparison of the spectra of the samples and of standards photographed on a separate plate. Report the mean of duplicate determinations in each case. The values for Mo and V should check those observed by Procedure 7.1-1.

Table XXX

Spectral Observations for Ten Elements of the Refractory Group

Element	Wave Length A	Intensity (MIT) arc	Spark	Remarks
Cb	3094.18	100	1000	3094.18 is reliable only if V is less than 50 ppm.
	3194.98	30	300	
Ga	2943.64	10	20r	If detected, check for contamination.
	2500.17	12	10r	
Hf	3399.80	60	100	Do not mistake background for Hf.
	2861.70	50	125	
Mo	3132.59	1000R	300R	
	3170.35	1000R	25r	
Pd	3404.58	2000R	1000R	
	3242.70	2000wh	600R	
Ta	2656.61	200R	2	2656.61 is reliable only if V is less than 50 ppm.
	2714.67	200	8	
Ti	3078.64	60	500R	Do not mistake Fe 3186.74 for Ti
	3186.45	150	80	
V	3183.41	200R	100R	3183.41 and 3183.98 must be present to report V. 2907.47 appears at 10 ppm and is useful when V is high.
	3183.98	500R	400R	
	2907.47	40	150h	
W	2946.98	20	18	
	2896.45	15	25	
Zr	3438.23	250	200	Hf interferes with 3438.23 at 200 ppm; however, Hf is usually not detected in samples.
	3387.87	100	100	

9.3. Determination of the Platinum Group Elements

This procedure provides for the spectrographic examination of the platinum-group concentrate in gold, prepared according to Procedure 8.3. The results of the examination for Ir, Pd, Pt, Rh, and Ru are obtained as concentrations in the original uranium-base samples. The concentrates are regularly prepared from samples of uranium metal, black oxide (U_3O_8), brown oxide (UO_2), and soda salts. Occasionally preparations are made from peroxide ($UO_4 \cdot 2H_2O$). The concentrates usually range in weight from 10 to 20 mg. If the weight exceeds 20 mg, the sensitivity of the method will be affected, and the standards of Section 5.5 will not apply strictly, but qualitative analyses may be made. The platinum metals are rarely detected. Sixteen arc exposures are photographed on one plate, representing a single run of each of 16 samples. The equipment employed is described in Section 3 of this report.

Procedure:-----The balance pans, spatula, and mortar of Section 9.2 are used in the preparation of the sample. The sample is broken up in the vial with the spatula, and a portion of 5 mg is weighed on the 50 mg balance. To the sample in the pan add 2 mg graphite powder (325 mesh). Mix the materials in the pan and transfer the mixture to an electrode with 1/32-inch cup held in an electrode block. Tap the electrode to distribute the charge evenly in the cup. Prepare the spectrograph and make the exposures according to the procedure for the zirconium concentrate (Section 9.2) with the exception that the exposure time is increased to one minute, 45 seconds. Examine the plate for the lines given in Table XXXI, and, if the element is present, estimate its concentration by reference to a plate on which standards 5.5 have been photographed. The determination of palladium by this method and by Procedure 9.2 should check.

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Table XXXI

Spectral Observations for the Platinum Metals

Element	Wave Length A	Intensity (MIT)		Remark
		arc	Spark	
Ir	3220.78	100	30	
	2661.98	150h	15	
Pd	2476.42	300r	50	
	2447.91	200r	100	
Pt	3064.71	2000R	300R	Note possibility of Ni interference by Ni 3064.62
	2997.97	1000R	200r	
Rh	2555.36	100	60	Note possibility of interference by Ni 2555.11
	3396.85	1000w	500	
Ru	2678.76	100	300	Do not mistake Fe 2679.06 for Ru 2678.76
	3436.74	300R	150	
	3428.31	100	100	

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REPORT A-2907(S)

A System of Methods for the Spectrochemical Analysis of
Uranium Base Materials

by

B. F. Scribner and H. R. Mullin

- Page 23. Par. 1, line 6: "over-present" should read "ever-present". ✓
- Page 59. Under standard solutions, column headed Source: The second entry should be "TiSO₄". ✓
- Page 66. Section 6.8, under list of apparatus, change "12 cm" to "1.2 cm". ✓
- Page 70. Line 3: The first chemical symbol should be "Ag" instead of "As". ✓
- Page 77. Par. 2, line 1: "733 mg" should read "735 mg". ✓
- Page 79. Under Exposure cycle, line 12: After "scrap" read "container". ✓
- Page 81. Line 10, opposite "Setting": Change "700A" to "7000 A". ✓
- Page 85. Line 7, opposite "Setting": Change "500 A" to "5000 A". ✓
- Page 87. Section 7.6, line 5: "7.1-7" should read "7.1-6". ✓
- Page 89. Opposite "Development": Change "Eastman 33" to "Eastman II-F". ✓
- Page 91. Heading of Section 8.1: Last word is "Concentrate". ✓
- Page 91. Par. 6, line 7: Change "ammoium" to "Ammonium". ✓
- Page 94. Par. 2, line 4: The second word is "until". ✓
- Page 95. Par. 4, line 3: After "1/32-" read "inch". ✓
- Page 96. Line 1: After "2.5 mg of", add "325-mesh". ✓
- Page 97. Table XXVIII, under Remarks, line 4: Strike out "this line" and substitute "Eu 3971.99". ✓

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