Date Issued: September 22, 1970

Document Y-1745

TID-4500

UNION CARBIDE CORPORATION
Nuclear Division

OAK RIDGE Y-12 PLANT

Operated under Contract W-7405-eng-26
With the US Atomic Energy Commission

THE QUANTITATIVE ANALYSIS OF MICROMETER-SIZE URANIUM
ALLOY POWDERS USING THE ELECTRON
MICROPROBE X-RAY ANALYZER

J. H. Stewart, Jr

This Report is based on a study by the author
as partial fulfillment of requirements for the
degree of Master of Science in Chemistry
from The University of Tennessee.

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ACKNOWLEDGEMENTS

The author is grateful to his advisor, Dr. John A. Dean, of The University of Tennessee, for his guidance, advice, and suggestions during this investigation.

Members of the Oak Ridge Y-12 Plant who contributed to the success of this work include the following: W. J. Hulsey and F. R. Winslow for materials and support, Anna G. Dobbins for metallographic specimen preparation, Mary R. Ferguson for chemical analyses, A. G. Hensley for electron microprobe analyses, and E. E. Johnson for statistical evaluations. Thanks are also extended to the Y-12 Plant for the educational assistance program which is available. This research was sponsored by the Union Carbide Corporation under its contract with the U. S. Atomic Energy Commission.

The Metals and Ceramics Division of the Oak Ridge National Laboratory provided the uranium alloys necessary for this study.

Finally, the author is indebted to his wife, Martha, and his son, Joe, for their understanding and encouragement during this endeavor.

ABSTRACT

Conventional chemical or microchemical analytical techniques, while quite satisfactory for homogeneous samples, have not proved adequate for determining the quantitative relationships between components of micrometer-size inhomogeneous nuclear fuel particles. In this study, the electron probe X-ray microanalyzer, which has been used extensively to qualitatively determine the distribution of elements within a wide spectrum of alloys, was extended to the quantitative analysis of individual microparticles of uranium-molybdenum and uranium-niobium-zirconium alloys. A computer program was applied to correct the characteristic X-ray intensities of the alloyed metals excited by the electron beam for absorption, fluorescence, and atomic number effects. The accuracy of the method is comparable to that of the conventional chemical analysis of homogeneous bulk samples.

Previous workers have reported that the precision of microprobe analyses is limited due to polymerized vapor (deposited on the surface of the specimen during a short counting period), causing reduction in the X-ray intensities. However, this factor was evaluated and found to be insignificant for the alloys examined.

A simplified specimen preparation and handling procedure was devised to prevent the usual rapid oxidation of the polished specimen

surface, which would introduce a significant nonreproducible bias into the analysis.

Comparison of the results obtained from conventional, high-precision techniques with those from the electron microprobe method for analyzing specially prepared homogeneous uranium alloy particles showed excellent agreement. Comparison of the same type of results for nonuniform particles showed that extreme deviations occur in the data from conventional techniques. Characteristic X-ray photographs of these particles support the results obtained with the electron microprobe and explain why the results from conventional techniques are in error.

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CHAPTER I

INTRODUCTION

A. Basis of the Investigation

The advent of new concepts in nuclear reactor fuel technology has created new demands on the analytical chemist for analyzing these materials. Reactor fuel elements contain micrometer-size particles of uranium alloys dispersed in other materials such as graphite, Zircaloy, stainless steel, and ceramics. Corrosion resistance of this fuel frequently depends upon the presence of stable gamma-phase uranium. The latter is normally obtained by forming an alloy of uranium with a second, or even third, metal. Homogeneity of the resulting alloy is essential in maintaining the uranium in the gamma phase.

Testing various types of powdered fuel materials has indicated poor corrosion resistance due to inhomogeneity of the alloys, but analytical techniques normally employed have failed to prove this assumption. Such techniques include potentiometry, absorption spectrophotometry, gravimetry, and monochromatic X-ray absorption analysis. Although these are all accepted methods of analysis, with well-established accuracy and precision criteria, they cannot overcome the basic problem of sampling and analyzing a micro-volume of the specimen and ascertaining its homogeneity.

Efforts to reduce the severity of the sampling problem included elaborate techniques for microanalysis using very small sample weights. Another approach was to sieve the powdered metal alloys into a series of particle size fractions and to analyze these fractions by conventional methods. Neither proved satisfactory, however, and a new approach to the problem became essential.

B. Historical Background

In 1949, R. Castaing presented a paper entitled "Application of Electron Beams to Metallographic Analysis" at a conference on electron microscopy.¹ This effort represented the first use of an instrument designed to utilize the focusing capability of the electron microscope as an excitation source to generate characteristic X rays, and to use these X rays to identify the elements present in the specimen. This original instrument rapidly evolved into an electron probe X-ray microanalyzer, which became available as a commercial instrument in the early 1960's. Since that time, the electron microprobe (or probe, as the instrument is now generally called) has become one of the most significant new analytical instruments for specialized chemical analysis. The original publications by Castaing² introduced the analyzer capability, which has gradually been extended to solve a wide variety of analytical problems.

From its inception, the electron microprobe was peculiarly suited to solving metallurgical problems. Its original uses included the qualitative identification of foreign material in metals, location of diffusion zones, semi-quantitative analysis of metals, and characteristic X-ray scanning to show the distribution of an element of interest in the specimen being examined. However, the complexity of specimen and electron beam interaction has resulted in serious problems in the development of an accurate quantitative procedure by electron microprobe techniques. The general physical nature involving the interaction of an electron beam with a specimen in the microprobe is understood, but many analytical results obtained using the best possible combination of theoretical calculations are not within the expected limits of experimental error. Two approaches to corrections for quantitative analysis are usually considered: (1) use of comparison standards of the same composition as the test specimen, and (2) use of pure standard elements for comparison with the specimen. Although the first case has the advantage of analytical simplicity, the preparation of such a set of standards, homogeneous on the microvolume scale, is often difficult and expensive. In such instances, the standards require chemical certification with attendant analytical limits of error and uncertainty about the specimen homogeneity on the microscale. The second case does not require a prepared set of calibration standards, but the theoretical assumptions are frequently based on uncertain X-ray absorption or fluorescence data.

C. Approaches to Quantitative Analysis

Quantitative electron microprobe analysis is based on a comparison of the primary characteristic X-ray intensities emitted by the specimen with those emitted by a standard element. This value is referred to as "a first approximation" since $C_A = I_A / (I_A)_S$, where C_A is the mass concentration of Element A in a complex target ternary alloy ABC. I_A represents the emergent X-ray intensity of Element A from the specimen, and $(I_A)_S$ represents the emergent X-ray intensity from the pure standard of Element A. Three major corrections must be considered to refine the "first approximation" into a quantitative value: (1) the absorption, (2) the fluorescence, and (3) the atomic number corrections. A stepwise illustration of the complexity of this computation was demonstrated by Adler and Goldstein.³ The absorption correction compensates for the reduction of X-ray intensity as the emergent beam traverses the distance from its point of generation within the specimen to the surface of the specimen. The fluorescence correction compensates for the increased intensity of a characteristic X-ray emission due to the additional direct excitation of that element caused by the stimulation from absorption of short-wavelength X-ray energy from a second, excited element of higher atomic number present in the specimen. The atomic number effect is defined as the composite of the interrelations that cause the primary X-ray intensity in the specimen to be a nonlinear function of concentration. This

effect becomes large as the difference between the atomic numbers of the specimen components increases. The effect also causes the characteristic X-ray intensities of elements with lower atomic numbers to be increased and the intensities of elements with higher atomic numbers to be decreased.

The quantitative analysis of multicomponent specimens is greatly simplified by using computer programs such as those recently published by Colby⁴ and by Brown.⁵ Quantitative results can be obtained using only pure elements as standards if: (1) the conditions under which the analysis is made are carefully chosen, (2) the observed intensities can be corrected to obtain the primary intensity actually produced in the specimen, and (3) the relationship between the primary intensity and concentration can be calculated. These computer programs have become increasingly important because quantitative analysis using empirical working curves has been only partially successful thus far. One problem has been the inability to reproduce analytical parameters. A problem of greater magnitude has been to obtain homogeneity of complex standard alloys on a microcrystalline scale.

Colby⁶ stated that the correction for fluorescence used by Castaing² does not adequately compensate for the electron accelerating voltage. He expected that a good correction could be obtained at one particular accelerating voltage but not for other accelerating voltages, since only the first term in Castaing's correction equation takes into account the accelerating

voltage. Thus, for large atomic number or fluorescence effects, the correction procedure would not be applicable at all accelerating voltages.

Heinrich⁷ stated that a lower accelerating voltage reduced the magnitude of the fluorescence correction factor by decreasing the depth from which the primary X-ray emission originated. This modification reduced the effect of the secondary fluorescence correction term in the Castaing² equation. Reed⁸ observed that the main approximation in Castaing's derivation of the fluorescence formula lies in the expression assumed for the ratio, I_B/I_A , of the primary X-ray intensities of Elements A and B present in the specimen. He further stated that this assumption is not strictly valid for the electron energies involved in electron microprobe analysis, and an improved formula was suggested. The effect of Reed's modification was to reduce the calculated fluorescence intensity compared with the value given by Castaing's original formula, and to introduce a stronger dependency on the electron beam energy.

All of the corrections discussed so far were found to apply to homogeneous samples. However, no satisfactory correction model is available for a precipitate of small particle size or for a highly segregated specimen in which fluorescence effects occur. Castaing² suggested that smaller X-ray emergence angles, coupled with low operating voltages, would tend to decrease the analytical error in these cases.

At the present time, a total of 23 different computer programs for the conversion of X-ray intensity ratios to chemical concentrations are available. All of the programs have been studied and critically evaluated for three separate alloy systems,⁹ using the same physical data. These alloy systems were: titanium-niobium, iron-chromium, and chromium-cobalt-molybdenum. Fourteen programs were judged to be incomplete on the basis of one or more of the following criteria: (1) accuracy of the correction scheme, (2) data handling capabilities, (3) utility for other than binary systems, (4) inadequate atomic number correction, and (5) nonavailability in a common computer language. Data from the nine other programs were tabulated, and Colby's Microprobe Analysis General Intensity Corrections (MAGIC) program was found to be in good agreement with the true chemical concentrations. His computer program was available and was used for this investigation.

1. Evaluation of Computer Correction Programs

The New York Metropolitan Probe Users Group¹⁰ evaluated 23 different correction procedures, including those of Brown and of Colby, using a set of four iron-nickel alloys. These values were compared with values obtained from the chemical analysis of the standard alloys. Colby's program yielded results within one per cent of the chemical composition for both iron and nickel on samples comprising up to approximately 70 per cent nickel.

The Colby program appeared to be generally more accurate over a wider concentration range than did Brown's program.

2. Effect of Electron Beam Incident Angle

A variable in microprobe quantitative analysis is the angle of incidence of the electron beam with the specimen surface. Manufacturers of commercial instruments have utilized a variety of incident angles, varying from 12° to 90° . The effect of the angle of incidence in quantitative microprobe analysis was recently studied by Colby¹¹ for three separate binary alloy systems: iron-chromium, copper-gold, and tantalum-aluminum. The data, corrected by the Colby MAGIC program, revealed only small random differences between the corrected results from microprobes with a normal (90°) electron beam incidence and microprobes having beam incidence angles of less than 90° . The normal beam angle usually requires a smaller absorption correction but a larger fluorescence correction.

D. Purposes and Objectives of This Investigation

A major objective of this investigation will be, first, to demonstrate the feasibility of a quantitative analysis of bulk uranium alloy metal or powder by means of the electron microprobe. If successful, this method will be extended to micrometer-size areas on such metals or powders. To assess the degree of homogeneity at the micrometer level, binary and ternary alloys

of uranium will be studied. While chemical analysis is satisfactory for homogeneous samples, the electron microprobe should be superior for revealing inhomogeneity in uranium alloy powder systems.

CHAPTER II

MATERIALS AND EQUIPMENT

A. Preparation of Standard Metal Alloys

Preparing homogeneous uranium solid alloy standards on a micro-volume scale is a complex and expensive task. To extend this preparation to micrometer-size particles is an even more formidable undertaking. The 14 uranium alloy disks used in this study were prepared by the Metals and Ceramics Division of the Oak Ridge National Laboratory. These standards were used to calibrate the electron microprobe, establish the optimum operational parameters, collect data on accuracy and precision, and test the MAGIC computer program.

Each of the 14 metal standards was arc melted for a minimum of six times, then drop cast into a water-chilled copper crucible, and finally thermally stabilized in a vacuum of 10^{-5} torr for 7 hr at 900° C. A 0.25-in.-thick disk was machined from each casting. The chemical certification of each standard was provided by four independent analyses of chips taken from the disk machining procedure. Monochromatic X-ray absorption edge techniques were used for an analysis of the uranium-molybdenum¹²⁻¹³ and the uranium-niobium-zirconium alloys.¹⁴

The Whittaker Corporation, Los Angeles, California, utilized a proprietary process to form homogeneous micrometer-size uranium-molybdenum particles. After receipt, these particles (or powders) were analyzed by the X-ray absorption edge technique. The degree of microhomogeneity of all standards was established by analyzing several hundred separate areas over the specimen surfaces with the microprobe.

The National Bureau of Standards (NBS) has recently prepared and evaluated the first standard that was fabricated specifically for electron microprobe calibration. This standard, designated SRM-480, was purchased to evaluate the precision and accuracy of the electron microprobe used in this investigation. The SRM-480 is a metal disk composed of an outer ring of pure tungsten, an inner ring of pure molybdenum, and a core of tungsten-21.50 per cent molybdenum alloy. Based on the NBS results of approximately 1500 microprobe determinations for both tungsten and molybdenum, the alloy was found to possess a high degree of homogeneity at the micrometer level. The reported coefficient of variation¹⁵ was 2.5 per cent for molybdenum and 1.5 per cent for tungsten.

B. Metallurgical Specimen Preparation

The importance of careful specimen preparation for microprobe analysis has frequently been underestimated. Comprehensive evaluations of the

influence of specimen preparation on the precision and accuracy of microprobe analysis have been published by Picklesimer and Hallerman,¹⁶ and by Yakowitz.¹⁵ A complete procedure for specimen preparation, emphasizing small particles of ores and minerals, has been reported by Taylor.¹⁷ A significant problem encountered was the development of a mounting and polishing procedure for the micrometer-size uranium alloy particulates. Several mounting materials were tested, which included a graphite-filled phenolic plastic, a silver conducting paint with a phenolic pressure mount, a low-melting bismuth-lead metal alloy, and a silver-filled epoxy plastic. The selected mounting material was copper-filled diallyl phthalate resin (ADP), which bonded with the specimen particles and produced a flat, well-polished surface. A 0.25-in.-diameter copper ring was inserted into the center of a conventional 1-in.-diameter copper (ADP) metallurgical mount, and the specimen particles were placed within the ring. This copper ring added mechanical strength to the mount, localized the particle distribution, and resulted in a flatter, more uniform specimen surface.

To obtain the final specimen surface, these mounts were polished with a series of silicon carbide abrasive papers beginning with 400 grit and ending with 600 grit. They were then successively polished with 9- and 6-micrometer diamond paste and ethanol lubricant on a cotton cloth. The final polish was with 3-micrometer diamond paste on a rotating polishing wheel

using nylon cloth. The polished specimens were ultrasonically cleaned in absolute ethanol to remove the diamond paste, and the wet specimens were immediately immersed under pure ethanol. Microscopic examination of the polished surfaces revealed no formation of an oxidized layer after 4 hr. This time interval was more than enough to transfer a specimen to the microprobe laboratory and prepare the instrument for the analysis.

Although a diameter of 1.0 in. would have been preferred for the ORNL standard metal disks, they were machined to a final diameter of approximately 0.75 in. due to the size of the available furnace and casting molds. The standard disks were polished using silicon carbide grits, then given a final polish with 0.25-micrometer diamond paste using pure ethanol as a lubricant. All disks were ultrasonically cleaned and immersed under pure ethanol to prevent oxidation of the surface in the same manner previously described for the mounted metal alloy particles. Since these disks would not fit into the 1.0-in.-diameter specimen holder in the microprobe, a 0.5-in.-thick, 1.0-in.-diameter brass cylinder was drilled with a 0.75-in.-diameter hole. A set screw through the side of this holder permitted orientation of the specimen surface with the top of the holder. When the set screw was tightened, the disk was held firmly in the proper orientation for placement into the microprobe specimen chamber.

C. Instrumentation

A Materials Analysis Company (MAC) 400S electron probe X-ray microanalyzer was utilized for this study. Figure 1 presents a schematic diagram of this instrument, illustrating the location of the essential components.

The electron beam column, which is the essential feature of the microprobe, contains the electron gun assembly, electromagnetic focusing lenses, beam defining aperture, and electron beam deflection scanning plates. These scanning plates make possible the deflection of a focused electron beam across a square area on the specimen surface. Those electrons that are reflected back from the surface (referred to as backscattered electrons) are detected and used to modulate the brightness of a cathode ray tube. This modulated signal, synchronized with the sweep of the electron beam, shows an electron-produced image of the specimen surface. Interaction of the electron beam with the specimen is illustrated in Figure 2.

The electron microprobe was equipped with three separate X-ray spectrometers and readout channels so that simultaneous analysis of the same microvolume of the specimen for as many as three components was possible. An optical microscope permitted accurate placement of any desired specimen surface under the electron beam. A high-resolution oscilloscope cathode ray tube with camera attachment was used to record the location of the individual components of the alloys. The accumulated X-ray counts were printed

Figure 1. Schematic Diagram of the Electron Probe X-Ray Microanalyzer

Figure 2. Schematic Drawing of Electron Beam Interaction with Specimen Surface

by a teletype and simultaneously punched on paper tape for use in the MAGIC computer program. A block diagram (Figure 3) details the interconnection of the separate electronic components into a complete electron probe micro-analyzer.

The electron probe is basically an instrument for the X-ray spectrochemical analysis of areas as small as 1.0 micrometer in diameter on the surface of a solid specimen. The instrument normally consists of six separate components: (1) the electron beam column; (2) X-ray spectrometers with their dispersing crystals; (3) the high vacuum system, including a fore-pump, a diffusion pump, and valving controls; (4) X-ray measuring and readout equipment; (5) a visual light microscope for positioning the specimen; and (6) a high-voltage power supply with regulating circuitry.

A positive, specific identification of the elements under the electron beam is achieved by using emission line energies of characteristic X rays to modulate the brightness of the cathode ray tube display. In the scanning X-ray mode, the location of any specific element, from boron through uranium, may be obtained by observing the X-ray responses on the cathode ray tube. The X-ray images are photographed to obtain permanent records of the elemental distribution of any desired number of components. A typical example of this use of the electron probe is given later (Chapter III). From back-scattered electron photographs (Figure 4), density gradients within the specimen

Figure 3. Block Diagram of Microanalyzer Interconnecting Components

Figure 4. Backscattered Electron Image of a Typical Specimen Surface

can be observed as different shades of gray, and these density changes can be related to the average atomic number of the component being examined.

After the desired photographs have been taken, the electron probe is normally positioned in a static mode on any desired area of the specimen surface. In this mode, characteristic X-ray responses, generated by the static electron beam, are accumulated in order to obtain the desired statistical counting precision.

CHAPTER III

DATA COLLECTION AND EVALUATION

A. Experimental Procedure

1. Electron Beam Alignment

The optimum conditions for instrumental operation were established with polished pure metal specimens of each element of interest. These standards were inserted, one at a time, into the microprobe specimen holder and the specimen chamber sealed. The combination of a mechanical forepump and an oil diffusion pump produced a vacuum of 10^{-5} torr in the entire microprobe beam column and specimen chamber. The high-voltage selector switch of the electron gun was then set to the desired potential and the high voltage initiated. The current through the electron-gun filament was then slowly increased until the point of optimum electron brightness, or saturation, was reached. This saturation point is recognized as the start of a plateau during a visual observation of the electron-gun current meter. Instructions for aligning the instrument were followed to orient the filament over the center of the grid cup aperture and the grid cup assembly over the anode plate and beam apertures, and then to complete the final alignment of the entire electron-gun assembly with the electron beam column. The aligned electron beam was focused with the auxiliary and objective electromagnetic lenses to form a

beam spot approximately 0.5 micrometer in diameter. This aligned, focused electron beam was used as the specimen excitation source.

2. Wavelength Calibration

The polished sample of the metal or alloy was rotated into position beneath the electron beam. The odometer dials of the X-ray spectrometers were set for the theoretical angular positions of the desired X-ray lines. These lines were selected so as to be free from any anticipated spectral interferences. The actual wavelengths were determined by slowly scanning the separate odometer dials across the theoretical position of the desired emission lines and noting the dial values for the maximum deflection of the X-ray ratemeters. A moving strip chart recorded these ratemeter pulses so that exact wavelength settings could be established. The odometer scans were all started at a higher wavelength than theoretical and moved toward the low-wavelength side of each emission line. This procedure removed "backlash" uncertainty from the gear drive mechanism on each scan in exactly the same manner. All spectrometer scans were started at least $0.20 \text{ \AA}$ before the peak on the long-wavelength side, and continued for at least $0.20 \text{ \AA}$ beyond the peak. Thus, any interfering emission lines would be detected throughout this wavelength interval. A background wavelength, free of spectral interference and located approximately $0.10 \text{ \AA}$ to one side of the peak, was selected for each emission line.

3. Electronic Discrimination

After the correct wavelength setting had been established, the base-line discriminator of the pulse height analyzer was set at 2 V to eliminate extraneous background pulses from the electronic circuitry. The amplifier gain control was increased until a maximum signal from the X-ray line was obtained on the pulse height analyzer. The voltage of the base-line discriminator was then increased until the X-ray intensity was reduced to the level of the background. This voltage, which was a measure of the voltage window span required to accept the pulses from the emission line, was recorded. The base-line voltage (E) was reset to 2 V, and an electronic window span ($E \approx 1.5V$) was set so that only the desired signal was accepted by the pulse height analyzer. This procedure was followed for each element to be determined. Next, an electronic timer was set so that a statistically desired total number of X rays were accumulated in the electronic scaler for each element.

4. Specimen Counting Procedure

Accurate setting of the spectrometers was essential to achieve optimum precision and accuracy. The following operating procedure was therefore devised which did not require any adjustment of the spectrometers after the background counts of each of the pure metal standards (maximum of three) were accumulated and each of the spectrometers had been set for the corresponding emission line peak of interest.

Five separate sets of background counts were taken for the first pure-metal standard at $0.10 \text{ \AA}$ beyond the peak position. Then, one of the spectrometers was carefully set to the predetermined peak position and five sets of counts were accumulated. Next, the second pure-metal standard was placed under the microprobe beam and the background and peak count procedure repeated, using the second spectrometer. If necessary, the same procedure was followed, with a third standard, for the third spectrometer. As many as eight different elements (the maximum for the Colby MAGIC computer program), but only three simultaneously, can be analyzed in this way. Next, count data for the emission lines were then taken on the alloy specimen to be analyzed. Any desired total number of separate points (usually 50) were analyzed; then the pure-metal standards were separately placed under the electron beam and the peak counts taken again. After all the emission-line peak counting had been completed, the spectrometers were moved to the background wavelengths and the alloy specimen was placed under the beam to accumulate its own background counts.

This counting procedure permitted averaging of the reference counts for the pure-metal standard, taken before and after the analysis of the specimen. It also served to determine whether any change had occurred in counting rates due to electronic or mechanical drift in the equipment. The count data were printed by a teletypewriter and simultaneously punched

onto a paper tape for subsequent computation by the IBM 360 computer.

5. Accelerating Voltage Study

The uranium-7.5 weight per cent molybdenum standard, prepared at the ORNL, was placed in the instrument along with freshly polished specimens of pure uranium and pure molybdenum. This particular standard represented the nominal alloy composition desired and was also near the middle of the set of prepared standards. Thus, a study of the effect arising from changes in the accelerating voltage on the electron gun would be expected to reveal the optimum voltage for obtaining unbiased quantitative uranium and molybdenum values with the MAGIC computer program. As the electron beam energy exceeds the minimum value, V_o , to excite an element, the characteristic X-ray intensity increases as a power of the overvoltage, V . This intensity increase is usually expressed as $(V - V_o)^x$, where x is believed to have a value between 1.5 and 2.0. According to Compton and Allison,¹⁸ the best value is probably 1.65. Thus, an optimum accelerating voltage for the uranium-molybdenum standard was expected at approximately 12 kV for the uranium M_{α} ($V_o = 5.5$ kV) and at 6 kV for the molybdenum L_{α} ($V_o = 2.9$ kV) emission lines. Decreasing the accelerating voltage reduces the extent of the electron beam penetration into the specimen; thus, the absorption correction factor in the MAGIC program is minimized. However, a low accelerating voltage

means reduced X-ray intensities, and the electron beam becomes more difficult to focus and control.

Curves showing the effect of accelerating voltages from 8 to 30 kV on the weight per cent of uranium and molybdenum, as computed by the MAGIC program, are given in Figures 5 and 6. Curves showing the effect of accelerating voltage on the K ratio (first approximation) are seen in Figures 7 and 8. The K ratio is the calculated percentage of uranium and molybdenum which was computer-corrected only for background X-ray counts and detector resolution time. Thus, differences in the curves are due to the increased accuracy resulting from correction for the absorption, fluorescence, and atomic number effects by the MAGIC program. A definite voltage dependency was observed in the K-ratio curves, whereas the MAGIC weight percentages frequently cluster about a median value for each element, regardless of the accelerating voltage.

A similar study of accelerating voltage versus weight per cent and K ratio was performed on NBS standard SRM 480. The responses of the tungsten M_{α} emission line ($V_o = 2.8$ kV) and the molybdenum L_{α} emission line ($V_o = 2.9$ kV) were expected to be similar to those from uranium and molybdenum in the ORNL standard. Again, the molybdenum K-ratio curve (Figure 9) had a definite voltage dependency, whereas the MAGIC correction (Figure 10) removed virtually all of the voltage dependency. The tungsten

Figure 5. Dependence of Uranium Response on the Electron Beam Accelerating Voltage for a Uranium-Molybdenum Standard Corrected by the MAGIC Program

Figure 6. Dependence of Molybdenum Response on the Electron Beam Accelerating Voltage for a Uranium-Molybdenum Standard Corrected by the MAGIC Program

Figure 7. Dependence of Uranium K Ratio on the Electron Beam Accelerating Voltage for a Uranium-Molybdenum Standard

Figure 8. Dependence of Molybdenum K Ratio on the Electron Beam Accelerating Voltage for a Uranium-Molybdenum Standard

Figure 9. Dependence of Molybdenum K Ratio on the Electron Beam Accelerating Voltage for NBS Standard

Figure 10. Dependence of Molybdenum Response on the Electron Beam Accelerating Voltage for NBS Standard Corrected by the MAGIC Program

K ratio (Figure 11) and MAGIC response curves (Figure 12) were almost independent of the accelerating voltage. The K ratio calculated percentages were less than the accepted values by 3.60 per cent for tungsten and 1.80 per cent for molybdenum, while the uncorrected MAGIC values were positively biased by 1.0 per cent for tungsten and were unbiased for molybdenum.

Microprobe examination of a ternary alloy of uranium-niobium-zirconium was requested by metallurgists.¹⁹ Consequently, a set of ternary alloys was prepared by the ORNL Metals and Ceramics Division. The standard, with a nominal concentration of 7.5 weight per cent niobium, 2.5 weight per cent zirconium, and 90 weight per cent uranium, was examined to determine the effects of changes in accelerating voltage on the computed weight percentages of the three components. The value of V_o for the niobium L_{α} emission line (2.7 kV) and for the zirconium L_{α} emission line (2.5 kV) suggested a close relationship to the tungsten and molybdenum curves obtained from the NBS standard (SRM 480) and the ORNL uranium-molybdenum standards. Examination of the uranium, niobium, and zirconium MAGIC curves (Figures 13, 14, and 15) revealed a voltage dependency for both uranium and niobium, while zirconium was almost independent of the accelerating voltage. The K-ratio voltage curves indicated a strong relationship between the response and accelerating voltage for the niobium (Figure 16) and for zirconium (Figure 17), but only a slight relationship for uranium (Figure 18).

Figure 11. Dependence of Tungsten K Ratio on the Electron Beam Accelerating Voltage for NBS Standard

Figure 12. Dependence of Tungsten Response on the Electron Beam Accelerating Voltage for NBS Standard Corrected by the MAGIC Program

Figure 13. Dependence of Uranium Response on the Electron Beam Accelerating Voltage for a Uranium-Niobium-Zirconium Standard Corrected by the MAGIC Program

Figure 14. Dependence of Niobium Response on the Electron Beam Accelerating Voltage for a Uranium-Niobium-Zirconium Standard Corrected by the MAGIC Program

Figure 15. Dependence of Zirconium Response on the Electron Beam Accelerating Voltage for a Uranium-Niobium-Zirconium Standard Corrected by the MAGIC Program

Figure 16. Dependence of Niobium K Ratio on the Electron Beam Accelerating Voltage for a Uranium-Niobium-Zirconium Standard

Figure 17. Dependence of Zirconium K Ratio on the Electron Beam Accelerating Voltage for a Uranium-Niobium-Zirconium Standard

Figure 18. Dependence of Uranium K Ratio on the Electron Beam Accelerating Voltage for a Uranium-Niobium-Zirconium Standard

Examination of the X-ray mass absorption coefficients compiled by Birks²⁰ indicated that uranium absorbed a large fraction of the niobium L_{α} and zirconium L_{α} radiation.

These studies of accelerating voltage indicated that 10 kV was an acceptable potential. They showed that the MAGIC correction yielded values near the theoretical, the electron beam stability could be maintained, and X-ray intensities from the specimens were sufficient to permit the accumulation of a statistically desirable number of counts within a counting time of 60 sec. or less.

6. Effects of Polymerized Surface Film

Oil vapors from the roughing vacuum pump and the oil diffusion pump are always present in high-vacuum systems. The electron beam polymerizes these vapors and deposits a visible film on specimen surfaces at the point of interaction with the beam. Therefore, it was necessary to determine the rate at which the film was deposited and the extent to which it reduced the counting rate at each of the analytical wavelengths.

The uranium-7.5 weight per cent molybdenum standard was freshly polished and placed in the microprobe. The electronic timer was preset to accumulate X-ray counts for 15 sec. and then print the results. After the automated motor drive advanced the specimen for a distance of 5 micrometers to a fresh specimen surface, the counting sequence was repeated. Forty

or more separate points were analyzed in this manner. The specimen drive motor was then disconnected, and separate sets of counts were taken at a single point on the specimen. Through the optical microscope a tan-colored spot could be observed after the fourth set of counts. The spot progressively darkened, apparently as the thickness of the polymerized film increased, until it appeared virtually black. The resulting curves for total accumulated uranium and molybdenum counts at each point, versus the corresponding point number, are shown in Figures 19 and 20. For a counting interval of 2.5 min., there is no significant decrease in X-ray intensity due to the contamination.

NBS standard SRM 480 was examined in the same manner as was the uranium-molybdenum standard. Data from a point-by-point count and a static count were again plotted versus the elapsed time intervals. Curves for the tungsten M_{α} and molybdenum L_{α} emission lines are illustrated in Figures 21 and 22, respectively. These curves showed that reliable counting data were accumulated for at least 5.0 min. before any significant decrease in the X-ray intensities occurred. During this time, 130,000 tungsten and 81,000 molybdenum counts were accumulated.

The uranium-niobium-zirconium standard was also similarly analyzed. Curves for the three components are seen in Figures 23, 24, and 25. No significant decrease in the X-ray intensity occurred for a total counting

Figure 19. Total Accumulated Uranium X-Ray Responses Versus Elapsed Counting Time in a Uranium-Molybdenum Standard

Figure 20. Total Accumulated Molybdenum X-Ray Responses Versus Elapsed Counting Time in a Uranium-Molybdenum Standard

Figure 21. Total Accumulated Tungsten X-Ray Responses Versus Elapsed Counting Time from an NBS Tungsten-Molybdenum Standard

Figure 22. Total Accumulated Molybdenum X-Ray Responses Versus Elapsed Counting Time from an NBS Tungsten-Molybdenum Standard

Figure 23. Total Accumulated Uranium X-Ray Responses Versus Elapsed Counting Time from a Uranium-Niobium-Zirconium Standard

Figure 24. Total Accumulated Niobium X-Ray Responses Versus Elapsed Counting Time from a Uranium-Niobium-Zirconium Standard

Figure 25. Total Accumulated Zirconium X-Ray Responses Versus Elapsed Counting Time from a Uranium-Niobium-Zirconium Standard

interval of 5.0 min. During this interval, 190,000 uranium, 24,000 niobium, and 10,000 zirconium counts were accumulated.

B. Analysis of the Metal Alloys Used for Calibration

1. NBS Standard Microprobe Sample

Analysis of a reference material with an accurately known composition and the highest possible microhomogeneity was necessary to establish the capability of the microprobe for quantitatively analyzing solid uranium alloys.

The SRM 480 standard was of particular interest in this study because of its microhomogeneity and because it possessed an accurately known composition. Furthermore, the molybdenum L_{α} emission line would be used in the analysis of the uranium-molybdenum alloy. Also, the tungsten M_{α} emission line was similar to the uranium M_{α} line so that the tungsten and uranium X-ray responses should be comparable. Similarly, the characteristics of the molybdenum L_{α} emission line should be comparable to those of the niobium and zirconium L_{α} emission lines.

Selected areas of the NBS sample were analyzed to: (1) determine the reproducibility of the MAC 400S microprobe under the established instrumental parameters, (2) determine any existing biases in the tungsten and molybdenum computer-corrected values, and (3) measure the degree

of homogeneity of the ORNL-prepared alloys as the difference in precision between the SRM 480 and the ORNL alloys. The data obtained in this study were statistically evaluated and are listed in Table I. The coefficients of variation reported by the National Bureau of Standards¹⁵ are 1.5 per cent for tungsten and 2.5 per cent for molybdenum; the coefficients of variation of the MAGIC corrected measurements are 1.4 per cent for tungsten and 1.3 per cent for molybdenum.

2. Uranium-Molybdenum Alloy

The uranium-molybdenum alloy disks prepared at the ORNL were successively polished and placed in the microprobe. On each specimen, approximately 25 separate sets of points were analyzed for each component. The only variation from the prior instrumental parameters was the increase in counting time to 40 or 60 sec. as the molybdenum concentration in the standards decreased. The standard set consisted of seven alloys of uranium with these nominal molybdenum contents (in weight per cent): 2.0, 4.0, 6.0, 7.5, 8.0, 10.0, and 13.0. The accepted chemical values, the MAGIC corrected microprobe values, and the limits of error (L.E.) at the 95 per cent confidence level (2σ) are reported in Tables II and III. Precision of the microprobe analysis was examined by repetitive measurements of the ORNL uranium-molybdenum alloy disk (Table IV).

TABLE I
COMPARISON OF MAGIC-CORRECTED MICROPROBE AND NBS
CHEMICAL RESULTS ON SRM-480 TUNGSTEN-
MOLYBDENUM STANDARD

Component	NBS Chemical Value (weight per cent)	MAGIC-Corrected Microprobe Value ^a (weight per cent)	Microprobe Value Minus NBS Value	Limit of Error of a Single Measurement (per cent)	Coefficient of Variation of a Single Measurement
W	78.50	78.95 ± 0.39^b	-0.45	± 2.3	± 1.4
		78.19 ± 0.68^b	+0.31		
		78.36 ± 0.48^b	+0.14		
		Average 78.50			
Mo	21.50	21.36 ± 0.14^c	+0.14	± 0.57	± 1.3
		21.80 ± 0.15^c	-0.30		
		21.34 ± 0.11^c	+0.16		
		Average 21.50			

^aEach value is the mean of 20 analyses plus or minus the L.E. of the mean.

^bThe MAGIC-corrected microprobe value for the weight per cent tungsten is calculated as follows: (1.2967 times the MAGIC-computed per cent tungsten) minus 29.67.

^cThe MAGIC-corrected microprobe value for the weight per cent molybdenum is calculated as follows: 0.9911 times the MAGIC-computed per cent molybdenum.

TABLE II

URANIUM CONTENT OF URANIUM-MOLYBDENUM ALLOY: COMPARISON
OF CHEMICAL AND MAGIC-CORRECTED MICROPROBE RESULTS

Sample Number	Means of Four Chemical Analyses (weight per cent)	MAGIC-Corrected Means of Twelve Microprobe Analyses ^a (weight per cent)	MAGIC-Corrected Microprobe Value Minus Chemical Value
702083	98.08	98.27 ± 0.61	+0.19
702084	95.98	95.21 ± 1.05	-0.77
702087	94.09	94.24 ± 0.87	+0.15
702069	92.49	92.58 ± 0.73	+0.09
702085	92.16	92.32 ± 0.86	+0.16
702088	90.09	90.22 ± 0.67	+0.13
702086	87.04	86.20 ± 1.31	-0.84

^aThe MAGIC-corrected microprobe value for the weight per cent uranium is calculated as follows: (1.1944 times the MAGIC-computed per cent uranium) minus 19.44.

TABLE III

MOLYBDENUM CONTENT OF URANIUM-MOLYBDENUM ALLOY: COM-
PARISON OF CHEMICAL AND MAGIC-CORRECTED
MICROPROBE RESULTS

Sample Number	Means of Four Chemical Analyses (weight per cent)	MAGIC-Corrected Means of Twelve Microprobe Analyses ^a (weight per cent)	MAGIC-Corrected Microprobe Value Minus Chemical Value
702083	2.02	1.83 ± 0.10	-0.19
702084	4.10	3.85 ± 0.05	-0.25
702087	5.98	5.73 ± 0.06	-0.25
702069	7.46	7.45 ± 0.09	-0.01
702085	8.00	8.37 ± 0.09	+0.37
702088	10.06	9.80 ± 0.10	-0.26
702086	13.04	13.30 ± 0.10	+0.26

^aThe MAGIC-corrected microprobe value for the weight per cent molybdenum is calculated as follows: 1.0857 times the MAGIC-computed per cent molybdenum.

TABLE IV

PRECISION OF MICROPROBE ANALYSES BASED ON ANALYSIS OF ORNL
URANIUM-7.5 WEIGHT PER CENT MOLYBDENUM ALLOY

Individual Analyses for Uranium ^a (weight per cent)		Individual Analyses for Molybdenum ^b (weight per cent)	
Run A	Run B	Run A	Run B
95.05	- ^c	7.07	6.74
95.77	96.33	7.25	6.82
94.13	94.74	7.50	6.80
93.62	93.34	6.85	6.92
94.84	92.05	7.21	6.76
93.67	92.87	7.03	6.91
93.25	93.97	7.14	6.81
95.07	93.61	7.17	6.65
92.44	93.76	7.17	7.15
95.14	93.40	7.17	7.10
94.01	93.66	7.17	6.93
95.65	93.95	7.19	6.76

^aThe L.E. of a single result is as follows: weight per cent, ± 2.2 ; relative per cent, ± 2.3 .

^bThe L.E. of a single result is as follows: weight per cent, ± 0.44 ; relative per cent, ± 6.3 .

^cDeviant result omitted.

3. Uranium-Niobium-Zirconium Alloy

The set of seven uranium-niobium-zirconium alloy disks prepared at the ORNL was also analyzed. These standards had the following niobium-zirconium compositions (in weight per cent): 5.0-2.5, 7.5-1.0, 7.5-2.0, 7.5-2.5, 7.5-3.0, 7.5-3.5, and 9.0-2.5. The accepted chemical values, the computer-corrected microprobe values, and the statistically evaluated limits of error are given in Tables V, VI, and VII.

Precision of the MAGIC-corrected microprobe analysis was established with multiple measurements taken on a disk of the ORNL uranium-niobium-zirconium, ORNL uranium-tungsten, and NBS tungsten-molybdenum alloys. This information is compiled in Table VIII.

C. Determination of Powder Homogeneity

Homogeneity of the powdered specimens of uranium-molybdenum and uranium-niobium-zirconium alloys was rapidly estimated by point counting several different areas on the surface of a few selected particles of various sizes. Another technique has been to photograph the characteristic X rays emitted from the powder particles. Examples of nonhomogeneous spheres of uranium-molybdenum can be seen in Figures 26 and 27. Corrosion resistance of such nonuniform material is extremely low. Spheres of the same alloy, showing homogeneous distribution of uranium and molybdenum, are

TABLE V

URANIUM CONTENT OF URANIUM-NIOBIUM-ZIRCONIUM ALLOY:
COMPARISON OF CHEMICAL AND MAGIC-CORRECTED
MICROPROBE RESULTS

Sample Number	Means of Four Chemical Analyses (weight per cent)	Microprobe Run Number	MAGIC-Corrected Means of Twelve Microprobe Analyses ^a (weight per cent)	MAGIC-Corrected Microprobe Value Minus Chemical Value
702138	88.03 ± 0.28	1	88.67 ± 0.75	+0.64
		2	86.32 ± 1.20	-1.71
702142	88.44 ± 0.28	1	86.79 ± 0.54	-1.65
		2	89.80 ± 0.52	+1.36
		3	88.13 ± 1.10	-0.31
		4	89.13 ± 0.58	+0.69
702141	89.38 ± 0.28	1	89.63 ± 0.90	+0.25
702137	90.02 ± 0.28	1	90.73 ± 0.16	+0.71
		2	89.81 ± 0.62	-0.21
		3	88.32 ± 0.41	-1.70
		4	88.84 ± 1.10	-1.18
		5	90.94 ± 0.99	+0.92
702140	90.22 ± 0.28	1	90.03 ± 1.10	-0.19
		2	90.75 ± 0.80	+0.53
702139	91.39 ± 0.28	1	92.65 ± 0.26	+1.26
		2	91.98 ± 0.89	+0.59
		3	91.96 ± 0.63	+0.57
702136	92.42 ± 0.28	1	91.58 ± 0.31	-0.84
		2	92.91 ± 0.62	+0.49
		3	92.96 ± 0.83	+0.54
		4	91.65 ± 1.20	+0.77

^aThe MAGIC-corrected microprobe value for the weight per cent uranium is calculated as follows: (1.1283 times the MAGIC-computed per cent uranium) minus 12.83.

TABLE VI
 NIOBIUM CONTENT OF URANIUM-NIOBIUM-ZIRCONIUM ALLOY:
 COMPARISON OF CHEMICAL AND MAGIC-CORRECTED
 MICROPROBE RESULTS

Sample Number	Means of Four Chemical Analyses (weight per cent)	Microprobe Run Number	MAGIC-Corrected Means of Twelve Microprobe Analyses ^a (weight per cent)	MAGIC-Corrected Microprobe Value Minus Chemical Value
702138	9.07 ± 0.11	1	9.05 ± 0.37	-0.02
		2	9.45 ± 0.53	+0.38
702142	7.90 ± 0.73	1	8.64 ± 0.21	+0.74
		2	7.63 ± 0.51	-0.27
		3	8.73 ± 0.72	+0.83
		4	8.21 ± 0.30	+0.31
702141	7.53 ± 0.11	1	7.31 ± 0.43	-0.22
702137	7.56 ± 0.11	1	7.99 ± 0.09	+0.43
		2	7.26 ± 0.26	-0.30
		3	7.62 ± 0.20	+0.06
		4	7.64 ± 0.19	+0.08
		5	7.38 ± 0.12	+0.18
702140	7.52 ± 0.11	1	6.72 ± 0.37	-0.80
		2	7.07 ± 0.30	-0.45
702139	7.49 ± 0.11	1	7.35 ± 0.09	-0.14
		2	6.67 ± 0.23	-0.82
		3	7.30 ± 0.45	-0.19
702136	4.95 ± 0.11	1	5.17 ± 0.09	+0.22
		2	5.04 ± 0.18	+0.09
		3	5.18 ± 0.25	+0.23
		4	4.96 ± 0.17	+0.01

^aThe MAGIC-corrected microprobe value for the weight per cent niobium is calculated as follows: 0.9815 times the MAGIC-computed per cent niobium.

TABLE VII
ZIRCONIUM CONTENT OF URANIUM-NIOBIUM-ZIRCONIUM ALLOY:
COMPARISON OF CHEMICAL AND MAGIC-CORRECTED
MICROPROBE RESULTS

Sample Number	Means of Four Chemical Analyses (weight per cent)	Microprobe Run Number	MAGIC-Corrected Means of Twelve Microprobe Analyses ^a (weight per cent)	MAGIC-Corrected Microprobe Value Minus Chemical Value
702138	2.52 ± 0.024	1	2.52 ± 0.05	0.00
		2	2.76 ± 0.14	+0.24
702142	3.51 ± 0.020	1	3.34 ± 0.06	-0.17
		2	3.38 ± 0.18	-0.13
		3	3.66 ± 0.26	+0.15
		4	3.50 ± 0.09	-0.01
702141	3.00 ± 0.024	1	2.95 ± 0.14	-0.05
702137	2.50 ± 0.024	1	2.11 ± 0.04	-0.39
		2	2.38 ± 0.11	-0.12
		3	2.61 ± 0.08	+0.11
		4	2.61 ± 0.13	+0.11
		5	2.46 ± 0.08	-0.04
702140	1.98 ± 0.024	1	2.00 ± 0.09	+0.02
		2	2.04 ± 0.08	+0.06
702139	0.97 ± 0.024	1	0.89 ± 0.02	-0.08
		2	1.08 ± 0.04	+0.11
		3	1.23 ± 0.06	+0.26
702136	2.52 ± 0.024	1	2.23 ± 0.06	-0.29
		2	2.46 ± 0.12	-0.06
		3	2.70 ± 0.10	+0.18
		4	2.63 ± 0.12	+0.11

^aThe MAGIC-corrected microprobe value for the weight per cent zirconium is calculated as follows: 0.9526 times the MAGIC-computed per cent zirconium.

TABLE VIII
PRECISION OF MAGIC-CORRECTED MICROPROBE ANALYSIS OF
ORNL AND NBS METAL DISK STANDARDS

Composition of Standard	Element Analyzed	Number of Results	Limit of Error for a Single Measurement	
			Weight Per Cent	Relative Per Cent
U-Nb-Zr	U	289	± 2.4	± 2.7
	Nb	278	± 0.94	± 13
	Zr	278	± 0.33	± 14
U-Mo	U	24	± 2.2	± 2.3
	Mo	24	± 0.44	± 6.3
W-Mo	W	60	± 2.30	± 2.9
	Mo	60	± 0.57	± 2.7

Figure 26. Characteristic Uranium X-Ray
Photograph of a Segregated Specimen

Figure 27. Characteristic Molybdenum X-Ray Photograph of a Segregated Specimen

seen in Figures 28 and 29. These photographs illustrate the need for an in situ analysis of small-diameter particles by the microprobe technique. Tables IX and X illustrate the poor agreement obtained on inhomogeneous uranium-molybdenum powder when comparing the chemical and microprobe methods. Individual uranium-molybdenum particles were analyzed; typical results obtained from three different screened fractions are tabulated in Table XI.

Table XII gives a comparison of chemical and microprobe results on uranium-niobium-zirconium alloy powders. It shows that the two techniques agree only if the inhomogeneous particles, labeled as statistically deviant outliers, are omitted from the comparison. The individual deviant results are shown in the table to indicate the degree of inhomogeneity of this particular set of screened particle sizes.

Conventional microchemical analysis, following careful screening of the powder into fractions, would reveal only the average concentrations of the uranium and molybdenum, but not their actual distribution.

Figure 28. Characteristic Uranium X-Ray
Photograph of a Homogeneous Specimen

Figure 29. Characteristic Molybdenum X-Ray Photograph of a Homogeneous Specimen

TABLE IX

URANIUM CONTENT OF INHOMOGENEOUS URANIUM-MOLYBDENUM
POWDER: COMPARISON OF CHEMICAL AND MAGIC-CORRECTED
MICROPROBE RESULTS

Sample Number	Particle Size (micrometers)	Number of Particles Analyzed by Microprobe	Means of Four Chemical Analyses (weight per cent)	MAGIC-Corrected Mean of Microprobe Analyses (weight per cent)	Corrected Microprobe Value Minus Chemical Value
702493	Unscreened	50	93.56	83.03	-10.53
702485	+30	50	91.58	87.04	- 4.54
702486	+20	50	92.65	89.73	- 2.92
702487	+10	50	93.46	94.08	+ 0.62
702488	-10	50	^a	87.02	-
702494	Unscreened	50	89.48	77.53	-11.95
702489	+74	50	89.78	87.54	- 2.24
702490	+53	50	90.68	79.68	-11.00
702491	+44	50	90.60	87.90	- 2.70
702492	-44	50	88.93	90.48	+ 1.55

^aInsufficient material for analysis.

TABLE X

MOLYBDENUM CONTENT OF INHOMOGENEOUS URANIUM-MOLYBDENUM
POWDER: COMPARISON OF CHEMICAL AND MAGIC-CORRECTED
MICROPROBE RESULTS

Sample Number	Particle Size (micrometers)	Number of Particles Analyzed by Microprobe	Means of Four Chemical Analyses (weight per cent)	MAGIC-Corrected Mean of Microprobe Analyses (weight per cent)	Corrected Microprobe Value Minus Chemical Value
702493	Unscreened	50	7.43	17.27	9.84
702485	+30	50	7.58	12.93	5.35
702486	+20	50	6.67	8.83	2.16
702487	+10	50	5.37	6.24	0.87
702488	<10	50	a	8.62	-
702494	Unscreened	50	9.68	19.65	9.97
702489	+74	50	9.43	11.64	2.21
702490	+53	50	9.04	16.26	7.22
702491	+44	50	9.15	19.80	10.65
702492	<44	50	10.43	15.78	5.35

^aInsufficient material for analysis.

TABLE XI

TYPICAL INDIVIDUAL RESULTS FROM ANALYSIS OF
THREE SCREENED FRACTIONS OF INHOMOGENEOUS
URANIUM-MOLYBDENUM POWDER

Sample Number								
702488 ^a			702494 ^b			702486 ^c		
Specimen Number	U	Mo	Specimen Number	U	Mo	Specimen Number	U	Mo
1	90.98	7.01	25	92.20	7.48	49	92.79	5.69
2	92.26	6.00	26	96.95	3.17	50	87.05	10.31
3	88.19	9.42	27	87.67	11.98	51	86.73	13.74
4	87.76	9.75	28	4.06	91.67	52	98.84	2.71
5	92.59	4.35	29	94.25	5.15	53	92.33	10.70
6	89.82	9.23	30	90.68	4.53	54	92.59	7.88
7	92.96	4.78	31	91.12	8.76	55	78.72	25.74
8	91.31	6.44	32	5.37	95.23	56	88.47	13.59
9	85.90	11.73	33	92.35	7.22	57	98.20	2.34
10	78.96	18.20	34	90.24	10.58	58	96.45	6.50
11	95.33	3.33	35	88.36	11.08	59	97.14	3.60
12	90.15	7.47	36	89.91	11.64	60	89.83	10.86
13	88.20	11.80	37	93.49	6.53	61	95.67	5.64
14	5.49	91.68	38	85.58	17.03	62	86.34	16.39
15	90.74	8.36	39	92.41	6.82	63	93.10	6.05
16	87.90	13.12	40	38.17	65.93	64	90.15	10.56
17	96.32	1.69	41	90.50	9.28	65	96.79	4.19
18	83.77	15.61	42	3.68	93.83	66	98.41	1.77
19	93.81	5.50	43	91.99	8.31	67	92.76	5.94
20	89.94	10.01	44	92.22	7.15	68	40.72	62.03
21	83.35	18.27	45	91.24	7.10	69	80.83	19.34
22	92.45	7.86	46	5.13	95.94	70	91.60	5.68
23	93.73	4.41	47	91.27	6.61	71	85.25	14.87
24	92.26	6.00	48	82.29	17.61	72	90.13	5.16

^aParticle size = < 10 micrometers.

^bParticle size = 5 - 100 micrometers.

^cParticle size = 44 micrometers.

TABLE XII

COMPARISON OF CHEMICAL AND MAGIC-CORRECTED MICROPROBE RESULTS ON
URANIUM-NIOBIUM-ZIRCONIUM ALLOY POWDER

Sample Number	Particle Size (micrometers)	Per Cent Uranium				Per Cent Niobium				Per Cent Zirconium			
		Chemical	Microprobe	Outliers ($> 3\sigma$)		Chemical	Microprobe	Outliers ($> 3\sigma$)		Chemical	Microprobe	Outliers ($> 3\sigma$)	
631908	Unscreened	89.78	89.09	67.63	- -	7.40	7.07	5.05	- -	2.60	2.52	1.92	- -
631908	+10	90.20	88.27	84.01, 76.08, 79.98		7.39	7.02	8.29, 6.20, 7.11		2.55	2.55	2.79, 1.83, 2.72	
631908	+20	90.08	88.15	-	- -	7.36	7.31	-	- -	2.50	2.77	-	- -
631908	+30	89.79	90.41	75.71, 84.16, 80.82		7.35	7.09	5.40, 6.61, 6.71		2.51	2.78	2.51, 2.58, 2.87	
631910	Unscreened	89.80	87.08	71.42	- -	7.35	7.41	6.18	- -	2.55	2.57	2.23	- -
631910	+10	89.79	87.51	94.03, 82.26, 80.02		7.31	7.23	6.83, 6.53, 6.65		2.47	2.54	2.73, 1.80, 2.31	
631910	+30	90.05	89.76	-	- -	7.38	7.39	-	- -	2.54	2.72	-	- -

CHAPTER IV

SUMMARY

From this investigation, the following conclusions concerning quantitative electron probe microanalysis of uranium-molybdenum and uranium-niobium-zirconium alloys may be drawn:

1. In general, the two powder specimens of uranium alloys examined were found to be inhomogeneous. Inhomogeneity of such alloys has been suspected but virtually impossible to substantiate by conventional analytical techniques.

2. Simple quantitative calculations, based on direct ratios of the specimen and pure metal X-ray emission intensities, are dependent on the accelerating voltage used. The Colby MAGIC computer program compensates for this and other variables. However, since the MAGIC program was designed to be applicable to the analysis of widely varied materials, biased values were obtained for the uranium alloys investigated in this study. Therefore, a single correction factor, which is valid throughout a wide concentration range, was experimentally determined for each of the elements in these alloys.

3. Polished specimens, handled under pure ethanol prior to analysis, did not require extensive inert-gas glove-box facilities to prevent oxidation of the specimen surface.

4. The formation of a polymerized surface film at the point of interaction of a sample with the electron beam did not significantly reduce the X-ray intensities in these analyses.

5. The electron probe microanalyzer, using a suitable correction program, is capable of quantitatively analyzing individual uranium-molybdenum or uranium-niobium-zirconium alloy particles of less than 10 micrometers in diameter. The precision and accuracy are comparable with conventional chemical techniques.

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