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Chemistry

**PURIFICATION OF URANIUM BY
ZONE-REFINING TECHNIQUES (U)**

J. L. Bieber
J. M. Schreyer
E. L. Williams

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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Oak Ridge, Tennessee

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ABSTRACT

A zone-refining technique has been established for purifying uranium in gram quantities to less than 30 ppm total impurities.

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SUMMARY

An investigation was made to establish the variables and parameters necessary to purify uranium by zone-refining techniques. After establishing the best cleaning procedure, molten-zone width, direction and rate of travel of the molten zone, length of the zone-refined area, and degree of vacuum, purified uranium was prepared with total impurities less than 30 ppm, as established by spark-source mass spectrometry.

INTRODUCTION

It is well known that the properties of elemental metals are markedly affected by the presence of even small amounts of impurities. Tungsten is an illustration. In its conventional state, with impurities amounting to as much as 200 ppm, tungsten is quite brittle at normal temperatures; on the other hand, it can be made ductile at room temperature by reducing the total impurities to less than 10 ppm. Beryllium shows a similar dependence of ductility on its impurity level. No extensive study on the properties of ultrapure uranium has been made up to this time because of the unavailability of sufficient quantities of the metal. Zone refining has been developed as a method of producing useful quantities of uranium for the study of its physical properties.

Previous attempts by researchers to produce ultrapure metals by zone refining were hampered when the impurity level reached the lower limits of detection of the emission spectrographic procedures. The spark-source mass spectrometer, which has been introduced recently as an analytical instrument, provides a versatile method for impurity analysis in materials. Detection limits for a single element are in the range of one part per billion, and the method provides good reproducibility and accuracy. The availability of this technique has made greater advances possible in the purification of metals by zone-refining techniques.

Some purification of uranium metal by zone refining has been accomplished by workers in the field.^(1 - 3) The evidence of purification was based largely on increasing resistivity ratios, which indicate a relative decrease in impurities.

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ZONE REFINING

PROCEDURE

Uranium rods, 1/8 inch in diameter, were zone refined in a commercial electron-beam floating-zone apparatus, (a) shown in Figure 1. In this instrument, a sample up to 18 inches in length is suspended vertically between two supports in a vacuum chamber, as illustrated in Figure 2. An incandescent thoriated tungsten filament, formed in a single loop around the specimen, emits electrons which are accelerated toward the specimen by the potential drop between the filament and the specimen.

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Figure 1. ELECTRON BEAM ZONE REFINER.

(a) MRC Manufacturing Corporation, Model EBZ-93A.

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Figure 2. MOUNTED URANIUM ROD IN VACUUM CHAMBER.

This beam of accelerated electrons is focused by the geometry of the filament enclosure and bombards the specimen rod in a narrow band around its circumference. The kinetic energy of the electrons is translated into thermal energy upon striking the

specimen, and this energy can be controlled to produce a molten zone supported entirely by surface tension. Travel of the filament and the resulting molten band up or down the length of the specimen is referred to in this report as a pass.

The first step in treating the uranium rods was degreasing in acetone. Alternating treatments of anodic cleaning in concentrated orthophosphoric acid for 20 seconds and rinsing in distilled water were continued until the surface was bright and lustrous. The sample, touched only by forceps or clean gloves, was loaded immediately into the instrument and the pump down to vacuum was begun. Typical rods are shown in Figure 3.

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Figure 3. URANIUM RODS.

Spark-source mass spectrometric analysis was made on each uranium rod for all elements with Z numbers less than 95 with the exception of the noble gas elements and lithium, beryllium, fluorine, chlorine, polonium, astatine, francium, actinium, tellurium, and promethium. All summations of total impurities were obtained by adding in the maximum possible values for elements reported as "less than". This approach would certainly indicate that the total impurities are less than the values described.

A commercial spark-source mass spectrograph^(b) was used for the analysis of the purified uranium rods.

(b) Manufactured by Associated Electrical Industries.

DISCUSSION

Due to the affinity between oxygen and uranium, an oxide layer quickly formed on the surface of the heated specimen even though the normal operating pressure was 10^{-6} torr or lower. If the previously described sample cleaning procedure was not carried out between successive passes, the oxide layer became so deep that the boundaries of the molten zone were entirely obscured, making control of the molten zone extremely difficult.

It was observed that a heavy uranium oxide film also prevented the liberation of ionized gases and therefore inhibited the removal of impurities. To verify this, a comparison was made between two rods which were subjected to the same conditions of treatment with one exception—one rod (Rod A) was cleaned only before the first pass and was not removed from the vacuum chamber between passes while Rod B was cleaned by the acetone-orthophosphoric acid procedure prior to each of the four passes. The results are summarized in Table 1. These data clearly show the inhibiting effect of a uranium oxide film on the removal of impurities from uranium.

Table 1
EFFECT OF THE REMOVAL OF THE OXIDE LAYER BEFORE EACH PASS

	Total Impurities (ppm)	Nitrogen (ppm)	Oxygen (ppm)
Original Material	837 - 888	35	262 - 403
Rod A (oxide allowed to build up)	439	35	200
Rod B (oxide removed after each pass)	316	2	80

One successful mechanism of the purifying process is to vaporize, under vacuum, the impurities in the heated sample. Under these conditions (vaporization and under vacuum), the undesirable elements will be more effectively removed from the parent metal. To confirm the advantage of this mechanism, one uranium rod was subjected to six passes with the electron beam held just below the energy level necessary to form a molten zone. Analysis of the rod at three different points along the treated five-inch length indicated that a 50 percent reduction in total impurities was effected. Further experiments indicated that after three such nonmolten passes, no further purification could be obtained by this method. Other experiments confirmed that nonmolten passes could not upgrade a sample which had been subjected to molten passes.

It was decided to make the passes from bottom to top in order to utilize another mechanism of purification, namely that the impurities can be separated from the parent metal if their densities are appreciably different. Because uranium is heavier than most of its impurities, they will float to the top of the molten pool. Also, most of the impurities lower the melting point of the pure metal. These two mechanisms worked together and caused most of the impurities to be deposited in a concentration gradient that increased toward the upper end of the specimen. Other impurities, notably carbon, that raise the melting point of the parent metal, concentrated at the end from which the passes initiated. Because some impurities concentrated at the top and others at the bottom, the center portion of the uranium rod, which was zone refined by this method, was purer than either end. The data of Table 2 confirm this conclusion.

Table 2
TOTAL OF SEVENTY-SIX ELEMENTS ANALYZED IN
URANIUM BY SPARK-SOURCE MASS SPECTROMETRY

Sample	Total Impurities (ppm)
Original Material	
Sample 1	878
Sample 2	888
Sample 3	837
Zone-Refined Rod (distance from the initial molten zone)	
One Inch	188
Two Inches	149
Three Inches	60
Four Inches	80

Movement of the molten zone over the length of the rod was investigated at various speeds ranging from $3/4$ inch per hour, the slowest rate obtainable on this instrument, up to five inches per hour. Analysis of the samples indicated that the slower speeds resulted in more purification. Presumably, this more effective removal was due to the fact that the greater time lag in the passage of a molten zone allowed the diffusion within the zone to more nearly approach equilibrium.

The results of each of the investigated variables were considered and parameters for the most efficient zone refining were chosen accordingly. The best cleaning procedure, zone width, direction and rate of travel of the molten zone, length of the zone-refined area, and degree of vacuum were utilized in the further treatment of the uranium rods.

The rod described in Table 2 was subjected to three passes from bottom to top of a five-inch section. The molten zone, about 1/4-inch wide, had traveled at a rate of 3/4 inch per hour under a vacuum maintained at or below 10^{-6} torr. The summation of 76 elemental impurities, given in Table 3, indicated that the impurity concentration had dropped from the original 850 ppm level to less than 60 ppm. The variance in the detection limits for the same element is caused by changes in the parameters used for the spark-source mass spectrometer as the impurities in the uranium decrease.

Table 3
SPARK-SOURCE MASS SPECTROMETRIC ANALYSIS OF URANIUM
ROD BEFORE AND AFTER ZONE REFINING
(All Values Expressed in Weight ppm)

Element	Original Material	After Three Passes ⁽¹⁾	After Six Passes ⁽²⁾	Element	Original Material	After Three Passes ⁽¹⁾	After Six Passes ⁽²⁾
Ag	<0.04	<0.01	0.01	Nd	<0.04	<0.01	<0.01
Al	6.1	0.70	3.1	Ni	21.8	2.0	1.1
As	<0.01	<0.01	0.01	Np	<0.03	<0.02	<0.05
Au	<0.07	<0.02	<0.01	O	403	13.4	4.7
B	0.10	1.1	0.50	Os	<0.08	<0.02	<0.01
Ba	<0.04	<0.01	<0.01	P	0.23	0.08	0.35
Bi	<0.03	<0.02	0.05	Pa	<0.03	<0.02	<0.05
Br	<0.01	<0.01	<0.01	Pb	0.96	<0.02	0.05
C	305	31.0	3.5	Pd	0.04	<0.01	<0.01
Ca	0.32	0.05	0.05	Pi	<0.04	<0.01	<0.01
Cd	<0.04	<0.01	<0.01	Pt	0.30	<0.02	<0.02
Ce	<0.04	<0.01	<0.01	Pu	<0.03	<0.02	<0.05
Co	0.04	0.02	0.02	Ra	<0.03	<0.02	0.05
Cr	0.85	0.50	0.24	Rb	<0.01	<0.01	<0.01
Cs	<0.04	<0.01	<0.01	Re	0.08	<0.02	0.01
Cu	7.0	0.20	0.35	Rh	<0.04	<0.01	<0.01
Dy	<0.04	<0.01	<0.01	Ru	<0.04	<0.03	<0.01
Er	<0.04	<0.01	<0.01	S	0.26	0.03	0.04
Eu	<0.04	<0.01	<0.01	Sb	<0.04	<0.01	<0.01
Fe	46.0	5.0	7.7	Sc	0.02	<0.01	<0.01
Ga	0.09	<0.01	0.01	Se	<0.01	<0.01	<0.01
Ge	<0.02	<0.01	<0.04	Si	45.5	5.0	22.7
Gd	<0.04	<0.01	0.01	Sm	<0.04	<0.01	<0.01
Hf	<0.04	<0.01	<0.01	Sn	<0.04	<0.01	<0.01
Hg	<0.07	<0.02	0.25	Sr	<0.01	<0.01	<0.01
Ho	<0.04	<0.01	<0.01	Ta	<13.7	<1.5	<0.68
I	<0.04	<0.01	<0.01	Tb	<0.04	<0.01	<0.01
In	<0.04	<0.01	0.01	Te	<0.04	<0.01	<0.01
Ir	<0.08	<0.02	<0.01	Th	<0.03	<0.02	<0.05
K	<0.02	<0.03	<0.01	Ti	0.16	0.15	0.08
La	<0.04	<0.01	<0.01	Tl	<0.07	<0.02	<0.003
Lu	<0.04	<0.01	<0.01	Tm	<0.04	<0.01	<0.01
Mg	0.54	<0.06	<0.01	V	<0.02	<0.01	<0.01
Mn	4.2	<0.01	0.01	W	<0.08	0.05	0.08
Mo	0.21	0.20	0.05	Y	<0.01	<0.01	<0.01
N	35.3	2.0	2.0	Yb	<0.04	<0.01	<0.01
Na	<0.01	<0.01	<0.01	Zn	10.1	0.30	0.17
Nb	<0.04	<0.01	<0.01	Zr	0.46	0.15	0.07

(1) Three inches from the initial molten zone.

(2) One inch from the initial molten zone.

Another rod was refined using similar starting stock and the same parameters, but the number of passes was increased to six. The analysis of a sample taken from this rod, containing less than 48 ppm impurities, is also given in Table 3.

Starting uranium stock with a lower concentration of impurities was utilized in the next zone-refining attempt to obtain greater purity. A rod originally containing about 100 ppm of the impurities was subjected to two bottom-to-top passes. Analysis, as shown in Table 4, demonstrated that the impurity content dropped to less than 30 ppm.

Table 4
SPARK-SOURCE MASS SPECTROMETRIC ANALYSIS OF HIGH-PURITY
URANIUM ROD BEFORE AND AFTER ZONE REFINING
(All Values Expressed in Weight ppm)

Element	Original Material	After Two Passes	Element	Original Material	After Two Passes
Ag	<0.04	<0.01	Nd	<0.09	<0.01
Al	3.0	0.86	Ni	7.3	1.1
As	<0.01	<0.01	Np	<0.04	<0.02
Au	<0.10	<0.02	O	7.0	4.0
B	0.01	0.01	Os	<0.08	<0.02
Ba	<0.03	<0.01	P	0.01	0.02
Be	0.1	0.1	Pa	<0.04	<0.02
Bi	<0.04	<0.1	Pb	4.6	0.30
Br	<0.03	<0.01	Pd	<0.07	<0.01
C	15.	8.5	Pt	<0.02	<0.01
Ca	0.1	0.2	Pt	<0.30	<0.02
Cd	<0.07	<0.01	Pu	<0.04	<0.02
Ce	<0.03	<0.01	Ra	<0.04	<0.02
Co	0.04	0.02	Rb	<0.02	<0.01
Cr	0.21	0.4	Re	<0.05	<0.01
Cs	<0.02	<0.01	Rh	<0.02	<0.01
Cu	5.4	0.75	Ru	<0.06	<0.01
Dy	<0.10	<0.01	S	<0.03	<0.05
Er	<0.08	<0.01	Sb	<0.04	<0.01
Eu	<0.05	<0.01	Sc	<0.03	<0.04
Fe	19.	7.0	Se	<0.03	<0.01
Ga	<0.03	<0.03	Si	7.8	2.2
Ge	<0.03	<0.01	Sm	<0.09	<0.01
Gd	<0.11	<0.01	Sn	<0.06	<0.01
Hf	0.11	<0.01	Si	<0.02	<0.01
Hg	<0.11	<0.02	Ta	<5.0	<0.50
Ho	<0.03	<0.01	Tb	<0.03	<0.01
I	<0.02	<0.01	Te	<0.06	<0.01
In	<0.02	<0.01	Th	<0.04	<0.02
Ir	<0.05	<0.05	Ti	0.11	0.58
K	<0.03	<0.03	Tl	<0.05	<0.02
La	<0.02	<0.01	Tm	<0.03	<0.01
Lu	<0.03	<0.01	V	<0.03	<0.01
Mg	9.6	<0.01	W	<0.10	<0.08
Mn	0.83	<0.01	Y	<0.01	<0.01
Mo	<0.07	<0.12	Yb	<0.09	<0.01
N	6.5	2.0	Zn	5.5	0.17
Na	<0.03	<0.01	Zr	<0.03	<0.1
Nb	<0.05	<0.01

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