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**SPARK SPECTROGRAPHIC CHARACTERIZATION
OF URANIUM METAL BY PART
SURFACE SENSITIZATION**

H. G. King

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ABSTRACT

Further studies of the in-situ spectrographic characterization of uranium metal have resulted in changes in methodology which reduce spectral background and improve the sensitivity of the method. The anode spot is sensitized by thermoelectrical bombardment from the ammonium bifluoride-packed cathode. Detection limits can be lowered by as much as twofold, and a more readable spectrogram is obtained.

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SUMMARY

A relatively sensitive spectrographic method has been developed for the characterization of impurities in semifinished and in-stream uranium parts. The cratered graphite cathode^(a) in a high-frequency spark discharge is packed with 40 mg of ammonium bifluoride (NH_4HF_2) which serves to generate a carrier action at the part surface on which the spark column impinges. The volatile impurity fluorides are rapidly released into the spark column from the uranium metal to provide greater sensitivity and to provide for better plate reading.

The corrosion effects on the part surface were studied, and it was found that no corrosion centers were formed, although the part is very slightly affected dimensionally. Additional surface explorations were made with an electron microprobe to more completely characterize the sensitizing phenomenon.

Sensitivity increases were evaluated by a simple comparison of the spectra taken from the graphite cathode and that obtained by this method. Increases in the sensitivity of essentially all elements sought were observed.

(a) The convention "cathode" is used to indicate phase as distinguished from ground.

INTRODUCTION

While the method developed previously for the in-situ spark spectrographic analysis of uranium metal for impurities does not suffer from intolerable levels of matrix radiation (both continuous and discrete), a reduction in this background could improve the lower limits of detection.^(b) Further, a number of uranium spectral lines, proximate to impurity lines, could be reduced in intensity and thus provide for easier visual intensity estimation of the impurity lines.

Essentially, the problem in this phase of methodological development centers around creating a phenomenon in which the impurities are brought into the excitation system in greater volume than in the previous method, without introducing a proportional amount of uranium matrix. Excitation control and, therefore, background can be reduced to some degree by characterizing the spark column through the selection of source parameters; but, with currently available sources, this is a limited effect. Shorter excitation periods have a serious effect on detection limits; although, ostensibly, the background is diminished.

In the light of extensive experience at the Oak Ridge Y-12 Plant^(c) in the use of carriers for analyzing uranium, it was determined that the proper approach to the problem was one in which the impurities in and near the analytical surface would be "sensitized" by converting them to volatile forms, while the matrix would convert to a relatively nonvolatile form. Ammonium bifluoride was selected as the sensitizer after the completion of initial studies, the selection being based on such considerations as performance, economics, and contamination.

(b) King, H. G.; *In-Situ Characterization of Common Impurities in Uranium Metal by Spark Spectrochemistry*, Y-1937; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; March 29, 1974.

(c) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

CHARACTERIZATION OF URANIUM METAL

EQUIPMENT

Spectrograph

The spectrograph used has a large quartz prism mounted after the manner of Littrow. The 30-degree reflecting prism is illuminated by parallel light from the collimator. The latter receives radiation from the spark column center which is focused on its front surface. After passing the condenser and slit, light from the spark is deviated from being perpendicular to the principal optical axis to a position that is parallel to the principal axis by means of a 90-degree reflecting prism. The camera is angled with respect to the principal axis to adjust to the very valuable polychromatic properties inherent in the Littrow mount. This tilt in the camera to achieve focus at the different wavelengths accounts for much of the dispersion so necessary in dealing with complex spectra. A flat sparking table with a counterelectrode clip is mounted on the optical bench to support the part. Alternatively, the cantilever optical bench can be used. (b) Figure 1 is a schematic drawing of the spectrograph; the operating parameters for the instrument are listed in Table 1.

Figure 1. ARRANGEMENT OF THE PRINCIPAL COMPONENTS OF THE SPECTROGRAPH.

Table 1
INSTRUMENT PARAMETERS

Spectrograph	Source Unit
Focus - 153.5 cm	Voltage - 24,000 V
Camera Tilt - 208 (protractor setting)	Current - 1.5 A (in primary)
Prism System - Quartz-9	Capacitance - 0.0063 μ F
Collimator - medium	Inductance - 500 μ H
Slit - 10 μ m	Spark Power - 8 (arbitrary units)
Plate - SA-I	Discharges - 4/half Hz
Exposure - 45 s	Resistance - 5 ohms

Source Unit

The source unit for the work is a condensed RF spark manufactured by the National Spectrographic Laboratories. The maximum potential of the source is 25,000 volts. As much as 0.0063 μ F of capacitance and 600 mH of inductance can be added. The source is equipped with an auxiliary gap interrupted by an air stream. Breaks per half cycle are adjustable over a range from two to twelve. The interrupter gap is adjustable to provide for changing the break-down potential and for phasing. The spark character can be observed on an oscilloscope mounted on the front panel. Table 1 also gives the operating parameters for the unit.

MATERIALS

The following materials were used in the investigation:

Uranium metal standards.

Wipers, paper.

Spectroscopic photographic plate, Eastman Kodak Type SA-I.

Photographic Supplies:

Developer, D-19, Eastman Kodak;

Fixer, Eastman Kodak.

Electrodes, spectroscopic, Carbon Products Division, UCC:

Cathode, graphite, crater 4 mm by 4 mm deep in nominal 0.25 in (6.34 mm) stock, undercut;

Boiler cap, graphite, to fit the graphite cathode.

Reagents:

Methanol, reagent grade;

Ammonium bifluoride, Bakers analyzed grade or Fisher;

Silver fluoride, carrier grade;

Hydrofluoric acid, electronic grade;

Potassium fluoride, Bakers analyzed;

Acetic acid, reagent grade.

EXPERIMENTAL PROCEDURE

General Considerations

The classical spectrographic spark discharge is characterized by a number of phenomena, two of which are prominent. First, is the very high thermoelectrical equivalent temperatures encountered in the spark; second, is the ionization power which it displays both in the spark

column and on the surfaces from which it emanates and impinges. The spark, running at a potential of 25,000 V, can have electron temperatures in the order of about 10^7 ° C, according to the following calculation:

$$I \approx \frac{2}{3} \frac{mv^2}{K}$$

or:

$$T \approx \left(\frac{10^{-28} \times (10^{10})^2}{1.4 \times 10^{-16}} \right)^{2/3}$$

where $m \approx 10^{-28}$ gram, the mass of an electron traveling at a velocity, v , of 10^{10} cm/s and K (1.4×10^{-16}) is the Boltzmann constant.

This value can be reported, conventionally, as the thermal environment required for 0.025 MeV electrons. The impact from these electrons can eject material from a part surface for excitation in the spark column. The ionization processes prevalent in the spark give rise to high-energy spectral lines which appear in a spectral region characteristic of such lines (ie, the ultraviolet and far ultraviolet).

These features of the spark have made it useful through the years in the spectrographic analysis of metals for matrix and submatrix elements, and more recently in the analysis of uranium metal for micro amounts of impurities. The latter uses source parameters (principally inductance) to generate additional amounts of vapor.

As in virtually all spectrographic analyses for residuals in a base metal, it is desired to excite as much of the impurity as needed, while holding the spectrum of the matrix to a minimum. Since the source parameters are optimal, the next step in the advancement of the methodology for the spark analysis of uranium metal is to arrange for the condition just described to prevail.

Preliminary Investigations

It became apparent after some study that some chemical effect at the part surface could increase the volatility of many of the elements present. Such an effect should be similar to one phase of carrier distillation. The Y-12 Plant Laboratory has had long and extensive experience with carrier techniques; and, although carriers have been used in analyzing uranium in the form of the octoxide (U_3O_8), there was no immediate reason seen why a carrier should not be used in the analysis of the metal.

Most carrier methods are characterized by three properties: (1) a "sweeping" action to carry vapor to the excitation site, (2) a suppression of the complex matrix spectrum, and (3) the formation of volatile compounds by chemical action between the elements sought and the carrier. For the purposes of this study, the latter action is the more important, since the goal is to sensitize the uranium part surface by such a process.

Methodology

Generally speaking, the volatile compounds of metals are the halides, particularly the fluorides. Table 2 lists the boiling points of the fluorides of the impurity elements, along with the boiling point of uranium tetrafluoride (UF_4). The boiling points and sublimation temperatures of the fluorides are well below that of UF_4 .

The first approach to sensitization was to apply a thin coat of 5% electronic-grade hydrofluoric acid to the metal surface, sparking when the surface was dry. However, this approach was found to be unsatisfactory. The layer was quickly and massively removed from the surface, and the latter suffered considerable etching. At this point it was obvious that the sensitization must be effected during the sparking period, that it should proceed at the optimum speed, and must be continuous during the cycle.

The conditions stated can be obtained in two ways: (1) hydrogen fluoride gas can contact the surface of the part by passing from a storage vessel through a tube, or (2) a fluoride compound can be volatilized from a crater in the cathode and react with the part surface during the excitation cycle. The latter course of action was taken.

The second attempt in surface sensitization was made with potassium fluoride. Using crater charges of 20 to 50 mg, there was insufficient vapor produced from the high-boiling material (1500°C) to effect a satisfactory sensitization. Experiments with silver fluoride succeeded in producing a considerable reduction in background intensity and, at the same time, there was an increase in the impurity line intensity. However, AgF is expensive, and there is the possibility of silver contamination. Ammonium bifluoride was found to be eminently satisfactory for the procedure. Forty milligrams of this sensitizer were packed in the 4 by 4-mm craters of the cathodes; and, after a two-hour period of desiccation, were used to spark the surface of the uranium metal standard parts. Figure 2 provides a comparison of the backgrounds of the method with that of the usual graphite spark, while Figure 3 indicates the sensitivity differences. By observing the line intensities of the lowest standard in both spectra (Figure 3), it can be seen that there has been a sensitivity increase in the elements which fall in this spectral region. The lines used for analysis are given in Table 3; a detailed procedure is given in the Appendix.

Sensitization Phenomenon

Immediately after the spark begins to operate, the electrode temperatures begin to increase rapidly due to the inductance (500 mH) placed in the internal power circuit. At a relatively low temperature of about 200°C , the NH_4HF_2 begins to vaporize into the spark column and is carried to the part surface being sparked. Following this, and as the interrupter gap spacing is being adjusted, the cathode suffers a current overload at which point in time it is carrying maximum ion and electronic current. The indication of this occurrence is that the cathode becomes acoustic; ie, it begins to "hiss" in much the same manner as the DC arc at the overload point. The spark under these conditions has good stability as, incidentally, does the DC arc.

Table 2
BOILING POINTS OF THE
IMPURITY FLUORIDES
(All Values in $^\circ\text{C}$)

CuF_2	$\sim 1000^{(1)}$
FeF_2	$\sim 1050^{(1)}$
MoF_6	35
NbF_5	236
NiF_2	$\sim 800^{(1)}$
SiF_6	86
TiF_4	284 (sublimes)
ZrF_4	600 (sublimes)
UF_4	1477
UF_6	Not Likely to be Formed

(1) Estimates only.

(a) Conventional Graphite Spark. (3X)

(b) Surface Sensitization. (2.8X)

Figure 2. BACKGROUND COMPARISON.

(a) Conventional Graphite Spark. (2.5X)

(b) Surface Sensitization. (3X)

Figure 3. LINE-INTENSITY COMPARISON.

The chemical action proceeds at the part surface, and the sensitization occurs with this action, whereby the volatile fluorides of such metals as iron, copper, nickel, and silicon are vaporized into the spark column. The uranium compound formed which is most likely UF_4 appears not to vaporize too readily, as is indicated in Spectrum b of Figure 2. Electron microprobe studies of the sensitized areas before and after sensitizing and sparking are illustrated in Figure 4. It is indicated that there is a chemical effect, as can be seen from a comparison of the two views of Figure 5. View b shows an area sparked with a simple graphite rod cathode. When the impurity level is low, the sensitization occurs principally in the metal crystal structure; since, at low impurity levels, the grain boundaries are small. Figure 6 shows a sensitized zone of a low-impurity-level standard and the area in this zone on which the spark impinged. Figure 7 shows a sensitized sparked area at low magnification, showing the effect on the metal surface.

Table 3
WAVELENGTHS OF SPECTRAL
LINES USED

Element	Wavelength (nm)
Copper	2618.37
Iron	2382.04
Molybdenum	2538.46
Niobium	2927.81
Nickel	2394.50, 2545.9
Silicon	2631.28
Titanium	2525.60
Zirconium	2571.39, 2678.63

DISCUSSION

From the spectra displayed in Figure 3 it can be seen that the exposure, It^n , could be increased by a factor of two without serious effects in the background. This effect could lead to a further increase in the sensitivity of the method.

No photoelectric measurements were made to compare the line intensities of the method described with the current method. However, if the low standards are visually compared it can be seen that there is an increase in sensitivity of from 1.5 to 2.0 times over the current method. Figure 3 shows a series of pairs of exposures of the lowest and highest level standards with a one-impurity element spectrum beneath each high-level standard for identification of the characteristic lines.

During the sparking cycle, the grain boundaries of the higher-level standards empty to an average depth of 22 micrometers. In the low-level standards, this measurement could not be made since the delineation is small. In the high standards, when the impurity concentrations exceed their solubility in uranium, there is an accumulation in the grain boundaries which can then be readily observed. It was predicted that the effect on the small boundaries would be similar to that on the impurity-filled boundaries, although an electron microprobe scan across the small boundaries could not show changes in the impurity levels because the concentration levels in the low standards were too low for detection by the probe.

When affected zones of specimens sparked by the technique are polished to a depth of 25 micrometers, the newly generated surface is bright and not deformed. Corrosion-resistant centers have been formed by the sensitizer and spark, which indicates refining of the metal at a greater depth than the topography disturbances show. Two of the specimens suffered no corrosion in air after several weeks.

(a) Electron Backscatter.

(b) X-Ray Videogram of Fe K_{α} . (c) X-Ray Videogram of Si K_{α} .

Figure 4. IRON AND SILICON URANIUM METAL STANDARDS. [Top Views were Taken before Sparking, Bottom Views were Taken after Sparking (sensitized); 300X]

(a) Sensitized and Sparked Surface.

(b) Classical Graphite Sparked Surface.

Figure 5. TWO SURFACES SHOWING A CHEMICAL EFFECT.

(a) Sparked Area.

(b) Sensitized Area Adjacent to the Sparked Area.

Figure 6. OPTICAL PHOTOGRAPHS OF A LOW-IMPURITY-LEVEL URANIUM STANDARD. (190X)

(a) At 190X.

(b) At 10X.

Figure 7. A SENSITIZED SPARKED SURFACE AREA AT TWO MAGNIFICATIONS. (Optical Views)

CONCLUSIONS AND RECOMMENDATIONS

The surface carrier-sensitizer procedure for the spark spectrographic analysis of uranium metal and uranium parts with tolerances up to 50 micrometers (0.002 in), which is twice the metamorphosed depth, involves a feasible methodology which produces a more readable spectrum and increased sensitivity over current procedures of this type.

This procedure is recommended in situations where it is necessary to furnish analytical information concerning allowable impurity levels lower than the specification limits, but higher levels than that obtained by the refined carrier distillation technique applied to U_3O_8 samples. In this method, copper, molybdenum, niobium, and nickel are seen at 10 ppm; titanium, under 4 ppm; zirconium, well under 50 ppm; and iron easily at 20 ppm. These levels should be adequate for more conservative process control.

The elements studied in this work are those in which a particular interest has been shown. The possibility of determining additional elements has not been pursued, but it seems likely that a number of other impurities could be determined by the method.

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APPENDIX

IN-SITU SPARK SPECTROCHEMICAL CHARACTERIZATION OF URANIUM METAL BY ANODE SENSITIZATION

A. Preparation of the instruments.

1. Inspect the area surrounding the instrumentation for safety of operation and cleanliness.
2. Set the source unit parameters to the values given in Table 1, and energize the unit.
3. Set the parameters for the spectrograph, as given in Table 1.
4. Load an SA-I spectroscopic plate in the plate holder and slide the holder into the camera.

B. Cleaning the part.

1. Carefully wipe the surface area to be sparked with a cellulose wiper.
2. Apply 10 to 15 ml of a solution of methanol-5% acetic acid and rub the area briskly.
3. Rinse the surface thoroughly with distilled water.
4. Dry the surface completely with a wiper.

C. Operational procedure.

1. Weigh 40 mg of NH_4HF_2 into a 4 by 4-mm undercut crater in a nominal 6.35-mm by 63.5-mm long graphite electrode, and tamp the charge lightly with a 3.18-mm graphite rod.
2. Place the electrode in a desiccator for two hours.
3. When properly desiccated, fasten the electrode in the V slot beneath the spring clips of the spark stand cathode.
4. By pressing the bottom of the electrode, bring the crater lip up to the level of the table and firmly place the boiler cap over the crater.
5. Bring the gap spacer, which is located on the right front corner of the table, gently down on top of the cap.
6. Holding the ring or little finger of the left hand on the bottom of the electrode and, with the fore and middle fingers over the spring clips, press down on the spacer to achieve a proper analytical gap.

7. Carefully place the part on the table with the cleaned area centered over the boiler cap. Note: In the event that the surface to be sparked is round, place nonconducting wedges or blocks on both sides of the table top to bring the circumference of the part tangent to the plane of the sparking table top.
8. Pull the dark slide on the plate holder to the "open" position and set the camera of the spectrograph in position to receive the first exposure.
9. Throw the spark control switch to the "on" position and press the "start" button.
10. Readjust the part to obtain a fresh surface and repeat Step 9.
11. After two exposures, immediately remove the part from the table and clean it thoroughly with methanol and paper wipers.
12. Spark the standards at the bottom of the plate.
13. Develop, fix, and dry the SA-I plate and compare the impurity lines of the samples with those of the standards.

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