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IN-SITU CHARACTERIZATION OF COMMON IMPURITIES IN URANIUM METAL BY SPARK SPECTROCHEMISTRY

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MASTER

UNION CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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ABSTRACT

A rapid spectrochemical method, involving the application of a condensed spark to finished or semifinished uranium metal surfaces, has been developed to analyze large numbers of parts (50 or more in a single day) for up to nine specification impurity elements. No sampling or preparation is required, and the on-site analysis is carried out by transporting the spectrograph and source to the production area. The procedure is used for process control and is supplemental to the more refined pyro carrier spectrochemical analysis used for product certification. Elements determined by the large quartz prism spectrograph include: copper, iron, molybdenum, nickel, niobium, titanium, silicon, and zirconium. Carbon is determined by a very slight change in procedure.

CONTENTS

SUMMARY

The present method for the spectrochemical analysis of uranium metal for specification impurities involves: (1) ignition of degreased and pickled turnings or drillings from the uranium part to the octoxide (U_3O_8), (2) mixing a weighed aliquot of the U_3O_8 with a carrier, (3) charging an electrode crater with a weighed amount of the charge, and (4) arcing the electrode in a DC arc for a given time under fixed conditions. When impurities are found at levels above the specified maximum, determination of the source of the contaminant may require the very rapid analysis of a large number of finished parts for which no sample is available. To achieve this capability, a study was initiated to develop a method which could generate analytical data quickly without significantly damaging the part and yet would be sufficiently sensitive to serve the specification limits. The study resulted in a spectrochemical method which will: (1) supply data very quickly (5 to 10 minutes per part), (2) perform the analysis on the scene by moving the equipment and instrumentation there to the part, (3) apply the spark, essentially nondestructively, to the surface of the part itself, (4) analyze material for which no sample is available, and (5) make the determination(s) at a very low cost.

INTRODUCTION

In the processing of uranium through the various Oak Ridge Y-12 Plant[a] streams and cycles, there is an inadvertent pickup of contaminants. This contamination is normally at a minimum due to careful handling and the exercise of good judgement in the selection and construction of process equipment. There are, however, situations arising from time to time in which contamination reaches intolerable levels. Contamination of machining chips, which are recycled, or the spauling of steel or steel alloys in power presses used to break uranium metal parts into meltable pieces are two examples. When this pickup occurs, it is important that analytical signals be generated quickly at various points in the cycle involved to relevantly characterize the contamination.

Ideally, a physicochemical methodology, such as spectrography, could supply such analytical data provided that: (1) the complexity of the uranium spectrum, when originated by sparking the metal directly, would not interfere too drastically with the spectra of the impurities, and (2) a spectrographic instrument could be made that was durable and stable enough to operate in the production areas. In-laboratory experimentation was initiated to study spark-originated spectra from uranium metal. Studies of the varying environmental conditions in production areas were initiated in order that prevailing conditions might be compared with normal operating criteria for spectrographic equipment of several types.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

CHARACTERIZATION OF COMMON URANIUM IMPURITIES

EXPERIMENTAL WORK

Optical System

The optical system chosen, after due consideration, is illustrated in Figure 1. Light enters the instrument through the slit and is reflected by the reflecting prism to the collimator lens. The light is made parallel by the lens since the slit is one focal length distant from the lens. The parallel rays are diffracted by the diffracting prism into the camera where the dispersed spectrum is focused as an image of the entrance slit, and is photographed. The camera and lens can be set to achieve a dispersion in the region from 2000 to 2900 A of 1.2 to 4.0 A/mm, which was found to be the most suitable spectral range for the procedure. Transmission of the quartz system is excellent in this region (97.1%/cm).

Source Unit

Use of a DC arc to excite the impurities in the uranium metal would present some special problems. For example, it would be most difficult to maintain dimensional tolerance for parts (as a matter of fact, it would be destructive).

A source unit consisting of a high-powered condensed spark was chosen on the basis of this one criterion, although there are other advantages of the spark over the sensitive DC arc. The spark, for example, tends to be more stable and can reach high excitation levels.

A spark unit manufactured by the National Spectrographic Laboratory was available and used in the work. A voltage level of 25,000 V can be attained at peak power. Added self inductance was available up to 600μh and capacitance up to 0.0088 μf. Five ohms of resistance could be added in five steps. The spark circuit contained an auxiliary gap which was periodically interrupted by an air jet at rates of from two to twelve times per half cycle. Certain special safety actions were taken, and these are discussed in the appendix.

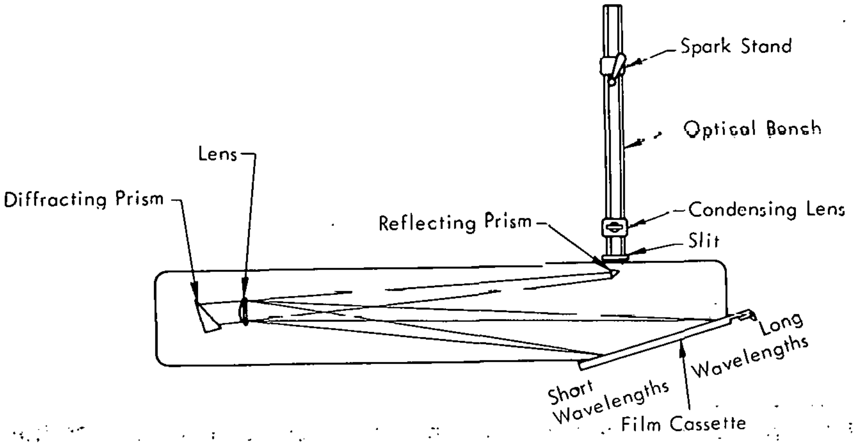

Figure 1. TYPICAL DESIGN OF A LARGE QUARTZ SPECTOGRAPH.

Preparation of Standards

Uranium metal standards were made to meet the following criteria:

1. The metallurgical history of the standards must be comparable to that of the metal to be analyzed:
2. The standards should be homogeneous to an extent equal to or better than the limit of error of the method, which was found to be ± 25% relative.
3. The physical shape of the standard should provide surfaces for comparison against round and/or flat surfaces of the part analyzed.

The standards were made from a depleted uranium rolled plate which was relatively low in the impurities sought. The plate, after being broken into small pieces, was loaded into a carbon crucible which had been coated with zirconite. The weighed impurities were placed in the center of the load when the crucible was half filled. The system was evacuated and the furnace brought to 1400° C. The melt was stirred occasionally with the pouring rod. After holding at 1400° C for 30 minutes, the material was poured into a billet mold; after twenty minutes, the system was backfilled with argon to 20 inches of mercury and cooled to room temperature.(1) The billet surface was removed by machining and a three-inch-thick, four-inch-diameter slice cut from the cylindrical billet. The turnings were used for chemical analysis. The disc was cut in half across the diameter to form two half-circular shapes with flat sides. Analyses of the four standards are reported in Table 1. A spectrographic analysis of the standards was made using the established pyro carrier distillation method. Repetitive analyses demonstrated that the standards met the homogeneity requirements. The carbon standards (Standards 5 and 6) were prepared in the same manner except that a 20% excess was added to compensate for losses.

Instrument Parameters

In studying the question of instrument settings, the predominant factor was dispersion. Complexity of the line spectrum of uranium and its compounds makes it mandatory that parameters be set to provide minimum interferences of uranium with the impurity lines. The "continuum" produced by uranium is not the serious problem it is commonly believed to be. The incandescence produced by "burning" uranium arises from hot particulates forced into the arc or spark, by the long persistence of the heavy element in the column, and other manageable factors. It was noted, in experimenting with deep anode craters, that well-vaporized uranium produces a background similar to iron.(2) However, lack of dispersion does greatly enhance the background effects. The prism system has a very high dispersion in the ultraviolet region (1.1 A/mm at 2000 A). After experimentation with several settings in the ultraviolet region, the optimum instrument parameters were selected. Table 2 provides a list of these parameters.

When the source unit is run as a condensed spark without added inductance it runs "cold", and no significant quantity of vapor is produced. To obtain the lower detection levels, generation of some sample vapor is desired and, thus, it is necessary to add nominal amounts of inductance to the circuit. The inductance, added in series, also served to prevent sparking

Table 1

CHEMICAL AND SPECTROGRAPHIC VALUES FOR STANDARDS
(All Values in ppm)

	Standard											
	1		2		3		4		5		6	
Element	Chemical	Spectrographic	Chemical	Spectrographic	Chemical	Spectrographic	Chemical	Spectrographic	Chemical	Spectrographic	Chemical	Spectrographic
Cu	16, 17	10, 12	57, 59	60, 50	97, 99	100, 85	194, 186	200, 150				
Average	15		55		95		185					
Fe	47, 51	45, 40	286, 236	200, 225	623, 672	400, 500	1062, 897	700, 1000				
Average	45		240		500		800					
Mo	< 10	< 10	70, 52	40, 30	200, 185	150, 200	176	150, 200				
Average	< 10		50		160		175					
Nb(1)		< 10, < 10		< 10, < 10		< 10, < 10		30, 40				
Average	< 10		< 10		< 10		35					
Ni	6, 8	10, 16	124, 116	100, 90	230, 222	300, 250	372, 324	400, 400				
Average	10		120		250		375					
Si	< 50, < 50	< 50, < 50	575, 525	500, 500	728, 602	1000, 800	1284, 1415	> 1000, >1000(2)				
Average	< 50		520		800		1350					
Ti(1)		< 4, < 4		4, 6		20, 20		30, 25				
Average	< 4		5		20		30					
Zr(1)		< 50, < 50		100		200, 200		250, 250				
Average	< 50		100		200		250					
C(3)	89, 86		238, 242		287, 305		680, 699		287, 313		199, 198	
Average	88		240		292		690		300		199	

(1) No suitable chemical method was available for these elements.
(2) Level above the pyro carrier standards.
(3) Only chemical values were determined.

at the first surge of current when the initial plasma has built up in the gap. A spark at this point in time produces unwanted background. The air-interrupted auxiliary gap, in series with a resistance, can be phased with the spark to provide a dampening effect for parts of the oscillatory train. The temperature of the sample surface increases due to the inductance which increases the amount of vapor. Insertion of capacitance reduces the number of oscillations, but there is a sharp increase in the energy input to the spark column; and, during the initial stages of plasma formation, there is a very high electron velocity in the analytical gap. This action provides much of the ionized vapor for obtaining the singly ionized spectra of the impurities. By adjusting the interrupter gap width, the discharge used can be varied.(3, 4) The breaks per half cycle are displayed on an oscilloscope in the source console. Table 2 also lists the source parameters that were used in the work.

Table 2

SETTINGS FOR THE LARGE QUARTZ PRISM SYSTEM AND SOURCE UNIT

Spectrograph	Source Unit
Focus - 153.5 cm	Voltage - 24,000 V Current - 1.5 A (primary)
Camera Tilt - 208	Capacitance - 0.0063 μf
Collimator - medium	Inductance - 500 μh
Slit - ~ 10 μm	Spark Power - 8 (arbitrary units)
Plate - SA-1	Discharges - 4 per half cycle
Exposure - 45 sec	
Illumination Mode - condenser lens set to focus source center on collimator	

Line Selection and Location

Lists of possible lines were made from the National Bureau of Standards monographs which give line intensities and transistion probability (gA) values for some 70 elements.(5) Since the population of the high upper states can be maintained easily with the powerful 24,000 V spark, the gA value of the lines should be indicative, to a high degree, of the line intensity. A series of spectrograms were then taken of the high and low standards with a spectrum of one of the impurities just below each set. The impurity lines selected from intensity and gA considerations were located by comparing the spectrum of the impurity to the standard spectra. Thus far, intensity has been the main goal, but it was necessary to observe the behavior of the line in real experiences. The standards were sparked on a petri table, using the conditions given, and some 20 spectrograms taken over a two-week period. No anomalies were noted, and the selection was completed. The lines are listed in Table 3.

Alterations for the Carbon Analysis

To analyze the uranium metal for carbon, the following equipment changes were made:

Source -	no change.
Spectrograph -	no change.
Counterelectrode -	1/4-inch by 4-inch-long copper tube with a 3/32-inch-diameter platinum wire loop filament attached to the spark end. A hose

for argon gas was attached to the bottom end of the tube. Argon flow was maintained at 19 scfh.

Spark Stand - Lucite box with light port placed over the petri table and resting on an optical bench.

The argon flow was started, and the uranium metal was sparked according to the normal procedure.

RESULTS

Sensitivity

The sensitivities achieved by the method are listed in Table 4 along with the specification upper limits of the metal parts. It can be seen from Table 4 that not only can the specification limits be met, but quality control data can be supplied by the method as well. Aluminum, magnesium, chromium, and manganese are also determinable by the method, but these are not usually troublesome in the contamination problem.

Concentration Measurements

Ten uranium parts were analyzed by the procedure and compared to results determined by the Quantometric[(b)] method. Carbon was not determined in these parts. It was, however determined in 25 different parts and compared with results from a combustion method. Tables 5 and 6 report the results. It appears from the values presented that there are no significant trends in differences. The only statistical study made was for iron (see Table 7). A very large number of parts were analyzed for that element alone. A precision of about ± 25% was obtained, which compares favorably with the Quantometric method.

Table 3

SELECTED SPECTRAL LINES FOR IMPURITIES IN URANIUM METAL

Element	Wave Length (A)	gA Value (10^8/sec)
Cu	2618.37	4.3
Fe	2382.04	92.0
Mo	2538.46	71.0
Nb	2927.81	17.0
Ni	2394.50	167.0
Si	2631.28	22.0
Ti	2525.60	13.0
Zr	2571.39	29.0
C	2836.61	Not Available

Table 4

SENSITIVITIES ACHIEVED FOR THE IMPURITIES

Element	Lower Limit of Detection (ppm)	Upper Limit, Specification (ppm)
Cu	25	50
Fe	50	250
Mo	30	100
Nb	10	10
Ni	20	100
Si	50	650
Ti	10	10
Zr	100	100
C	80	600

(b) Direct-reading spectrographic method.

Table 5

COMPARISON OF IN-SITU SPARK AND QUANTOMETRIC SPECTROANALYSES

Part Number	Element Cu	Fe	Mo	Nb	Nr	Si	Ti	Zr
1 C(1)	24	191	15	< 10	36	325	< 4	-
S(2)	< 25	200	< 30	< 10	30	250	< 10	< 100
2 C	9	119	28	< 10	69	208	< 4	-
S	< 25	150	< 30	< 10	80	200	< 10	< 100
3 C	9	80	26	< 10	62	218	< 4	-
S	< 25	100	< 30	< 10	60	250	< 10	< 100
4 C	9	90	15	< 10	51	177	< 4	-
S	< 25	100	< 30	< 10	60	200	< 10	< 100
5 C	9	94	12	< 10	57	188	< 4	-
S	< 25	125	< 30	< 10	60	250	< 10	< 100
6 C	18	117	19	< 10	72	174	< 4	-
S	< 25	120	< 30	< 10	50	200	< 10	< 100
7 C	8	121	11	< 10	84	175	< 4	-
S	< 25	125	< 30	< 10	55	180	< 10	< 100
8 C	-	623(3)	-	-	-	-	-	-
S	< 25	600	< 30	< 10	40	150	< 10	< 100
9 C	8	108	15	< 10	55	224	< 4	-
S	< 25	125	< 30	< 10	25	200	< 10	< 100
10 C	11	118	28	< 10	64	240	< 4	-
S	< 25	120	< 30	< 10	45	225	< 10	< 100

(1) Quantometric method.
(2) Spark method.
(3) Iron only, requested.

Table 6

COMPARISON OF SPARK SPECTROCHEMICAL AND CHEMICAL VALUES FOR CARBON IN URANIUM

Part Number	Spectrochemical (ppm)	Chemical (ppm)
1	300	352
2	350	374
3	250	328
4	300	330
5	200	178
6	120	153
7	200	246
8	200	246
9	100	118
10	200	209
11	200	188
12	180	116
13	200	203
14	200	219
15	200	181
16	200	203
17	180	166
18	180	156
19	100	80
20	100	78
21	135	112
22	100	70
23	100	80
24	100	76
25	100	62

Table 7

IRON RESULTS FOR STATISTICAL EVALUATION

	Fe Concentration (ppm)		Fe Concentration (ppm)		Fe Concentration (ppm)
Day 1	350	Day 2	400	Day 3	400
	400		450		450
	400		400		450
	400		450		450
	375		450		400
	400		450		400
	400		450		400
	400		450		400
			400		400
			400		400
Average	390	Average	430	Average	415
	LE(1) = ± 44		LE(1) = ± 59		LE(1) = ± 56

(1) Limit of error, absolute, at 95% confidence.

CONCLUSIONS

In-situ characterization of the specification elements in uranium by spark spectrochemistry is a feasible methodology which can be applied in house or on site. Satisfactory standards have been prepared for the method. Large numbers of uranium parts can be studied quickly and economically for the control of quality in finished and semifinished forms. Parts of various shapes and sizes can also be characterized by the method.

REFERENCES

(1) Tweed, E. A.; *Personal Communication*.

(2) King, H. G.; *Unpublished Work*.

(3) Twyman, F.; *The Spectrochemical Analysis of Metals and Alloys*; Chemical Publishing Company, Inc (1941).

(4) Jarrell, R. F.; "Excitation Units", *The Encyclopedia of Spectroscopy*; Reinhold Publishing Corporation, New York, New York (1961).

(5) Corless, C. H. and Bozman, W. R.; "Experimental Transition Probabilities for Spectral Lines of Seventy Elements", *NBS Monograph 53* (1962).

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APPENDIX

SPECIAL SAFETY ACTIONS

Since the source unit runs at nearly maximum power, the possibility of arcing between terminals and breakdown in the induction coils becomes greater. The safety factor must be increased in this respect by: (1) isolating the capacitor terminals with a sheet of electrically insulating materials, and (2) guarding against continued operation of the source, after a coil breaks down, by strict attention to the oscilloscope pattern which shows a very-low-amplitude, irregular sine wave at breakdown. A CO_2 fire extinguisher should be placed near the equipment.

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