Analysis of Trace Elements in Uranium Oxide Using the Prodigy DC Arc Spectrometer

Introduction

Uranium oxide is an oxide form of uranium metal and exists in several different forms, including: uranium(IV) oxide (UO_2), uranium(VI) oxide (UO_3), triuranium octoxide (U_3O_8) and uranyl peroxide (UO_2O_2). Triuranium octoxide is the most stable form of uranium oxide and the form most commonly found in nature.

Prior to 1960, uranium oxide was used in glazes to color glass and ceramic materials. When fired, these glazes become green or black under reducing atmospheric conditions and they become yellow or orange in an oxidizing atmosphere. These glazes are no longer produced and uranium oxide is now predominantly used as a fuel source for nuclear reactors. Uranium is enriched for use in nuclear power generation and in nuclear weapons. Uranium oxide is also used to produce mixed oxide (MOX) fuel, so-called because it contains more than one oxide of nuclear fission material. As an alternative to using low-enriched uranium for fuel in nuclear power reactors, MOX fuel contains a blend of plutonium and natural, reprocessed or depleted uranium.

This application note contains data to demonstrate the ability of the Teledyne Leeman Lab's **Prodigy DC Arc** to determine trace elements in high-purity triuranium octoxide, which will hereafter be referred to as uranium oxide.

Experimental

Operating Parameters

All standards and samples were prepared for analysis by mixing each with a carrier-containing buffer that consisted of gallium oxide (Ga_2O_3) and cobalt oxide (Co_3O_4) mixed at a ratio of 68.44:1 by weight. Each standard was mixed with the buffer such that the ratio of sample to carrier was 98:2. All mixtures were thoroughly blended with a mixer/mill (SPEX SamplePrep, Metuchen, NJ) for a minimum of 5 minutes.

Standards and samples were weighed directly into sample electrodes such that 125 mg of material was loaded into each electrode. Each loaded electrode was carefully vented prior to analysis. As uranium oxide is hygroscopic, all samples were weighed out and loaded into electrodes using a platinum spatula, weigh boat, funnel and a stainless steel packing tool to avoid transfer losses.

All analyses were performed on the Teledyne Leeman Lab's **Prodigy DC Arc** in atmosphere without the use of the Stallwood Jet. All elements were grouped into a single integration period from 4 to 45 seconds. The integration delay provided a 4 second pre-burn and excluded occasional emission from uranium when arc ignition caused small matrix ejections from the sample electrode. The remaining instrument and method conditions used are listed in Table I.

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The sample and counter electrodes were purchased from Bay Carbon Inc (Bay City, MI) and used as received. The sample electrodes used were pedestal electrodes, 1/8" in diameter (part # S-1) with 1/4" diameter, thin-walled boiler cups (part # S-3). The counter electrodes used for all analyses were 1/8" in diameter and pointed (part # C-1). A 4 mm analytical gap was used and the position of the electrodes was adjusted during the sample burn to maintain a distance of 4 mm between the sample and the counter electrode.

Table I DC Arc Operating Conditions

Parameter	Setting
DC Arc Stand	
Current	Ignite at 12A, hold at 12A for 45 s
Stallwood Jet	None
Analytical Gap	4 mm
Electrodes	
Counter Electrode	1/8" diameter and pointed (ASTM #C-1)
Sample Electrode	Pedestal 1/8" in diameter and 1/4" diameter, thin-walled boiler cup (ASTM #S-1 and #S-3)
Sample	
Sample Size	125 mg weighed, venting tool used
Buffer	Ga_2O_3:Co_3O_4 68.44:1 by weight
Internal Standard	Co using Co 304.401 nm wavelength
Integration Time	4-45 s

An alternate method for running these samples involves the use of a thick-walled boiler cup electrode (ASTM #S-2) with 100 mg of material loaded into each electrode. Both the S-2 and S-3 electrodes will produce good results for trace analyses in uranium oxide; however, it is important to modify the sample mass according to which electrode is being used (100 mg samples for S-2 electrodes, 125 mg for S-3 electrodes).

Calibration

The instrument was calibrated with several high-purity uranium oxide standards that were purchased from New Brunswick Laboratory (U.S. Department of Energy, Argonne, IL) and contained elements of interest from <0.1 to 400 ppm. All standards were weighed, mixed and prepared for analysis as described above.

An example calibration curve for elements measured in uranium oxide is illustrated in Figure 1 for B at 249.678 nm. The calibration curve for B demonstrates typical precision and accuracy for the concentrations over which the instrument was calibrated.

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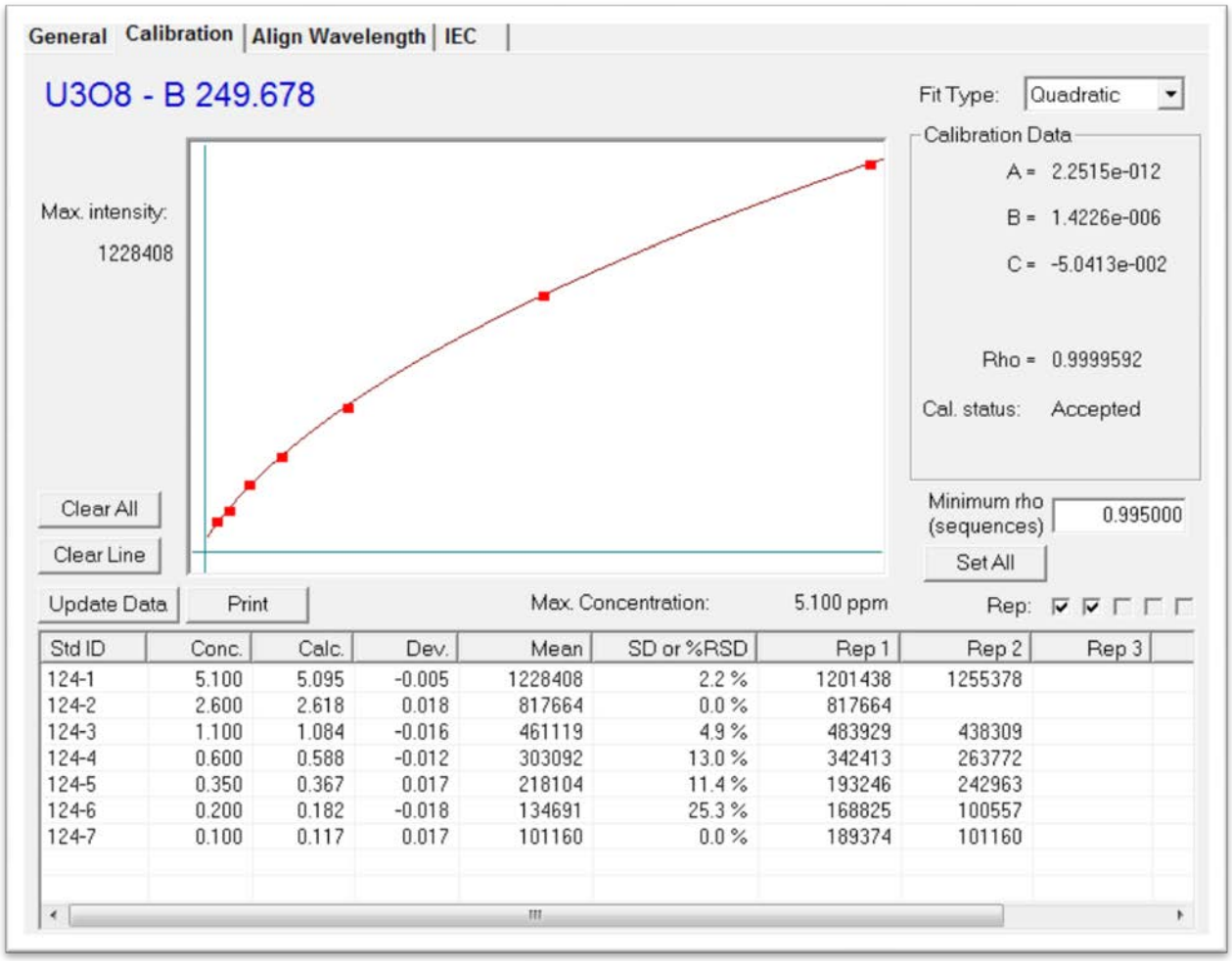
Figure 1 Calibration Curve of B at 249.678 nm in High-Purity Uranium Oxide



Std ID	Conc.	Calc.	Dev.	Mean	SD or %RSD	Rep 1	Rep 2	Rep 3
124-1	5.100	5.095	-0.005	1228408	2.2 %	1201438	1255378	
124-2	2.600	2.618	0.018	817664	0.0 %	817664		
124-3	1.100	1.084	-0.016	461119	4.9 %	483929	438309	
124-4	0.600	0.588	-0.012	303092	13.0 %	342413	263772	
124-5	0.350	0.367	0.017	218104	11.4 %	193246	242963	
124-6	0.200	0.182	-0.018	134691	25.3 %	168825	100557	
124-7	0.100	0.117	0.017	101160	0.0 %	189374	101160	

Results

Detection Limits

A study was performed to determine the instrument's detection limits for the elements of interest. Detection limits were calculated based on 3 times the standard deviation of 7 replicate measurements of CRM 124-7 and are listed in Table II in units of parts per million (ppm). Elements that were measured with a Co internal standard ratio are noted in Table II as well. As results in Table II are based upon a low standard, detection limits are slightly higher than those that could be obtained if pure uranium oxide material was available to make a calibration blank.

An additional, less sensitive wavelength for Na was included in this method (330.232 nm) to widen the dynamic working range for this element. The decrease in sensitivity for this Na wavelength is reflected in its detection limits in Table II.

Table II Detection Limits in High-Purity Uranium Oxide							
Element	Wavelength (nm)	Detection Limit (ppm)	Internal Std Used?	Element	Wavelength (nm)	Detection Limit (ppm)	Internal Std Used?
Ag	328.068	0.12	No	Mg	279.553	3.8	Yes
Al	396.153	0.028	Yes	Mn	257.610	1.2	Yes
B	249.678	0.083	No	Mo	313.259	1.3	Yes
Be	234.861	0.015	Yes	Na	588.995	1.3	No
Bi	306.772	0.50	Yes	Na	330.232	9.0	No
Ca	393.366	4.7	Yes	Ni	305.082	2.7*	Yes
Cd	228.802	0.11	No	Pb	283.307	0.39	No
Cr	284.325	4.8*	Yes	Si	288.160	4.5*	Yes
Cu	324.754	0.32	No	Sn	317.502	0.13	Yes
Fe	248.327	19.5*	Yes	Zn	213.856	0.33	No

*Contaminations present for these elements; actual detection limits should be lower than stated

Conclusions

The analysis of uranium oxide using the **Prodigy DC Arc** demonstrates that the current-controlled DC Arc power supply, combined with the simultaneous data collection of both peak and background data, provides reproducible sample burns that are reflected in the detection limits obtained for trace elements in a uranium oxide matrix.

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