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Danish Atomic Energy Commission
Research Establishment Risö

CHEMISTRY DEPARTMENT

SPECTROCHEMICAL DETERMINATION
OF TRACE IMPURITIES IN URANIUM OXIDE
BY CARRIER DISTILLATION METHOD
USING THE DC ARC CATHODE-CENTRAL REGION

by

A. Aziz and P. Solgaard

August 1974

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<p>Title and author(s)</p> <p>Spectrochemical determination of trace impurities in Uranium oxide by carrier distillation method using the DC arc Cathode-Central region</p> <p>by</p> <p>A. Aziz and P. Solgaard</p>	<p>Date August 1974</p>
<p>15 pages + 5 tables + illustrations</p>	<p>Department or group</p> <p>Chemistry Department</p>
<p>Abstract</p> <p>Spectrochemical determination of various elemental impurities in U_3O_8 is made by direct and carrier distillation method using exposures from full 4 mm arc gap and that from a 4 mm arc strip containing the cathode and central region of the arc from 6 mm arc gap. The spectra from the Cathode-Central region is found free of Uranium spectral background and is suitable for quantitative determination of impurities in U_3O_8. B, Cd, V, Fe, Cr and Pb gives reproducible results when 5% NaF is used as carrier in the Cathode-Central region method measurements while 5% AgCl and 5% of the mixture AgCl + NaF (4:1) is found a suitable carrier for Ni, Co, Mn, Zn and Mo. AgCl, although good for the visual detection of low level of some elements, is found an unsuitable carrier for quantitative analysis because it creates a heavy background from the Uranium spectra. Representative working curves of B and Cd for quantitative analysis are made and at 0.1 ppm concentration level of B and Cd a percent coefficient of variation of ± 7 and ± 9 is found respectively.</p>	<p>Group's own registration number(s)</p>
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INTRODUCTION

The requirement of high purity Uranium compounds for use in the nuclear reactor necessitates the development of methods of analysis capable of detecting and determining parts per million level or less of multielements impurities. The elemental impurities with high neutron absorption crosssection depresses the neutron flux and therefore decrease the efficiency of reactor fuel. Table I illustrates the amount of various elements in ppm which gives a thermal neutron absorption of 0.01% relative to Uranium (19).

Various methods have been used in the determination of trace elements in Uranium and its compounds. The simultaneous detection and determination of a large number of elements in Uranium oxide by emission spectrographic method (1-38) is the most popular and has been used in various laboratories of the world for the past thirty years. Spectrographic methods differing from each other by the special treatment of the Uranium oxide refractory matrix has been used in such an analysis. The notable among these are:

1. Direct burning of U_3O_8 in the DC Arc (12)
2. The chemical separation of impurities from Uranium prior to their excitation (1-11)
3. Concentration of impurities by evaporation-condensation prior to excitation (12-14)
4. Distillation of impurities from the Uranium matrix into the arc plasma using chemical carriers (15-34)
5. Direct cathode region method (35-37)

In the direct burning of Uranium oxide the spectra from the whole arc region is so replete with Uranium lines that it will obscure many of the lines of the impurities. The chemical separation and evaporation-condensation of impurities from the matrix prior to excitation is disadvantageous because of loss of impurities, contamination, and manipulation. However the determination of rare earths and some heavy elements down to one tenth or less of part per million level in U_3O_8 requires the concentration prior to such an analysis. In the carrier distillation method developed first by Scribner and Mullin (15), the carriers like Ga_2O_3 and alkali halides (38-40) added to Uranium oxide distills off the impurities into the arc plasma by their high vapour pressure and lowers the abundance of the atoms or ions spectral lines

of the Uranium on the photographic plate by depressing the plasma temperature (38-40). The method because of its speed and low detection limits for large number of metals has been very much in use in the routine analysis of Uranium compounds. Various carriers and their mixtures have been applied with varying degree of success in order to improve the sensitivity and precision of analysis.

Table I

Absorption of thermal neutrons by various elemental impurities in Uranium

element	neutron cross section (barns)	neutrons absorbed by impurity relative to absorption by equalent weight of Uranium	ppm (U basis) which gives absorption of 0.01% relative to Uranium
Gd	46,617	9,090	0.011
B	762	2,150	0.045
Sm	5,828	1,830	0.050
Eu	4,406	1,100	0.1
Cd	2,537	703	0.14
Co	36.3	19	5
Ag	64.8	18	5.6
Mn	13.2	7.4	14
Ti	5.8	3.6	28
V	5.0	3.1	32
Ni	4.6	2.6	39
Cu	3.9	1.8	56
Cr	3.1	1.7	58
Fe	2.6	1.4	71
Mo	2.7	0.81	127

Recently Avni (35-37) developed a new direct method in which the cathode region - a strip of 0.3 mm - is exposed on the photographic plate instead of the entire arc of 3 or 4 mm normally used. The matrix dense spectra in this method is almost eliminated and an abundancy of impurities spectral lines is obtained when U_3O_8 is excited by a DC arc in the anode without adding any carrier.

At a 6 mm arc gap Avni (35) found the following characteristic arc parameters in the vicinity of the cathode region:

1. The axial temperature gradient reaches its maximum value of 7300°K compared to the value in the anode showing a rise of 800°K .
2. The voltage decreases by 12 volts.
3. The relative intensity normalised to the value found in the anode zone for almost all the impurity elements is about 18 times higher in the cathode region.
4. The relative intensity of the Uranium spectral lines decreases by a factor of 2.5.
5. Free electron density is the highest in the cathode region.
6. The cathode region has lowest Uranium particle concentration.

Attempts were made to use a similar method with our stigmatic spectrograph without limiting ourselves to Sirks focus position. Preliminary work using the spectrum of the cathode region plus part of central region of a total 6 mm arc gap showed the same freedom of heavy Uranium background. The method with these arc parameters is therefore studied in the presence and absence of different carriers for the quantitative determination of some of the common metal impurities in U_3O_8 .

EXPERIMENTAL

Spectrographically pure materials from Johnson and Matthey Ltd., England, are used for the preparation of U_3O_8 standards. U_3O_8 and AgCl are prepared and purified in this laboratory by the method described by UKAEA (17).

Table II

Equipment and operating conditions

Spectrograph	3 meter Baird Atomic-Eagle mount concave grating, model GX-1
Grating	590 grooves/mm
Source	Baird Atomic spectrosource model IW1
Photoprocessor	Jarrell-Ash model JA-3410
Densitometer comparator	Baird Atomic model CBI
Reciprocal linear dispersion	2.72 Å/mm (second order)
Wave length range, Å	2040 - 3440 (2nd order) 4080 - 4550 (1st order)
Spectrographing setting	
Grating angle	9940
Focus	4849
Tilt	9348
Slit width	25 μ
Slit height	2.5 mm
Electrodes	High purity graphite electrodes supplied by Ringsdorff Werke GmbH Bonn-Bad Godesberg, W.Germany
Cathode (counter electrode)	Type RW0063
Anode (sample electrode)	Type RW0044 with pedestal type RW0048
Anode charge	50 mgm with vent hole
Electrode gap	6 mm. The part of the arc gap for exposure is defined by the diaphragm at the grating
Atmosphere	Air
DC arc current	8 Amps
Exposure time	40 sec
Photographic plates	Kodak SA-1, 10x25 cm two plates
Developing	Kodak D-19, 18°C, 3 min

Procedure

The pure oxides of the elements and U_3O_8 are mixed in an agate mortar and heated for 2 hours at $900^{\circ}C$ for complete homogenisation. Series of standards are prepared by dilution with U_3O_8 . The carrier is mixed with the standards in an agate mortar and 50 mgm of this mixture is placed into the anode (sample electrode) crater, pressed and a vent hole is formed with a venting tool. The arc is struck by touching the two electrodes and the arc gap is kept constant to 6 mm by setting the cathode and anode at positions described above in table II and marked on the Arc stand. The samples are arced in triplicate or quadruplicate. The intensity of spectral lines on the photographic plate is measured densitometrically. For quantitative determination only those lines of the elements are considered whose intensities are at least three times higher than their background.

RESULTS AND DISCUSSION

The spectra exposed from the entire 4 mm arc gap and that from the cathode-central zone of the 6 mm arc gap are discussed.

DC-arc excitation with 4 mm Arc gap

The detection limits of various elemental impurities in the U_3O_8 standards when arced in the presence of 5% each of carriers NaF, NaCl, AgCl and their mixture 5% NaF + 5% NaCl and 4% AgCl + 1% NaF are shown in Table III. The spectra is exposed on the photographic plate from the whole of 4 mm arc gap used. It is found that the spectrum over the whole wave length range is masked with high background from Uranium line spectra. The background increases in different carriers in that order



The intensity of spectral lines for B, Cd, V, Pb, Cr and Fe at a certain concentration was found highest in NaF compared to other carriers and their mixture. The chloride carriers, specially AgCl, are the most suitable for elements Ni, Co, Mn and Mo at low concentrations. These observations show that no single carrier or their mixture is suitable for the detection of all the elements to their lowest detection limit. It is seen that chloride and fluoride show different chemical activity in boiling off different

Table III

Detection limit of impurities in U_3O_8 by
carrier distillation method using 4 mm arc gap

Element	Spectral line λ°	Detection limit in ppm (U basis)					
		5% NaF P.w	5% AgCl P.w (Ref.17)	5% NaCl P.w	NaF (1%) AgCl(4%) P.w	NaCl (5%) NaF (5%) P.w	
B	2417.73	0.05	0.5	0.05	0.05	0.1	0.1
Cd	2786.02	0.1	0.5	0.2	0.5	0.5	0.5
Co	3405.12	10	5.0	1.0	10	10	10
	3412.34	10	5.0	-	10	10	10
Mn	2794.82	5.0	1.0	-	1.0	5.0	10
	2576.1	-	-	0.5	-	-	-
Cr	4254.34	5.0	5.0	-	10	5.0	10
	2677.2	-	-	5.0	-	-	-
Cu	3247.54	0.5	0.5	-	1.0	0.5	1.0
Zn	3345.02	10	10	20	20	10	20
Ni	3414.76	20	5.0	-	10	20	20
	3002.5	-	-	0.5	-	-	-
Pb	2833.06	2.0	2.0	-	5.0	2.0	5.0
	2677.2	-	-	1.0	-	-	-
Fe	2483.27	1.0	5.0	-	10	5.0	10.0
	2599.50	-	-	10	-	-	-
Mg	2795.53	0.1	0.5	-	0.5	0.5	0.5
	2779.8	-	-	5.0	-	-	-
Mo	3132.59	10	5.0	0.5	20	10	20
V	3183.98	2.0	2.0	1.0	5	5	5

P.w = Present work

impurity elements when comparing the carrier effect of NaF and NaCl. AgCl and NaCl show different cationic activity, as AgCl boils off more of Uranium and some impurity elements compared to that of NaCl. The sodium compounds are found more favourable for elements of low atomic mass like Mg, B, Si etc. The determination of various elements in NaF is found reproducible compared to other carriers used, showing the stability of the arc in respect of its constant temperature, volatilization and less wandering of the anode spot (38-40). The mixtures of carriers did not give improvement in the detection power over the individual carrier.

DC Arc excitation with 6 mm gap - Exposure from Cathode-Central region of Arc

The spectra from about 4 mm arc containing the entire cathode region and part of central region of the 6 mm Arc gap is found free of Uranium spectral background when U_3O_8 is arced directly without a carrier. The detection limit of various elements in U_3O_8 (Table IV) is found higher than that reported by Avni (36) and the carrier distillation method with 4 mm arc gap (Table III). The high arcing current of 13 Amps and 35 sec exposure time used by Avni in his 0.3 mm cathode region method might be responsible for such low detection limits. A high background was observed with our system when excitation is made with 12 Amps current and 40 sec exposure time. The 8 Amps current and 40 sec exposure time are found the optimum arcing conditions to produce the most intense impurity elements spectra with lowest background.

By incorporating the carriers 5% each of NaF, AgCl and the mixture AgCl + NaF (4:1) in U_3O_8 the detection power of the majority of the elements is increased by a factor of 10 to 100 in comparison to that obtained when U_3O_8 is arced directly. Table IV shows the detection limit of some important common elemental impurities by Cathode-Central region method. The method is found very sensitive for the quantitative determination of B, Cd, Pb, V, Fe, Mg, Cr and Cu in the presence of sodium fluoride carrier with detection levels given in Table IV. Co, Ni, Mn, Zn and Mo can only be detected and determined using the carrier AgCl and mixture AgCl + NaF. A background from Uranium spectra is observed when AgCl is used as carrier in this arcing method but is very much less than that when exposures are made from the entire 4 mm

Table IV

Detection limit of impurities in U_3O_8 by DC arc excitation using Cathode-Central zone of 6 mm arc gap

Element	Spectral line λ°	Detection limit in ppm (U basis)				
		Without carrier	5% NaF	5% AgCl	4% AgCl 1% NaF	Avni without carrier (36)
B	2497.73	0.5	0.01	0.1	0.2	0.1
Cd	2288.02	2.0	0.01	0.1	0.2	0.2
Co	3405.12	20	10	1.0	10	-
	3453.50	-	-	-	-	1.0
Mn	2794.82	10	5.0	0.1	1.0	-
	2576.10	-	-	-	-	0.5
Cr	4254.34	10	0.1	1.0	1.0	1.0
	(1st order)					
Cu	3247.54	0.5	0.1	0.1	0.1	0.2
Zn	3345.02	20	5.0	5.0	5.0	10
Ni	3414.76	20	20	2.0	5.0	-
	3002.49	-	-	-	-	0.5
Pb	2833.06	5.0	0.5	1.0	2.0	1.0
Fe	2483.27	10	0.5	1.0	1.0	1.0
Mg	2795.53	0.5	0.05	0.1	0.1	0.2
Mo	3132.59	10	5.0	0.5	1.0	2.0
V	3183.98	10	0.5	2.0	2.0	5.0
Eu	4435.56	100	50	50	50	15
	(1st order)					
Gd	3362.23	100	50	50	50	15
Sm	4424.34	100	50	50	50	25
	(1st order)					

arc gap. Rare earths impurities like Gd, Sm and Eu could not be detected at such low levels as reported by Avni (37). Therefore to determine the maximum permissible level (0.1 to 0.01 ppm) of these elements in reactor grade Uranium it is necessary to concentrate these by chemical separation from Uranium oxide prior to spectrographic analysis.

Representative working curves for B and Cd were made by arcing U_3O_8 standards in presence of NaF carrier. The results from the two separate runs in duplicate to quadruplicate are reproducible as noted in table V. Fig. 1 represents the working curves from the average value of measured optical density of the spectral lines. A percent coefficient of variation at 0.1 ppm level is found 1.7 and 1.3 for B and Cd respectively. These results show that an internal standard is not needed for B and Cd determination in U_3O_8 . Similar reproducible results without an internal standard are observed for Pb, V, Cr and Fe but an internal standard is needed for other elements determined in presence of AgCl carrier where a large spread in density-concentration curve is observed.

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Table V

Determination of B and Cd in U_3O_8 by
 clean fluoride carrier using Cathode-fall
 region of 6 mm arc gap

Concentration in (ppm)	Optical Density $\times 10^4$ Background correction*				+ coefficient of variation	
	B ^{2497.73}		Cd ^{2288.02}		B	Cd
	Run I	Run II	Run I	Run II		
1.0	140	130	64	55		
	132	136	57	52		
		128		60		
0.5	91	88	47	46		
	84	85	46	50		
		93		45		
0.1	43	34	28	32	± 7	± 9
	36	32	31	28		
	39	37	25	26		
	42	39	27	30		
0.033	22	19	19	18		
	24	20	20	17		
		25		21		
0.01	14	13	20	13		
	12	15	15	16		
		14		14		

* Constant background 3 to 4 is observed with both lines.

+ % coefficient of variation = $\frac{100}{\bar{x}} \sqrt{\frac{\sum d^2}{n-1}}$

where \bar{x} = average density

d = difference from mean

n = number of determinations

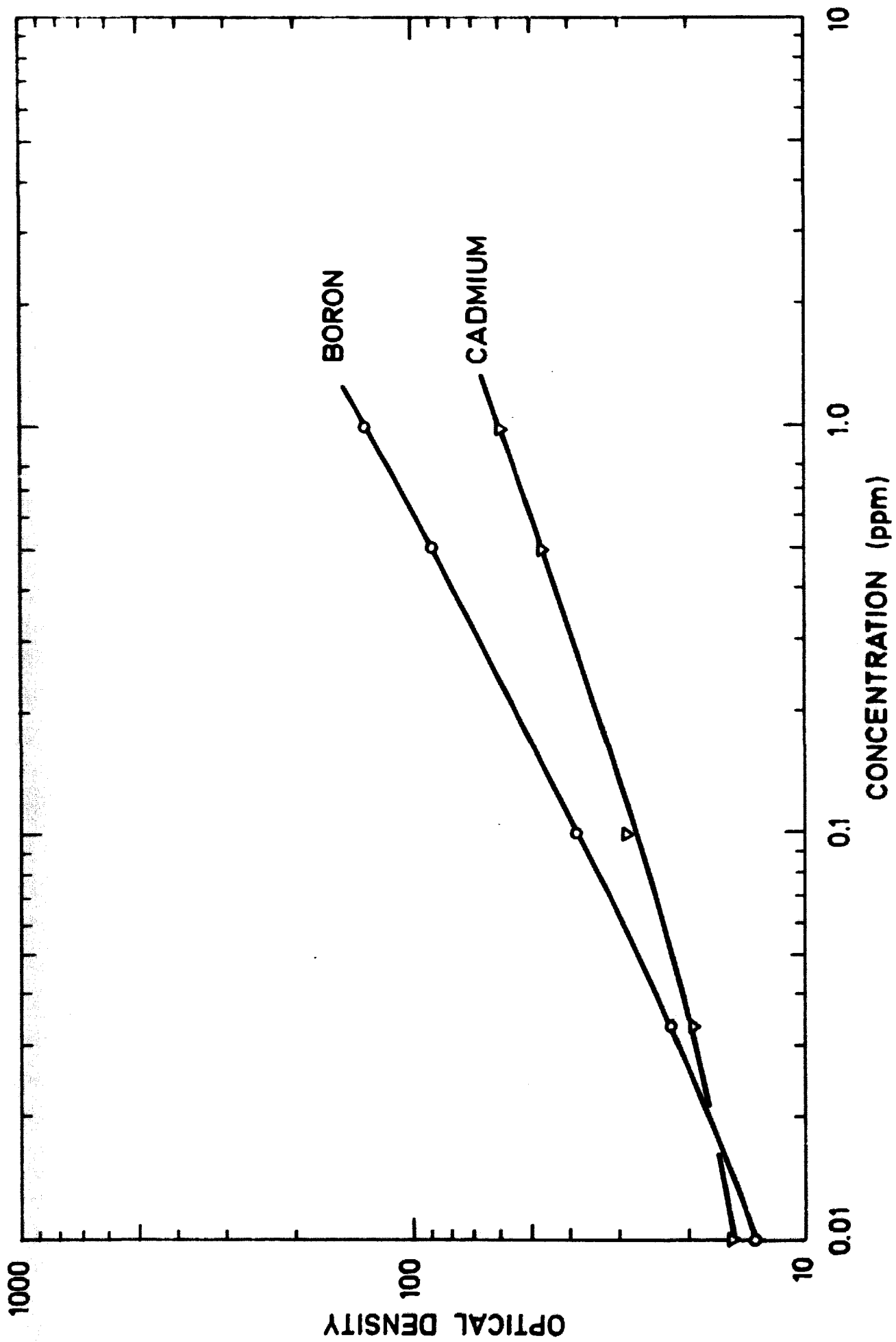


Fig.1 Working curve for B and Cd

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