

## SPECTROCHEMICAL PROCEDURES FOR ANALYTICAL CONTROL OF EIGHTEEN GENERAL IMPURITIES AND FOURTEEN RARE EARTH ELEMENTS IN $UO_2$ PELLETS AND OTHER URANIUM-BASE MATERIALS.

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A comparative study of the efficiency of five spectrochemical carriers for the direct quantitative spectrographic analysis of eighteen trace elements in uranium-base materials is presented. The volatility behavior of the impurities was verified by means of the moving plate technique. For more accurate comparisons a computer program was introduced to calculate the relative areas of the volatilization curves. Depending on the elements the best results were obtained with 4%  $In_2O_3$ , 6%  $AgCl$  and 6%  $NaF$  in a  $U_3O_8$  matrix. The precision is approximately in the range 4-20%.

The rare earth elements must follow a previous enrichment procedure and separation from uranium so as to get the required sensitivity. The method is based upon the sorption of thorium and rare earths when acid solution of uranyl nitrate, 0,3M in HF, is percolated through a small column of alumina / ( $Al_2O_3$ ), the uranyl ion being not sorbed. The technique of excitation involves a total burning of the sample in a 17 amp. direct current arc. The sample is not mixed with graphite or any other spectrochemical buffer. A controlled atmosphere in the arc region was not used. The coefficient of variation for Pr, Ho, Dy, Er, Tm, Lu, Gd and Tb amounts to  $\pm 10\%$ .

### 1. INTRODUCTION

The determination of impurities in the ppm and fractions of ppm ranges in a variety of nuclear / grade uranium compounds is a routine requirement of any atomic energy program and many spectrochemical procedures have been developed for this purpose. Because of the complex emission spectrum of the uranium, the techniques used must, in general provide either for the removal of uranium prior / to excitation or prevent the uranium in the sample from entering the arc region. Chemical separation methods are generally used when required detection limits cannot be reached with more / direct spectrographic approaches.

The most used direct method for determining / the so-called "general impurities" has been carrier distillation. Adequate detection limits for many impurities of nuclear interest, particularly for those having large neutron-capture cross-sections, can be obtained with some form of the carrier distillation technique.

The introduction of a carrier is useful because when a rather large amount of it is evaporated the temperature of the sample is maintained almost constant (in general, it does not exceed 2000 -2200°C), such that the uranium oxide does not enter the flame of the arc.

The first application of the carrier distillation technique to the analysis of uranium-base materials was reported by Scribner and Mullin in 1946. The sample was converted to the refractory oxide  $U_3O_8$  and gallium oxide was added as a carrier (2 parts  $Ga_2O_3$ , 98 parts  $U_3O_8$ ). Besides 2% / gallium oxide, many other compounds have been / used, such as 5%  $NaF$ <sup>(21,7)</sup>, 5%  $AgCl$ <sup>(3,22)</sup>, 10%  $AgCl$ <sup>(11)</sup>, 7%  $NaCl$ <sup>(22)</sup>, 35%  $ZnO$ <sup>(2)</sup>, and 12%  $NH_4F$ <sup>(25)</sup>. Mixtures of carriers have also been reported: 4% (4 parts  $AgCl$ , 1 part  $NaF$ <sup>(3)</sup>), 20% / (4 parts  $AgCl$ , 1 part  $AgF$ <sup>(14)</sup>), 4% (1 part  $SrF_2$ , 2 parts  $Ga_2O_3$ <sup>(8)</sup>). For the following mixtures details on their rate or proportion among the car-

riers were not available: (6  $AgCl$ , 2  $Ga_2O_3$ , 1  $NaF$ <sup>(4)</sup>), (6  $AgCl$ , 2  $SrF_2$ )<sup>(10)</sup>, (3  $AgCl$ , 3  $AgF$ )<sup>(16)</sup>, ( $AgCl$ ,  $LiF$ )<sup>(6)</sup> and ( $AgCl$ ,  $LiF$ , graphite) -<sup>(17)</sup>.

The rare earths are usually analysed as a separate group. The generally low level of concentration and the highly refractory nature of the rare earth elements in the normal uranium products submitted to analysis make any direct spectrographic method of determination unpractical. To overcome these difficulties, a procedure of separation and concentration must be used. After removal of the uranium and pre-concentration of the rare earths they may be determined by a number of different - spectrographic methods. Very low detection limits can be achieved by varying the original sample - size.

The most frequently outlined methods for the separation of rare earths from uranium for spectrochemical purpose include precipitation (co-precipitation with carriers)<sup>(16)</sup>, solvent extraction<sup>(24,26,18)</sup>, ion exchange<sup>(5,15)</sup> and other chromatographic methods<sup>(23,9)</sup>. One of the most widely used technique is the solvent extraction of / uranium with tributyl phosphate (TBP)<sup>(24,26,18)</sup>.

Several techniques have been used for the spectrochemical excitation of the rare earths. The most usual procedure is that of burning the sample placed in a cup type graphite electrode, in a d.c. arc<sup>(24,18)</sup>. In this case, the residue is usually mixed with graphite, which acts as a buffer. The cyanogen bands can be eliminated by the d.c.<sup>(20,23)</sup>. The copper spark method has also been used<sup>(12)</sup>. Under the carrier distillation technique the solution containing the rare earths can be dropped and dried on graphite powder mixed / with a proper carrier<sup>(13,19)</sup>.

### 2. PROPOSED METHOD FOR THE DETERMINATION OF EIGHTEEN GENERAL IMPURITIES IN $UO_2$ -PELLETS AND OTHER URANIUM-BASE MATERIALS.

A carrier distillation method was elected for / this purpose because it provides the best combination of versatility, sensitivity and precision.

### 2.1. Studies on five spectrochemical carriers.

The relative effectiveness of five spectrochemical carriers related to the volatilization behavior of eighteen trace elements from  $U_3O_8$  matrices was studied by means of the moving plate technique. The carriers LiF, NaF,  $In_2O_3$  and AgCl were tried in the concentrations of 2%, 4% and 6%. The final aim of this study was the selection of the best / carriers for the determination of trace amounts / of Ag, Al, B, Bi, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, Si, Sn, V and Zn in any uranium compound / convertible to a  $U_3O_8$  matrix.

For more accurate comparisons a computer program was introduced to calculate the relative areas of the volatilization curves. In a first approach, / was may consider that the larger the area, the / greater sensitivity. Results are shown in Table 1, 2 and 3.

The results shown in Tables 1, 2 and 3 are not absolute. It means that the largest area may not correspond to the best carrier or the greatest / sensitivity. Nevertheless, the volatilization / curves or their corresponding relative areas give the researcher a first approach for selecting a more specific group of carriers and the elements which may be determined with good sensitivity. Various experiments were done before pointing out the carriers to be used. Finally, the eighteen / elements were distributed in three groups:

- I. 6% AgCl : Cd, Cr, Fe, Mg, Mo, Ni and Zn.
- II. 6% NaF : Ag, Al, Bi, Cu, Pb, Sn and V.
- III. 4%  $In_2O_3$ : B, Mn, P and Si.

TABLE 1

Relative areas of the volatilization curves integrated from 0 to 40 sec. Concentration of each carrier:2%.

Element	Carrier				
	LiF	NaF	$In_2O_3$	$Ga_2O_3$	AgCl
Ag	34,2	25,1	24,6	19	----
Al	21,2	28,9	----	----	8,1
B	10,4	12,7	24,7	16,3	20,1
Bi	29	28,5	23,6	26	23,3
Cd	2,4	2,5	8,1	4,8	6,2
Cr	4,7	----	8,9	11,3	----
Cu	39,4	46,4	39,1	40,3	39,8
Fe	18,6	22,8	25,9	21,4	19
Mg	16,4	----	10,3	11,7	3,2
Mn	16,4	25,6	32,6	30,1	23,5
Mo	----	6,3	12,3	6,1	6,9
Ni	7,8	8,7	16,1	11,1	19,6
P	----	6,8	14	7,7	11,2
Pb	35,8	29,6	17,1	23,9	14,7
Si	36,5	41,4	42	31,1	21,7
Sn	26,7	33,6	27,5	28	22,2
V	21,1	25,1	1,1	----	----
Zn	10,3	10,6	18,2	14,1	16,2

- : Spectrum not recorded because of low volatilization

### 2.2. Preparation of standards and samples

The standards were bought from New Brunswick - Laboratory (N.Jersey, USA) and correspond to the analyzed samples numbered from 95-1 to 95-7. The  $U_3O_8$  samples 95-1 to 95-6 are synthetic materials prepared by adding solutions of the impurity elements to pure  $U_3O_8$ . Sample n° 95-7 is the matrix material to which the impurities were added.

Any uranium sample can be initially converted / to  $U_3O_8$ . This can be easily done by ignition in a muffle furnace at 900°C for 1 or 2 hours such as for uranium metal, ammonium diuranate, uranium / dioxide and uranium trioxide. The conversion of / halide salts by this procedure, such as uranium /

tetrafluoride, may result in losses of volatile / impurities as halides. To avoid losses, the salts may be hydrolyzed and the ignition completed as before.

To minimize the matrix effect arising from samples and standards having different physical properties, all of the standards and  $U_3O_8$  samples / are then dissolved with nitric acid. The solutions are dried slowly and the residues are ignited / again to  $U_3O_8$  as before. In the case of  $UO_2$  pellets or powder and metallic uranium the transformation to  $U_3O_8$ , prior to the dissolution with nitric acid, is not necessary and the samples can be directly dissolved with acid.

Details on mixing standards and samples with /

TABLE 2

Relative areas of the volatilization curves integrated from 0 to 40 sec. Concentration of each carrier:4%

Element	Carrier				
	LiF	NaF	In <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	AgCl
Ag	31,7	39,8	32,8	11,9	----
Al	20,7	38,8	----	----	----
B	10	10,8	21,4	16,5	20,4
Bi	27,2	39,8	37,3	20,3	25,3
Cd	2,9	6,3	11,3	2,7	4,9
Cr	9,4	9,5	13,1	7	7,6
Cu	33,4	39,6	54,3	31,1	47
Fe	18,3	25,6	34,3	16,8	31,8
Mg	6,4	13,5	19,1	6,9	5,8
Mn	13,1	17,1	43,9	23,2	34,7
Mo	----	----	15,9	----	11,8
Ni	0,8	1,4	21,1	----	30,9
P	----	----	13,5	6	9,8
Pb	36,2	42,5	32,1	20,2	16,1
Si	38,1	31	62,1	23	17,1
Sn	42	43,9	40,3	24,5	28
V	26,8	32,1	1,5	----	12,5
Zn	2	13,4	24,7	----	15,1

: as described in Table 1.

TABLE 3

Relative areas of the volatilization curves integrated from 0 to 40 sec. Concentration of each carrier: 6%.

Element	Carrier				
	LiF	NaF	In <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	AgCl
Ag	10,9	35,4	31	----	----
Al	----	0,4	----	----	----
B	21,2	10,8	18,9	14,8	22,7
Bi	10,8	22,7	40,3	18,8	27,1
Cd	4	5	9,1	----	5,5
Cr	----	13,9	10,5	----	14,9
Cu	29,1	33,3	24,6	27	----
Fe	5,5	29,8	25,4	12	41,7
Mg	----	11,5	11,5	----	12,7
Mn	9,9	28,1	32,4	18,4	43
Mo	----	3	16,4	----	19,1
Ni	----	13,6	9,5	----	46,4
P	14,1	----	13,6	4,6	5
Pb	12,4	32,3	33,5	18,4	17,4
Si	26,8	45	38,6	17,7	9,4
Sn	13,6	42,6	38,1	26	31
V	----	29	1,3	----	26,9
Zn	7,8	8,8	22,9	----	23,1

- : as described in Table 1

carriers, filling up the electrodes and forming / the vent hole in the U<sub>3</sub>O<sub>8</sub> charge are well known.

### 2.3. Equipments and experimental conditions.

Spectrograph : Jarrel-Ash 3.4 meter spectrograph having a 15,000 lines per inch grating. This grating. This grating gives a reciprocal linear dispersion of 2.47 Å / mm in the second order.

Excitation Source: Jarrel-Ash Standard Varisour ce.

Microphotometer: Non-recording Jarrel-Ash Micro-photometer.

Emulsion and Processing: Kodak Spectrum Analysis n° 1 (SA-1). The plate was developed in D-19 developer for 3 minutes at 18°C.

Electrodes: Pre-formed graphite electrodes supplied by National Carbon Company.

a. upper - SPK-L-4236

b. lower - AGKSP-9066 ("Scribner-Mullins" type)

c. pedestal-AGKSP-9068

Grating Angle: 10.00, to cover the range 2200-3450 A in the second order.

Voltage: 230 volts.

Current: 10 amp., d.c. arc.

Pre-burn period: 5 sec.

Exposure time: 35 sec.

Charge: 120 mg ( $U_3O_8$  + carrier)

Slit width: 10 $\mu$

Analytical Gap: 4 mm

Filter: none.

## 2.4. Results

This procedure provides for the determination of eighteen trace elements in nuclear grade uranium compounds and fulfills the requirements of / sensitivities for the analytical control of such materials. The use of an internal-standard (Co) did not introduce appropriate corrections in the working curves. The analytical lines, the concentration ranges and the precision data are given in Table 4. The precision has been calculated in terms of coefficient of variation from twenty values of concentrations.

## 3. PROPOSED METHOD FOR THE DETERMINATION OF FOURTEEN RARE EARTH ELEMENTS IN NUCLEAR GRADE URANIUM COMPOUNDS.

### 3.1. Separation of rare earths from uranium.

The separation and concentration of microquantities of rare earths from uranium, as a group, is achieved by the technique published by Abrão <sup>(1)</sup>. The method is simple and efficient and is based upon the sorption of rare earth elements / on an alumina column from uranyl nitrate 0.3M in HF. The method allows complete separation from / uranium and the great majority of all commonly / associated elements, except thorium which is also retained on the alumina. The experiments done by Abrão were performed for the separation of / thorium and lanthanides from uranyl nitrate of / 50-250 g/l  $U_3O_8$  and adjusted to be 0.3M in HF / and pH 0.5 to 2.5. The retention of thorium and rare earths was higher than 98%. After the percolation of the uranyl solution through a 3-5 ml  $Al_2O_3$  column, a washing step with 1% HF solution is followed for the complete elimination of uranium. The elution of the rare earths and thorium from  $Al_2O_3$  can be achieved with hot 1M  $HNO_3$  or 1 M HCl, 50-60 ml being enough.

### 3.2. Preparation of standards and samples.

The standards are prepared on a  $La_2O_3$  base. / For lanthanum determination another set of standards is prepared, in a  $Y_2O_3$  matrix. Lanthanum / and yttrium are both used as internal standards. A concentrated standard, containing 2% of each rare earth, is prepared by dissolving specpure / lanthanum oxide (or  $Y_2O_3$ ) with nitric acid, adding proper amounts of standard solutions of rare earths, precipitating with a saturated solution of oxalic acid, filtering and igniting at 800°C for 1 hour. Lower standards are prepared by successive dilutions with  $La_2O_3$  or  $Y_2O_3$ . Following the same procedure as described above.

To a sample solution, containing the eluted / rare earths, one's adds 5 mg of lanthanum oxide

the coprecipitation of the rare earths. After / precipitating the oxalates the residue is filtered off, dried and ignited at 800°C for 1 hour.

### 3.3. Spectrochemical procedure

Five milligrams of the sample (residue ignited at 800°C) or standard are placed in the crater of a shallow cup electrode (AGKSP-4031, National Carbon Co.). The electrode is tapped to distribute the charge evenly and the mass is compressed with the aid of a stainless steel small rod. For the very refractory nature of the rare earth elements a total burning method of excitation was selected. The sample is not mixed with graphite or any other buffer..

A serious problem of graphite in air is the / obscuring of spectral region 3600 to 4200 A by / the cyanogen bands. Many of the more sensitive / rare earth lines may be thereby hidden. The intensity of the cyanogen bands is greatly diminished, or even eliminated, if the graphite arc is maintained in a controlled atmosphere chamber, free from nitrogen. A mixture of 80% Ar-20%  $O_2$  has / been widely used for this purpose but was not / available by the time this work was developed. Nevertheless, a very careful selection of analytical lines was, fortunately, enough for the / success of the results. The use of a controlled / atmosphere, although leads the suppression of the CN bands, may cause a weakening of the spectral lines

### 3.4. Experimental Conditions.

Spectrograph, Excitation Source, Microphotometer, Emulsion and Processing: as described in 2.3.

Electrodes : pre-formed graphite electrodes - supplied by National Carbon Co.

- a. upper - SPK-L-4236
- b. lower - AGKSP-4031 ("shallow cup" type)
- c. pedestal -AGKSP-L-3919

Grating Angle: 13.00, to cover the range 3100-4350 A in second order.

Voltage: 230 volts.

Current: 17 amp., d.c. arc.

Pre-burn period: none.

Exposure time: 60 sec.

Charge: 5 mg.

Slit width: 10  $\mu$ .

Analytical gap : 4 mm.

Filter: Seven Step Filter, placed for 100 and 42,1 % transmission.

### 3.5. Precision

Ten micrograms of each rare earth was added to an uranyl nitrate solution, free from rare / earths, containing 100 g U (0,1  $\mu$ g / g U). This solution was submitted to the  $Al_2O_3$  chromatographic separation method, being the final residue excited according to the proposed spectrochemical procedure. This experiment was repeated ten times. The results are shown in Table 5.

### 3.6. Results

The proposed separation method and spectrochemical procedure can be applied to the determination of fourteen rare earth elements in a va-

is good considering that most of the rare earths exhibit complex but weak spectra. The concentration ranges will vary depending on the amount of uranium available for the separation and concentration step. A hundred grams of metallic uranium

or an equivalent amount of another compound are quite suitable for determining the rare earths at low level concentrations. The analytical lines internal standard, filter and concentration ranges are given in Table 6.

TABLE 4  
Analytical Lines, Concentration Ranges and Precision

Element	Wavelength (Å)	Concentration Range (ppm/U)	Coefficient of Variation (%)
Ag	3280.68	0.2 - 5.1	20.1
Al	2567.99	4 - 500	5.8
B	2497.73	0.4 - 0.6	6.7
Bi	3067.72	2 - 50	11
Cd	2288.02	0.15 - 5	11.1
Cr	2843.25	3 - 95	18
Cu	3273.96	1.5 - 52	19.8
Fe	3047.60	14 - 520	11.6
Mg	2795.53	3 - 101	14.7
Mn	2794.82	1 - 54	11.1
Mo	3132.59	0.4 - 51	15.8
Ni	3050.82	2 - 110	15.3
P	2553.28	25 - 500	3.8
Pb	2833.06	2 - 50	3.4
Si	2514.32	6 - 260	9.5
Sn	2839.99	1.2 - 50	14.3
V	3183.98	3 - 100	6.6
Zn	3345.02	10 - 500	13.1

TABLE 5  
Precision of the method

Element	ppm / U		Coefficient of Variation (%)
	Added	Found	
Dy	0.10	0.10 ± 0.01	10.0
Ce	0.10	0.12 ± 0.03	25.0
Nd	0.10	0.11 ± 0.03	27.3
Ho	0.10	0.097 ± 0.01	10.3
Tb	0.10	0.089 ± 0.01	11.2
Er	0.10	0.10 ± 0.008	8.0
Sm	0.10	0.09 ± 0.03	33.3
Pr	0.10	0.10 ± 0.008	8.0
Tm	0.10	0.11 ± 0.009	8.2
Lu	0.10	0.11 ± 0.01	9.1
Gd	0.10	0.098 ± 0.09	9.2
Yb	0.10	0.10 ± 0.02	20.0

TABLE 6

Analytical lines, internal standard, filter and concentration ranges (for a 100g U sample size)

Analytical Lines	Internal Standards Lines	Filter (% Transmission)	Concentration Ranges (ppm/U)
Eu 2727.78	La 2695.47	42.1	0.005 - 0.5
La 3265.67	Y 3280.91	42.1	0.01 - 0.5
Lu 3312.11	La 3772.02	42.1	0.005 - 0.25
Tm 3362.62	La 3701.81	42.1	0.005 - 0.25
Gd 3422.47	La 3701.81	42.1	0.005 - 0.25
Yb 3464.36	La 3672.02	42.1	0.005 - 0.25
Tb 3676.35	La 3701.81	42.1	0.01 - 0.5
Er 3692.64	La 3701.81	42.1	0.005 - 0.25
Sm 3885.29	La 3701.81	42.1	0.01 - 0.5
Pr 3908.43	La 4036.59	42.1	0.01 - 0.5
Ce 3999.24	La 4036.59	100	0.01 - 0.5
Dy 4000.48	La 4036.59	42.1	0.01 - 1.5
Nd 4061.09	La 4036.59	100	0.01 - 0.5
Ho 4103.84	La 4104.87	100	0.01 - 0.25

## 4. DISCUSSION

The results of sensitivity and precision obtained with both procedures are quite satisfactory for the analytical control of impurities at low level concentrations in uranium compounds of nuclear interest.

Better detection limits could be reached for some elements, such as V, Al and Si, by using the same proposed experimental conditions, but standards lower than 95-7 are not available. Although gallium oxide is still used in many laboratories, new carriers have been continuously introduced so that better precision and higher sensitivities can be achieved. 4% In<sub>2</sub>O<sub>3</sub>, 6% AgCl and 6% NaF have been extensively used in our laboratory for spectrochemical analysis of general impurities in UO<sub>2</sub>-pellets and nuclear grade ammonium diuranate.

The procedure for separating the rare earths is limited by the concentration of thorium and rare earths in the uranyl nitrate solutions since the presence of HF starts the precipitation of their fluorides, Abrão<sup>(1)</sup> concluded that when the thorium or rare earths are above 20 ppm in the uranyl nitrate solutions of 100-200 g/l U<sub>3</sub>O<sub>8</sub> the corresponding fluorides begin to precipitate 20-30 minutes after the addition of HF. Nevertheless, most of the samples submitted to spectrochemical analysis exhibit a total concentration of thorium and rare earths lower than 20 ppm. The presence of thorium in such low concentrations does not interfere in the spectrochemical procedure. Like for general impurities, the proposed method for the determination of rare earths has been applied to a number of different uranium compounds, such as UO<sub>2</sub>-pellets or powder, U<sub>3</sub>O<sub>8</sub> and ammonium diuranate.

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#### Discussion:

B. Riley (Combust.Eng.-Windsor, USA)

Have you obtained any variability in the proportion of the rare earths from various sources of yellow cake? I ask this because the rare earth analysis is expensive and can delay production. Can one rare earth element be used as a tracer for the others?

A.R. Lordello (Inst.d.En.At.-Sao Paulo, Bras.)

The total amounts of rare earths may vary from one source to another but the proportion among them remains, to some extent almost constant and the determination of one rare earth may be used as a rough estimation for the others.