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Determination of isotopic composition and concentration of uranium and boron by thermal ionization mass spectrometric isotopic dilution technique

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Abstract: In this study, the determination of isotopic composition and concentration of uranium and boron by mass spectrometric isotopic dilution have been performed .The isotopic composition was measured using thermal ionization mass spectrometer methodology employing U-233 and B-10 as spike isotope standards. The accuracy and reproducibility of the isotopic ratio and concentration measurements were evaluated.

Keywords: Mass Spectrometry, Boron Isotopes, Uranium Isotopes, Isotope Dilution Technique

1. Introduction

Boron and uranium are extremely important elements in the field of nuclear science researches, due to the nuclear fuel backbone of uranium and the ^{10}B (n,α) ^{7}Li neutron capture reaction [1]. Furthermore, boron is used in a primary coolant system in pressurized water reactors in the form of boric acid to control the reactivity in the core [2]. Accordingly, the precise quantification of their isotopic composition is of great interest in nuclear industry and also in environmental studies [3] .Isotope dilution technique (IDT) has been extensively employed by several authors for the determination of boron [4-7] and uranium [8-10].

The key stipulation of IDT analysis is existence of at least two stable isotopes for the element under consideration, because the method is based on the ratios of the isotopes [11-12] .This limitation, however, is somewhat less restrictive because a number of elements have artificial isotopes of long half-life which undergo negligible decay over the duration of the determination. The stable isotope dilution method can be used for the analysis of about 80% of the elements. The sensitivity of the method varies from element to another, from a few μg to 10^{-3} gm or even less.

In step with development of mass spectrometry, Isotopic dilution technique has found widespread application in solving complicated analytical problems, in the determination of geological age, in establishing yields of fission products and conditions of radioactive splitting and in studying a number of other nuclides as burn up monitors [13-15] for the burn up determination of the isotopic composition of fissile elements in the initial and irradiated fuel or the measurement of some stable fission products which serve as burn up monitors.

2. Experimental

2.1. Apparatus

Thermal ionization mass spectrometer (MAT 261), Finnegan Mat Co. (Germany)

The conditions for boron isotope analysis were as follows:

The applied current on evaporation and ionization filaments was 1.5-1.7 A

Temperature range 750-1000 ^{0}C

Ion measured $Na_2BO_2^+$

Mass: 88 correspond to $Na_2B^{10}O_2^+$

: 89 correspond to $Na_2B^{11}O_2^+$

The currents of evaporation and ionization filaments were step wise increased (0.2A every 3 min.) so a stable and intense isotope peak of B^{10} and B^{11} is reached in a period of twenty minutes [16].

The experimental parameters for uranium isotopes determination were as follows:

Applied current: evaporation filament 2 A
Ionization filament 5.6 A
Ion measured: U^+
Masses: 233, 234, 235 and 238
Pilot isotope: 238

2.2. Boron Measurement Reagents

National Bureau of Standards (NBS) reference material of boron was employed for this type of analysis and it includes the following:

NBS 951 boric acid with the following certificate of analysis: H_3BO_3, acidimetric assay, wt. % 100.00 ± 0.10
Absolute abundance ratio, B^{10}/B^{11} 0.2473 ± 0.0002
Boron 10, Atom% 19.827 ± 0.013
Boron 11, Atom% 80.173 ± 0.013

NBS 952 (Enriched boric acid) used as spike with the following specifications:

Absolute abundance ratio B^{10}/B^{11} 18.80 ± 0.02
Boron 10, Atom% 94.949 ± 0.005
Boron 11, Atom% 5.051 ± 0.005
H_3BO_3, acidimetric assay, wt. % 99.97 ± 0.02

2.3. Boron Measurement Procedure

Boric acid solution (3400 ppm boron) was prepared by dissolving 0.1034 gm of certified NBS 951 boron standard in distilled water and then was titrated with 0.05 M NaOH to reach a pH range of 8-8.5 using Hanna HI2209 pH meter. This range of acidity value is very essential to ensure complete conversion of boric acid to sodium tetraborate according to the following stoichiometric equation:

$$4H_3BO_3 + 2NaOH \rightarrow Na_2B_4O_7.7H_2O$$

The formation of sodium borate is necessary [17-18] and was performed completely since in thermal ionization mass spectrometer, the conversion of $Na_2B_40_7$ gives almost exclusively $Na_2BO_2^+$ ions having the masses 88 (B^{10}) and 89 (B^{11}). Similarly another solution of NBS boron isotope standard No.952 (spike) was prepared (3151 ppm) for the purpose of isotopic ratio measurements of samples of unknown isotopic abundance and also to measure the concentration using the isotopic dilution technique. An aliquot of 14 μg of the above mentioned boron standard was loaded on the rhenium filament of the mass spectrometer, and the isotopic ratio measurements of boron (B^{10}/B^{11}) were conducted.

2.4. Uranium Measurement Reagents

Uranium secondary standards of different enrichments (0.32, 0.72, 10% U^{238})

Spike standard of U^{233}, mass analysis expressed as atom percent:

U^{233} 99.7035 ± 0.0005
U^{234} 0.2355 ± 0.0001
U^{235} 0.0125 ± 0.0001
U^{236} 0.00
U^{238} 0.00485 ± 0.0002

2.5. Uranium Measurement Procedure

A series of different concentrations of uranium solutions (natural isotopic abundance) were prepared using uranyl nitrate hexahydrate dissolved in l M HNO_3, After complete loading of uranium samples on the rhenium thermal ionization filaments (melting point ~3180C°), the magazine, holding 13 filaments, was then inserted in the ion source chamber and the analyzer head was evacuated to a workable pressure of ~ 10^{-7} mbar.

3. Results

3.1. Boron Measurements

Precision and accuracy of boron measurements were calculated and compared with the certified value as shown in Table 1. To evaluate the net peak heights of the masses 88 and 89, a correction was made for oxygen-17 portions in the mass 89 which corresponds to the B^{11} isotope in the ion $Na_2B^{11}O_2^+$.

The formula applied for such correction is listed below [19]:

$$(B^{10}/B^{11})_{\text{corrected value}} = \frac{(B^{10}/B^{11})_{\text{measured}}}{1 - (B^{10}/B^{11})_{\text{measured}} \text{ x } 0.00079}$$

However for the application of isotopic dilution technique, a series of boron mixtures were prepared by mixing a known aliquot of spike solution (3151 ppm boron) with certain portion of freshly prepared standard solution (3400 ppm boron) exploiting N.B.S boron standard No.951. The mixture was chosen to represent a series of different ratios of the standard to the spike as shown in Table 2. For the calculation of boron concentration in the standard (taken as unknown), the following equation is usually used for isotopic dilution analysis [20].

$$Cx = Cs \cdot \frac{ms}{mp} \cdot \frac{Mp}{Ms} \cdot \frac{H^s_{10}}{H^p_{11}} \cdot \frac{[(1/V_{10})_{mix} - (1/V_{10})_s)]}{[1 - (V_{10})_p/(V_{10})_{mix}]}$$

Where
Cx = Boron concentration in the standard (unknown) in $(\frac{\text{mg boron}}{\text{gm. sol.}})$
Cs = Boron concentration in the spike (NBS-952) in $(\frac{\text{mg boron}}{\text{gm. sol.}})$
ms = Amount of spike solution (weight) in mg
mp = Amount of standard solution (weight) in mg
Mp = mean atomic weight of boron in the unknown solution
Ms = mean atomic weight of boron in the spike solution
H^S_{10} = Atomic % B^{10} in the standard (unknown)
H^P_{11} = Atomic % B^{11} in the spike
$(v_{10})_P$ = Atomic ratio of B^{10}/B^{11} in the unknown
$(v_{10})_S$ = Atomic ratio of B^{10}/B^{11} in the spike

$(v_{10})_{mix}$ = Atomic ratio of B^{10}/B^{11} in the mixture

The isotopic ratio measurements of six mixtures were determined by the mass spectrometer and the boron isotope ratios (B^{10}/B^{11}) were also corrected for the presence of oxygen-17. The concentration of boron samples determined by isotopic dilution method is compared with the given values as shown in Table 3.

3.1. Uranium Measurements

Isotopic composition measurements for each concentration of uranium were performed and the isotopic ratios, abundance and atom% were then calculated along with the standard deviation as shown in Tables 4 and 5. For further scrutinization the impact of uranium concentration on the precision and accuracy of isotopic ratio determination has been studied employing a series of different uranium concentrations of similar enrichment value as the results are presented in Table 6. Furthermore, different uranium enrichment solutions were prepared with the same uranium concentration (2000 ppm U) and then an amount of 10 µg of each sample was loaded onto the rhenium evaporation filament. The isotopic ratio determinations are shown in Table 6.

For isotopic dilution analysis of uranium, two mixtures were prepared by mixing U-233 spike standard (1000 ppm U) with a natural abundance uranium secondary standard (2422 ppm U). The mixture then evaporated to dryness and redissolved in 1 M nitric acid to ensure a complete isotopic exchange. The amount taken and the measured ratios of (U^{233}/U^{238}) of these two mixtures are shown in Table 7. Other isotopic ratios were also calculated including U^{234}/U^{238}, $U235/U^{238}$, $U236/U^{238}$ and U^{235}/U^{233}. Furthermore 238/238 has been calculated according to the following expression [21]:

$$238/238 = \left[\left(\frac{234}{235}\right)\left(\frac{235}{238}\right)\right] / (234/238)$$

The concentration of the spike solution taken as unknown were calculated using the following formula:

$$[U^{233}] = \frac{Rm - Ri}{1 - (\frac{Rm}{Rp})} \cdot \frac{Wi^{238}}{Wp^{233}} \cdot [U^{238}]$$

Where

$$R = \frac{U^{233}}{U^{238}}$$

Rm = R in mixture

Ri = R in spike (taken as unknown)

$Ri = \frac{U^{233}}{U^{238}}$ in spike (U^{238} in this work)

$Rp = \frac{U^{233}}{U^{238}}$ in the unknown (spike U^{233})

w = weight (wt)

i = spike (U^{238}), g

P = unknown (U^{233}), g

4. Discussion

For isotopic analysis of boron which is performed with thermionic mass spectrometer, precise value maintenance of filament current is essential to produce a stable intense peak and to avoid or minimize the isotopic fractionation usually appears in the analysis of light element using a thermal ionization mass spectrometer [22]. The results of analysis of two N.B.S boron standards as shown in Table 1, represents the reproducibility and accuracy of boron isotope measurements. The reproducibility of isotopic composition determination depends on the abundance of the individual isotopes. The error in the isotopic ratio measurements obtained for boron standards is higher by a factor of 0.1 for (N.B.S-951) and 0.64 for (N.B.S-952). The measurements of boron concentration by isotopic dilution analysis as represented in Table 3, reveals an average value of 3185 ppm of the determined boron in comparison to the given value of 3151 ppm. Variation in the isotopic ratio of standard to spike sample results in obtaining different ratios of B^{10}/B^{11} isotopes .The variation in the isotopic ratios in these mixtures of boron samples showed a little effect on the measurement of boron concentration. The error of boron concentration measurements (1.08%) is acceptable and in a good agreement with that published in the literature [18, 22].

Tables 4 and 6 represent the measurements of isotopic ratio composition of uranium samples with a scan of various concentration and different enrichment values to verify the feasibility of the mass spectrometer, the precision and the accuracy of the analysis. It is known that the isotope ratio measured in thermal ionization mass spectrometry is not the same as the actual isotope ratio of sample on the filament. The measured ratio varies during the analysis due to isotope fractionation occurring in the ionic emission process and this fractionation limits the accuracy of most of the isotopic analysis [12]. Reasonable isotopic ratio measurements were accomplished for depleted natural and enriched uranium samples. Data for the measurements of uranium concentration by isotopic dilution technique is given in Table 7 which shows the mixing ratio of U^{238} and U^{233} for the isotopic dilution analysis of U^{233}. It is seen also from Table 7, that the ratio 3:1 gives better results in comparison with ratio 12:1. This could be attributed to the large difference in the peak height of these isotopes. Consequently one can conclude that lower ratio could give more reliable results because of the similar peak intensity of the mixed isotopes. Based on the above results, one could conclude that precision of an isotopic abundance measurement varies with the number of average observations and with the abundance level of the isotope in question. Total error in concentration measurements of uranium samples by isotopic dilution analysis consists of the following errors:

A. Absence of N.B.S uranium primary standards.
B. Different errors of mass-spectrometric measurement; error caused by contamination of the sample and the filament, error of mass spectrometer calibration, statistical error of the measurement and error due to the interfering isotopes.
C. The errors emerged from weighing of sample and spike.
D. Errors caused by incomplete isotope exchange between spike and sample.

Table 1. *Test of the reproducibility and accuracy of boron isotope analysis.*

sample	No. of measurements	$R(B^{10}/B^{11})$	
		Certified	**Measured**
NBS 951	15	0.2473 ± 0.0002	0.2475 ± 0.00006(σn)
NBS 952	15	18.8000 ± 0.0130	18.6366 ± 0.00563(σn)

Table 2. *Mixtures of boron representing a series of different ratios of standard to the spike sample*.*

No.	Amount of (NBS-951), g	Amount of (NBS-952), g	Ratio of (951) / (952)
1	0.0997	0.0498	1:0.5
2	0.0997	0.1000	1:1
3	0.0991	0.1987	1:2
4	0.0993	0.4936	1:5
5	0.0988	0.9980	1:10
6	0.0497	1.0008	1:20

* Densities of NBS-951 = 1.005 g/m1 and of NBS-952 = 1.0008 g/m1

Table 3. *Boron concentration measurements by isotope dilution analysis.*

Mixture No.	No. of runs	$R(\frac{NBS\ 951\ std.}{NBS\ 952\ spike})$	$R(B^{10}/B^{11})_{mix}$ After correction For O^{17}	Boron conc. (ppm) taken	Boron conc. (ppm) found
1	4	1:0.5	0.81292 ± 0.0002	3151	3174
2	5	1:1	1.3532 ± 0.0018	3151	3187.5
3	4	1:2	2.3323 ± 0.002	3151	3193.2
4	4	1:5	4.6481 ± 0.0171	3151	3178.5
5	6	1:10	7.4055 ± 0.0017	3151	3182.5
6	4	1:20	10.5164 ± 0.0708	3151	3195
				Mean x = 3185	

Table 4. *Determination of isotopic ratio of uranium at different concentrations using natural uranium standard (0.72% enrichment).*

	Sample No. 1. Conc. : 4000 ppm; No. of runs = 5, Vol.: 5 µ1= 20 µg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	0.997532	0.000001	0.007314	0.000054
Std. deviation	0.0034977	0.000002	0.00000102	0.0000009
Atomic%	99.2667	0.0001	0.7278	0.0054
Mean wt.	236.2548	0.000236	1.710330	0.012636
wt.%	99.2759	0.001	0.7287	0.0053
Mean atomic wt.		237.978		
	Sample No. 2. Conc.: 3000 ppm; No. of Runs = 5, Vol.: 5 µ1= 15 µg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	1.000783	0.000000	0.07316	0.00061
Std. deviation	0.0049412	0.0000007	0.0000849	0.00000192
Atomic%	99.2683	0.000000	0.7257	0.006
Mean wt.	236.2585	0.0000	1.7054	0.0140
wt.%	99.2774	0.0000	0.7166	0.0059
Mean atomic wt.	237.9780			
	Sample No. 3 Conc. : 2000 ppm; No. of Runs = 5, Vol.: 5 µ1= 20 µg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	0.998252	0.000000	0.007296	0.0000
Std. deviation	0.0048696	0.0000066	0.00000256	0.0000
Atomic%	99.2687	0.0000	0.7255	0.0000
Mean wt.	236.2595	0.0000	1.7049	0.0000
wt.%	99.2779	0.0000	0.7164	0.0000
Mean atomic wt.	237.9779			

Table 5. *Determination of isotopic ratio of uranium at different concentration (μg /filament) at natural uranium solutions.*

Ratio, μg/filament	U-238	U- 236	U-235	U-234
20	0.997532	0.000001	0.007314	0.0000054
15	1.000783	0.000000	0.007316	0.000061
10	0.998252	0.000000	0.007296	0.000085
8	1.004333	0.000004	0.007300	0.000052
6	1.001872	0.000003	0.007291	0.000056
4	1.008944	0.000000	0.007300	0.000055
2	1 .003127	0.00000	0.007283	0.000054

Table 6. *Determination of isotopic ratio of uranium at different concentration enrichments.*

	Sample No. 1 10% enrichment., Conc.: 2000 ppm ; No. of Runs = 10, Vol.: 5 μ1 = 10μg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	1.000000	0.000688	0.110323	0.000795
Std. deviation	0.0000	0.0000019	0.000053	0.0000026
Atomic%	89.9438	0.0618	9.9228	0.0715
Mean wt.	241.0662	0.1459	23.3186	0.1673
wt.%	90.0580	0.0613	9.8101	0.00703
Mean atomic wt.		237.7980		
	Sample No.2 0.32% enrichment. Conc. : 2000 ppm; No. of Runs = 10, Vol.: 5 μ1= 10 μg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	1.000000	0.00168	0.003496	0.0000206
Std. deviation	0.0000	0.0000054	0.0000071	0.0000045
Atomic%	99.6328	0.0167	0.3483	0.0020
Mean wt.	237.1260	0.0394	0.8185	0.0048
wt.%	99.6374	0.0165	0.3439	0.0020
Mean atomic wt.		237.9887		
	Sample No.3 0.72% enrichment. Conc. : 2000 ppm; No. of Runs = 5, Vol.: 5 μ1= 1μg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	0.998252	0.0000	0.007296	0.000085
Std. deviation	0.004870	0.0000	0.000003	0.000066
Atomic%	99.2687	0.0000	0.7255	0.0058
Mean wt.	236.2595	0.0000	0.7049	0.0135
wt.%	99.2779	0.0000	0.7164	0.0056
Mean Atomic wt.		237.9779		
	Sample No.4. Conc. : 1600 ppm; No. of Runs = 5, Vol.: 5 μ1= 15 μg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	1.004333	0.000004	0.007300	0.000052
Std. deviation	0.0034038	0.0000015	0.00000886	0.000004
Atomic%	99.2729	0.0003	0.7215	0.0051
Mean wt.	236.2695	0.0070	1.6955	0.00 19
wt.%	99.2822	0.0002	0.7124	0.0050
Mean atomic wt.		237.9776		
	Sample No.5. Conc. : 1200 ppm; No. of Runs = 5, Vol. : 5 μ1= 20 μg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	1.001872	0.000003	0.007291	0.000056
Std. deviation	0.0054849	0.00000292	0.00000109	0.0000023
Atomic%	99.2717	0.0002	0.7224	0.0055
Mean wt.	236.2666	0.0004	1.6976	0.0129
wt.%	99.2811	0.0004	0.7133	0.0054
Mean atomic wt.		237.9775		
	Sample No.6. Conc. : 800 ppm; No. of Runs = 5, Vol.: 5 μ1 = 15 μg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	1.008944	0.000000	0.0073	0.0000
Std. deviation	0.0046957	0.0000054	0.0000046	0.0000
Atomic%	99.2711	0.0000	0.7233	0.0000
Mean wt.	236.2647	0.0000	1.6998	0.0000
wt.%	99.2804	0.0000	0.7143	0.0000
Mean atomic wt.		237.9781		
	Sample No.7., Conc.: 400 ppm; No. of Runs = 5, Vol.: 5 μ1= 15 μg / filament			
Isotope	U^{238}	U^{236}	U^{235}	U^{234}
Mean ratio	1.003127	0.000000	0.007283	0.000054
Std. deviation	0.0037031	0.00000262	0.00000697	0.000001
Atomic%	99.2739	0.0000	0.7208	0.0053
Mean wt.	236.2718	0.0000	1.6939	0.0124
wt.%	99.2830	0.0000	0.7118	0.0052
Mean atomic wt.		237.9781		

Table 7. *uranium concentration measurements by isotope dilution technique.*

[U^{238}] spike wt., g	[U^{233}] sample wt., g	Mixing ratio	Mean ratio U^{233}/U^{238}	U^{233} found (ppm)	R.E [%]
1.029	0.2453	12:1	0.0803	943	18
0.2520	0.2440	3:1	0.3740	975	6.5

[U^{238}] = 2422 ppm [U^{233}] = 1000 ppm taken as unknown. $R = U^{233} / U^{238}$ Ri = 0.000154 Rp = 1483

5. Conclusions

On the basis of the above findings, the isotopic dilution analysis for the determination of uranium and boron concentrations could be carried out with reasonable and reliable accuracy and reproducibility. The accuracy of the method depends on the purity of the isotopic material added (spike) as well as on the accuracy of the isotope analysis. The total weight of material containing the enriched isotope which is added is generally known with great accuracy.

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