RESEARCH ARTICLE

Study on Detection Method of Uranium Content in Uranium Dioxide-Beryllium Oxide Pellets

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Abstract: The uranium content detection method of UO2-BeO pellets was studied. The sample was dissolved in phosphoric acid, and then heated to be completely dissolved at 200℃ by adding 3 drops of nitric acid. In concentrated phosphoric acid solution containing sulfamic acid, excess ferrous sulfate was used to reduce uranium (vi) to uranium (vi), the rest ferrous sulfate was oxidized by nitric acid using molybdenum (vi) as catalyst, vanadyl sulfate was added, and uranium was titrated by potassium dichromate standard solution. The precision of the method is better than 0.1%

Keywords: UO2-BeO core; uranium content

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1 Method Principle

In concentrated phosphoric acid solution containing sulfamic acid, excessive ferrous sulfate is used to reduce uranium (vi) to uranium (vi), excessive ferrous sulfate is oxidized by nitric acid with molybdenum (vi) as catalyst, vanadyl sulfate is added, and uranium (vi) is titrated to the end of potential with potassium dichromate standard solution.

2 Reagent Materials

Unless otherwise specified, all reagents used in the analysis are analytical pure reagents that meet the national standards, and the analysis water is deionized water that meets the national laboratory water level.

2.1 sulfuric acid, excellent grade pure.

2.2 phosphoric acid, excellent grade pure.

2.3 nitric acid, excellent grade pure.

2.4 sulfamic acid, excellent grade pure.

2.5 ferrous sulfate (FeSO4·7H2O).

2.6 Ammonium molybdate [([(NH4)6Mo7O24·4H2O]].

2.7 Sulfuric acid solution: 50%, prepared with sulfuric acid (2.1) and water.

2.8 sulfamic acid saturated solution: prepared with sulfamic acid (2.4) and water.

2.9 ferrous sulfate solution, ρ (FeSO4) = 280g/L;

2.10 U3O8: GBW04205, burned at 900℃ for 2h before use.

2.11 nitric acid-ammonium molybdate solution;

Weigh 2±0.1g ammonium molybdate (2.6) in a 500mL beaker, add 200mL water and stir until it is completely dissolved, add 250mL nitric acid (2.3) and transfer it to a 5000mL volumetric flask, add water to the marking line and shake well.

2.12 potassium dichromate: GBW06105a, baked at 130℃ for 4h before use.

2.13 vanadyl sulfate.

2.14 potassium dichromate a solution: = 2.4mg/g. ρ_a= 2.4mg/g.

2.15 potassium dichromate b solution: =0.5mg/mL. ρ_a= 0.5mg/mL.

2.16 vanadyl sulfate solution:

Weigh 15.5g vanadyl sulfate (2.13) in a 500mL beaker, add 200mL water and stir to dissolve it, add 15mL sulfuric acid (2.1) and stir, transfer to a 500mL volumetric flask, dilute with water to scale, and shake well.

2.17 hydrofluoric acid, excellent grade pure.

2.18 phosphoric acid, excellent grade pure.

3 Instruments and Equipment

3.1 millivolt meter.

3.2 Platinum electrode.

3.3 Saturated calomel electrode.

3.4 Electromagnetic stirrer.

3.5 Temperature-regulating electric heating plate.

3.6 Analytical balance: the sensitivity is 0.01mg

3.7 Analytical balance: sensitivity 0.1mg.

3.8 Microburette: 2mL, the dividing value is 0.02mL.

4 Experimental Methods

4.1 Preparation of Sample

Beryllium oxide and uranium dioxide pellets are crushed and ground for analysis.

4.2 Sample Dissolution

4.2.1 Weigh out 0.2g () of the sample, accurate to 0.00001g, and put it in a 250mL glass.m_5)

4.2.2 Add 10mL nitric acid (2.3) to the cup, cover it with watch glasses, heat it at 200 ℃ for 15min, add 3 drops of hydrofluoric acid (2.17) and continue heating it for 15min, remove the watch glasses and evaporate it to dryness, add 40mL phosphoric acid (2.18) and heat it until the sample is completely dissolved, remove it and cool it to room temperature.

4.3 Sample Determination

4.3.1 Weigh the quality of the titration bottle containing potassium dichromate A solution (). Accurate to 0.0001 g ..m_6)

4.3.2 Place the dissolved solution on the electromagnetic stirrer (3.4), add 0.5mL sulfamic acid (2.8) solution while stirring, and then add 5mL sulfuric acid solution (2.7), 4.5mL sulfamic acid solution (2.8) and 5mL ferrous sulfate solution (2.9) in turn after 0.5min.

4.3.3 After fully stirring for 1.5min, add 10mL nitric acid-ammonium molybdate solution (2.11), at this time, the solution changes from light green to brown and then to light green.

4.3.4 Continue to stir for 2.5min, then place for 0.5min, add 10mL vanadyl sulfate solution (2.16) and then add 90mL water.

4.3.5 Insert the electrode with stirring, the potential is generally (350400)mV, and drop the potassium dichromate A solution (2.14) by titration weighing bottle until the potential is (480500)mV.~400~500

4.3.6 Continue to add 0.10mL of potassium chromate B solution (2.15) dropwise with a 2mL micro burette (3.8), and record the potential value and the corresponding volume number when the potential reading changes less than 1mV within 5s. After dropping to the end point, drop 0.10mL of solution, and write down the corresponding potential value. According to the example in Table 1, the volume of potassium dichromate B solution (2.15) consumed to reach the equivalence point is calculated by the second-order Wechat business.V .

4.3.7 Weigh and titrate the mass of weighing bottle (), accurate to 0.0001gm_7)

4.4 Calculation and Expression of Analysis Results

Uranium content is calculated according to formula (1).

Table 1 Volume calculation of potassium dichromate B solution consumed by titration

Adding volume mL	MV potential	dv	dv2
3.200	470	20	140
3.300	490		
		160	
3.400	650		-125
		35	
3.500	685		
Titration V = 3.300+0.100 {140/[140-(-125)]} = 3.3528 (ml)			

$$W(u)=\frac{\left[\rho_a \bullet (m_6-m_7)+\rho_b \bullet V\right]\times 2.4273\times G}{m_5\times 1000}\times 100 \tag{1}$$

Type:

$W(u)$—— Uranium content in the sample, expressed in percentage (%);

ρ_a—— the mass fraction of potassium dichromate A, in mg/g;

ρ_b—— the concentration of potassium dichromate B solution, in milligrams per milliliter (mg/ml);

m_5—— the quality of the sample, in grams (g);

m_6—— The quality of the titration bottle with potassium dichromate A solution before titration, in grams (g);

m_7—— The quality of the titration bottle containing potassium dichromate A solution after titration, in grams (g);

V—— The volume of potassium dichromate B solution consumed at the end point, in milliliters (ml);

2.4273—— Conversion factor of potassium dichromate to natural uranium;

G—— Concentration factor of uranium = relative atomic weight of uranium in the sample /238.029.

The result has four significant digits.

5 Results and Discussion

5.1 Beryllium Interference Experiment

Using uranium dioxide powder and adding 1%, 3% and 5% beryllium oxide respectively, the uranium content in the sample was determined according to the experimental method, and beryllium interference experiment was carried out. The results were calculated according to the sample weight of 0.2g The experimental results are shown in Table 2.

From the data in Table 2, it can be seen that the uranium content of the uranium dioxide powder used in the experiment is 87.25%, and the average uranium content measured after adding 1%, 3% and 5% beryllium oxide into the uranium dioxide powder is consistent with the background value of the sample, so it can be judged that the addition of beryllium oxide has no interference on the determination of uranium content.

Table 2 Beryllium oxide interference experiment

Sample background uranium content (%)	87.25	Average (%)
Beryllium oxide content added	Determination of uranium content (%)	
1% beryllium oxide content	87.29	87.24
	87.21	
	87.26	
	87.22	
	87.19	
	87.29	
3% beryllium oxide content	87.31	87.26
	87.27	
	87.25	
	87.18	
	87.24	
	87.29	
5% beryllium oxide content	87.21	87.24
	87.32	
	87.18	
	87.25	
	87.23	
	87.26	

5.2 Sample Dissolution

5.2.1 Selection of Sample Dissolving Temperature

Sample dissolution experiments were carried out on the temperature-controlled electric heating plate at 150 ℃ , 180 ℃ , 200 ℃ and 250 ℃ , respectively. The results are shown in Table 3.

Table 3 Temperature selection experiment of surface dissolution sample

Temperature (℃)	Complete dissolution time of sample (min)	Dissolution phenomenon
150	45	The dissolution process is stable.
one hundred and eighty	35	The dissolution process is stable.
200	30	The dissolution process is stable.
250	20	The dissolution process is intense and the solution boils.

From Table 3, it can be seen that when the sample dissolving temperature is lower than 200℃ , the samples can be dissolved smoothly, while when the temperature reaches 250℃ , the solution boils, which leads to sample splashing and sample loss, which affects the detection results. Therefore, in this method, after comprehensively considering the phenomenon of the dissolution time and the dissolution process of the sample, the dissolution temperature of the sample is selected to be 200℃ , so that the purpose of dissolving the sample quickly and stably can be achieved.

5.2.2 Addition Amount of Hydrofluoric Acid

Heat at 200 ℃ on a temperature-controlled electric heating plate, add different amounts of hydrofluoric acid, and follow the experimental method for other steps. See Table 4 for the experimental results.

Table 4 Addition amount of hydrofluoric acid

Hydrofluoric acid dosage	Experimental phenomenon
1 drop	Some samples failed to dissolve.
2 drops	Some samples failed to dissolve.
3 drops	Sample completely dissolved
Continuous drip	Steaming time is longer.

It can be seen from Table 4 that when the amount of hydrofluoric acid is insufficient, the sample can't be completely dissolved; when the amount of hydrofluoric acid is 3 drops, the sample can be completely dissolved; when the hydrofluoric acid is continuously dropped, it takes a long time to evaporate the excess hydrofluoric acid due to the large volume of acid, so after comprehensive consideration of the detection time and detection results, the method selects the amount of hydrofluoric acid as 3 drops.

5.3. Preparation of Vanadyl Sulfate

The preparation period of vanadyl sulfate solution prepared by vanadium pentoxide method is usually one to two days, and the preparation process is rather tedious. If the middle link goes wrong, the preparation will fail. In this paper, vanadyl sulfate is chosen to prepare vanadyl sulfate solution. Preparation method: Weigh 15.5g vanadyl sulfate in a 500mL beaker, add 200mL water and stir to dissolve it, add 15mL sulfuric acid, stir, transfer to a 500mL volumetric flask, dilute with water to scale, and shake well.

5.4 Precision Experiment

Beryllium oxide with beryllium content of 3% is added into uranium dioxide powder with uranium content of 87.25%, and a simulation sample of beryllium oxide uranium dioxide pellets is prepared. The uranium content in the sample is determined according to the experimental method. The experimental results are shown in Table 5.

Table 5 Precision experiment

Measurement times / element	one	2	three	four	five	six	Average%	RSD%
Uranium content (%)	87.31	87.29	87.27	87.18	87.25	87.24	87.26	0.05

It can be seen from the results in Table 5 that the average value of uranium content in the determination results is 87.26%, and the relative standard deviation is RSD=0.05%.

6 Conclusion

A detection method of uranium content in beryllium oxide uranium dioxide pellets was established, and the experimental conditions were given. According to this method, the uranium content in beryllium oxide uranium dioxide pellets could be accurately and quickly determined, and the determination results met the requirements of technical indexes, with a relative standard deviation of 0.05%.

References

[1] ISO 9989:1996(E) Determination of uranium content in uranium dioxide powder and pellets by ferrous sulfate reduction/potassium dichromate oxidation titration .1996 (01): 23-24.