RESEARCH ARTICLE

Determination of Zirconium, Niobium, Iron, Nickel, Copper and Manganese in Uranium Alloys-Emission Spectrometry

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Abstract: This method established an inductively coupled plasma emission spectrometry method to determine the contents of zirconium, niobium, iron, nickel, copper and manganese in uranium and uranium alloy through the sample pretreatment, sample weighing, dissolution method, uranium separation method, interference test between coexisting elements, precision and recovery test. This method separated the uranium matrix, and avoided the influence of uranium matrix on zirconium, niobium, iron, nickel and manganese.

Keywords: Uranium and uranium alloy; Zirconium content; Niobium content; Iron content; Nickel content; Copper content; Manganese content; Emission spectrometry

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1 Experimental Part

1.1 Method Principle

After the sample was decomposed by nitric acid, hydrochloric acid and hydrofluoric acid, and a large amount of uranium was extracted and separated by xylene-tributyl phosphate in dilute nitric acid medium, the contents of components and impurity elements were measured by standard curve method under the measurement conditions of inductively coupled plasma emission spectrometer selected by the method.

1.2 Reagents or Materials

Nitric acid: excellent grade pure, (HNO3) = 1.42 g/ml, used after re-steaming in sub-boiling distiller.

Nitric acid solution: c(HNO3)=5.5mol/L, mixed with nitric acid (1.2.1) and water.

Hydrochloric acid: excellent grade pure, r(HCl)=1.19g/mL, used after re-steaming in sub-boiling distiller.

Hydrochloric acid solution: c(HCl)=6mol/L, prepared with hydrochloric acid (1.2.3) and water.

Mixed acid solution: it is prepared by hydrochloric acid solution (1.2.4) and nitric acid (1.2.1) in a volume ratio of 3: 2.

Hydrofluoric acid: (HF) = 1.19g/ml.

Tributyl phosphate: excellent grade pure.

Xylene: excellent grade pure.

Extractant: tributyl phosphate (1.2.7) and xylene (1.2.8) in a volume ratio of 1: 3.

Sample washing acid: nitric acid (1.2.1) and deionized water are prepared according to the volume ratio of 1: 3.

Anhydrous ethanol.

National standard solution of elements to be measured.

Series standard solutions: prepare the national standard solutions (1.2.12) of each element to be tested into series standard solutions according to Table 1.

Table 1 Series standard solutions

grade	Element concentration μg/mL		Nitric acid medium mol/L
	Fe、Ni、Cu、Mn	Nb、Zr	
blank space	0	0	5.5
Standard 1	0.20	2	5.5
Standard 2	0.40	four	5.5
Standard 3	0.80	eight	5.5
Standard 4	one point six	16	5.5
Standard 5	2.0	20	5.5

1.3 instruments and Equipment

Inductively coupled plasma emission spectrometer: Optima5300DV.

Electric heating plate: the maximum temperature is 350℃ .

Electronic balance: the dividing value is 0.1mg.

Shi Ying separatory funnel: 60mL.

Instrument Parameters

See Table 2 for instrument parameters:

Table 2 Main working parameters of the instrument

project	ask	project	ask
RF generator power	1300W	Atomizer flow	0.8L/min
Plasma gas flow rate	15L/min	Sampling speed	1.5mL/min
Auxiliary air flow	0.2L/min	Observation mode	Horizontal observation

1.5 Experimental Methods

Sample treatment: take about 2g of sample in a 100mL beaker, heat it with washing acid (1.2.10) until it has metallic luster, rinse it with deionized water for three times, then clean it with absolute ethanol (1.2.11) for dehydration, and dry it with electric heating plate (1.3.2) at 140℃ for later use.

Blank test: Do blank test with the sample.

Sample dissolution: Accurately weigh 0.4000g of the sample to 0.1mg, put it in a Shi Ying beaker, add 3mL of mixed acid solution (1.2.5), put it on an electric heating plate (1.3.2), and heat it at 230℃ ~ 260℃ for dissolution. After the sample reacts violently completely, add 0.25mL hydrofluoric acid (1.2.6), and continue heating at 230 ℃ ~ 260℃ for 2min. After the sample solution is bright yellow, take it off and cool it to room temperature. Transfer all the test solutions with nitric acid solution (1.2.2) into Shi Ying separatory funnel (1.3.4) with 20mL extractant (1.2.9), and clean the beaker three times, each time about 3mL, to ensure that all the test solutions in the beaker are transferred into Shi Ying separatory funnel (1.3.4). Shake the separatory funnel for 30s and then let it stand for 10min. Transfer the water phase into a 100mL volumetric flask after the stratification is complete. Clean the inner wall of the separatory funnel with nitric acid solution (1.2.2) for three times. Transfer all the solutions cleaned each time into the volumetric flask, dilute to scale with nitric acid solution (1.2.2) and shake well. On the inductively coupled plasma emission spectrometer (1.3.1), a series of standard solutions 2(1.2.13), blank solutions and sample solutions were determined in turn under the selected working parameters and procedures, and the contents of zirconium, niobium, iron, nickel, copper and manganese were determined by the standard curve method.

2 Results and Discussion

2.1 Sample Pretreatment

Uranium and uranium alloy samples are lathe chips. After turning, oil stains and other impurities on the surface of the alloy are entrained on the lathe. Direct detection will greatly affect the accuracy of the samples, and it is more likely to affect the detection equipment, contaminate the detection equipment and affect the detection results.

According to the pre-treatment experience of uranium alloy, cold nitric acid (1+3) soaking or hot nitric acid (1+3) heating treatment is generally adopted. After the metallic luster appears, deionized water and absolute ethanol are used for cleaning, and then air-dried for later use. During the experiment, it was found that hot nitric acid (1+3) heat treatment of metals needed short time and high cleanliness, so this method chose hot nitric acid (1+3) heat treatment.

2.2 Selection of Weighing Sample Quantity

The weighing amount is too small, the weighing error is large, and it is greatly influenced by blank and instrument fluctuation. At the same time, if the peak value is too small, the sensitivity of spectrometer will be insufficient. Generally speaking, the weighing error can be reduced by appropriately increasing the sample weighing amount, but the sample weighing amount is too large, which increases the difficulty of sample dissolution, and the strength of component elements may exceed the detection range of the instrument. In actual operation, the minimum sample weight representing the sample should be taken. Under the same detection conditions, different sample weighing amounts were selected for the experiment. The experimental results showed that when the sample weighing amount was greater than 0.4g, the precision of the results all met the requirements, and the minimum sample weighing amount that met the requirements was 0.4g.

2.3 Selection of Dissolution Methods

When the uranium alloy contains zirconium and niobium, because zirconium and niobium are refractory metals, whether they can be completely dissolved is directly related to the accuracy of the determination results. When hydrofluoric acid is not added to the sample, mixed acid with nitrate can dissolve the sample, but the sample solution is not clear and the result is low, which is caused by the hydrolysis of zirconium and niobium in the sample solution. Hydrofluoric acid has strong complexing ability to niobium and zirconium, and it is the best solvent for dissolving zirconium and niobium.

At the same temperature, the solution was dissolved with nitrate mixed acid and hydrofluoric acid was added. During the experiment, it was found that when the amount of hydrofluoric acid was too little, the solution was turbid, which led to the blockage of atomizer and brought difficulties to the detection. Adding more than 3 drops of hydrofluoric acid can completely dissolve niobium and zirconium, but in order to avoid the corrosion of hydrofluoric acid to Shi Ying torch tube, the minimum amount of hydrofluoric acid is selected, that is, adding 3 drops of hydrofluoric acid when dissolving the sample.

2.4 Selection of Separation Methods

When the measurement solution contains a certain amount of uranium matrix, the uranium element will have a significant influence on the measured element, so it should be considered to fully separate the uranium matrix in the sample from the measured element in the measurement. Therefore, for 0.1g uranium and uranium alloy, the reverse chromatography separation method and extraction separation method are used for uranium separation determination and comparison, and 12 samples of the same sample of 0.1g are respectively weighed and divided into two groups. After one group is dissolved, a 7cm high reverse chromatography column is used to separate uranium. After the first group is dissolved, 20 mL extractant is used to extract and separate uranium, and then the amount of residual uranium in the sample solution is measured to calculate the extraction rate of uranium.

From the experiment, it is known that the extraction rate of reversed-phase chromatographic separation method is the same as that of extraction separation method. However, because the chromatographic column is too high to be cleaned and the effect of adsorbing uranium is obviously reduced with the increase of separation times, extraction separation is used to separate uranium from uranium and uranium alloy.

2.5 Interference Test between Coexisting Elements

The simulated sample solutions containing the upper limit point of interference elements (niobium and zirconium content 2%) and the lower limit point of analysis elements (impurity content 20ug/g) were prepared respectively, and niobium, zirconium, iron, nickel, copper and manganese elements were determined, and the measured results of each analysis element were compared with the actual content.

The experimental results show that there is no interference between high content Zr and Nb, and there is no interference between high content Zr and Nb and low content Fe, Ni, Cu and Mn.

2.6 Precision and Recovery Experiment with Standard Addition

24 samples of the same sample were weighed and divided into four groups. The first group is the background; In the second group, 0.2% of the lower limit of niobium and zirconium elements and the lower limit of iron, nickel, copper and manganese elements are added; In the third group, 2% of niobium and 2% of zirconium and the lower limit of iron, nickel, copper and manganese were added. In the fourth group, 2% niobium and 2% zirconium, 5 times lower limit of iron, nickel, copper and manganese elements were added, and the samples were measured under the same treatment conditions. See Table 3 for the recovery and precision experiments of niobium and zirconium elements, Table 4 for the recovery and precision experiments of iron, nickel, copper and manganese elements, and Table 5 for the recovery and precision experiments of iron, nickel, copper and manganese elements.

From the measurement results in Tables 3, 4 and 5, it can be concluded that the recovery rates of niobium and zirconium are between 95% and 105%, and the precision is better than 1%. The average recoveries of Fe, Ni, Cu and Mn are between 95% and 103%, and the precision is better than 10%, which meets the detection requirements.

Table 3 Recovery and precision of niobium and zirconium

element	Background content	addition	Measured value%						average value	Recovery rate%	Precision %
Nb	1.02	0.2%	1.20	1.19	1.22	1.21	1.20	1.21	1.21	95	0.87
Nb	1.02	2.0%	3.04	3.05	3.00	3.04	3.03	3.09	3.04	101	0.96
Zr	0.98	0.2%	1.19	1.18	1.19	1.21	1.19	1.20	1.19	105	0.87
Zr	0.98	2.0%	2.98	3.00	3.05	2.98	2.99	3.01	3.00	101	0.88

Table 4 Recovery rate and precision of lower limit of method for elements Fe, Ni, Cu and Mn

element	Background content	addition	Measured value（μg/g)						average value	Recovery rate	Precision %
Fe238.204	34.7	20	56.2	52.8	54.4	54.2	55.3	54.9	54.6	100	1.8
Ni231.604	8.71	20	29.2	28.4	28.6	27.7	27.9	29.1	28.5	99	2.1
Cu224.700	10.2	20	29.7	28.4	31.3	29.5	32.1	31.5	30.4	101	4.7
Mn260.568	24.3	20	43.0	42.2	43.9	43.1	42.8	44.6	43.3	95	2.0

Table 5 Recovery rate and precision of five times lower limit of method for elements iron, nickel, copper and manganese

element	Background content	addition	Measured value (μg/g)						average value	Recovery rate%	Precision%
Fe238.204	34.7	100	134	127	143	144	138	130	136	101	3.7
Ni231.604	8.71	100	102	114	106	100	105	110	106	97	4.8
Cu224.700	10.2	100	122	104	105	113	109	103	109	99	6.6
Mn260.568	24.3	100	115	119	122	128	131	120	122	98	4.9

3 Conclusion

A method for the determination of niobium, zirconium, iron, nickel, copper and manganese in uranium and uranium alloy by inductively coupled plasma emission spectrometry was established through sample pretreatment, sample weighing, dissolution method, uranium separation method, interference test between coexisting elements and precision and recovery experiment with standard addition. The recovery rates of niobium and zirconium are between 95% and 105%, and the precision is better than 1%.

References

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