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Determination of impurity content in the reactor zirconium by atomic absorption spectrometry with electrothermal atomization in the graphite furnace

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The paper discusses the possibility of quantitative determination of metal impurities in pure zirconium materials using atomic absorption spectrometry with electrothermal atomization in graphite.

Keywords: *Atomic absorption spectrometry · graphite furnace · zirconium materials*

For nuclear power engineering to be effective and safe it is important to have constructional appropriate materials for the nuclear reactor core. Zirconium plays a key role here. The production of metallic zirconium requires a control of undesired impurities during the entire technological process to obtain the final product of "nuclear purity". To solve this problem, effective methods for analysis of zirconium materials with the use of modern physical devices must be developed.

There is a lack of information in literature about the use of atomic absorption spectrometry method for determination of "traces" of metal impurities in zirconium. But there are some publications about application of other spectral analysis methods for materials which contain zirconium.

G. Schneider and V. Krivan [1] determined the lower limit of electrothermal detection of 15 elements in zirconium dioxide in the range from 1 to 200 ng/g and noticed the necessity of application of chemical modificators in analysis of several elements.

For content determination of 22 elements in zirconium and hafnium N. Gordon Jr. and R. Jacobs [2] used spectrochemical method with graphite electrodes and photoplate, but the metrological characteristics of methodic were not presented.

It turned out that the most close correspond to our task is the work of A.V. Grigorova and Y.V. Sirobaba, where they use atomic emission spectrometry with inductively coupled plasma for determination of the metal impurity content in zirconium of high purity [3]. The authors noted the large matrix disturbance and intersection of spectral lines of zirconium with the lines of determinated elements. Potassium (K), Lithium (Li), Magnesium (Mg) and Calcium (Ca) were reliably determined by this method. Determination of other elements requires nontrivial approaches to decrease the influence of zirconium matrix on analytical signal.

The atomic absorption spectrometry, as the most suitable method for determination of "traces" of metal impurities in various samples is mostly used in industry and research due to its high sensitivity (10^{-4}–-10^{-7}%), excellent selectivity and relatively low cost of the analytical equipment. This main analytical method combined with complementary methods like mass-spectrometry with laser ablation, resonance nuclear reactions analysis with the use of a gamma-ray spectrometer etc., allows solving the problem of quantitative analysis of the element composition in zirconium materials.

In recent years the use of so-called permanent modifiers has been proposed to improve analytical characteristics of electrothermal atomic absorption spectrometry (ET AAS). They change conditions of analyzable element interaction with the graphite surface of the furnace during the analysis of elements which form refractory carbides on the furnace surface [4–6].

Zirconium is one of such elements and its determination in samples in graphite furnaces is a relatively complicated analytical problem. Its ability to form carbides with the furnace graphite can be used as modification of the graphite surface for reliable analysis of other metals – impurities in zirconium materials.

The aim of this work is to test this idea in analytical practice and to study the possibility of using electrothermal atomic absorption spectrometry in graphite furnaces for determination of the metal impurity content in zirconium materials.

Experimental

Sample preparation

Three differently prepared samples of metallic zirconium were analyzed: iodide (TC95.46-82), calcium

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thermal (TC95.166-83) and magnesium thermal (ASTM-B-350). Each sample was washed in hot double distilled water with ultrasonic treatment, then it was placed into a vacuum-tight fluoroplastic (Teflon) autoclave where it was completely dissolved at room temperature in 10% hydrofluoric acid. Obtained solutions were diluted by 0.1N nitric acid to appropriate concentrations and were analyzed for the impurities content.

The aqueous solutions for calibration were prepared from standard samples of metal salts aqueous solutions (state standard samples of composition of metal salts aqueous solutions). All solutions were prepared with double distilled water and chemically pure acids.

A lot of mineral acids and their mixtures were investigated to dissolve the samples of zirconium. There are sulfuric acid, hydrofluoric and nitric acid, hydrochloric acid, the mixture of hydrochloric and nitric acids (3:1) "aqua regis", the mixture of hydrofluoric and nitric acid (3:1). Strong sulfuric, nitric and hydrochloric acids and the mixture of hydrochloric and nitric acids (3:1) dissolve zirconium very slowly (2–10% for week), even through temperature were increased to 50°C and left a solid sediment. That is the reason, why these acids were ineligible to dissolve zirconium.

Such discrepancy with literature connected with fact that chemical experiments were made with zirconium, which contain not less than 10% of impurities whereas we used the high-purity material. Therefore high chemical inertness of zirconium of "nuclear purity" results from high purity of material.

Table 1. Spectrometric conditions of analysis

Element	Analytical condition		
	Wavelength, nm	Slit width, nm	Atomization temperature, K
Al	309.3	0.4	2700
Cd	228.8	1.0	1800
Co	240.7	0.1	2500
Cr	357.9	0.4	2600
Cu	324.7	0.4	2500
Fe	372.0	1.0	2500
Li	670.8	1.0	2700
Mg	285.2	1.0	2000
Mn	Triplet	1.0	2500
	279.5		
	279.8		
	280.1		
Ni	232.0	0.1	2600
Pb	283.3	0.4	2000
Si	251.6	0.1	2500
Sn	286.3	0.4	2500

Equipment

Measurements were performed using the double-beam atomic-absorption complex KAS 120.1 (Selmi, Ukraine) with a deuterium corrector of non-atomic absorption. Hollow cathode lamps served as sources of radiation. An A-5 electrothermal atomizer with a standard pyrolytic graphite furnace, 28 mm long and with inner diameter of 6 mm, was used. The sample of 20±0.4 μl was dosed by an MD-20 sampler onto the inner surface of the furnace. The atomic absorption signal was scanned and processed on the computer.

Spectral mode of the measurements were standard [7]. Temperature program was selected for each element separately to achieve optimal conditions of analysis. This data are presented in table 1. No additional spectrum buffers and modifiers were used to make easier the problem posed.

Results and discussion

Results from the determination of the impurity content in the zirconium samples are presented in table 2 and compared with standard specifications for their production.

The adequacy of technique was proved by method "added-obtained". In this case the inaccuracy of concentration determination was not more than 8%. As we can see from table 2, obtained results agree with standard requirements (specifications) for each sample. At the table 3, values of characteristic mass for pure water solutions (specification of device) and for described methodic were presented. As we can see from table 3, for the most of elements the decrease of characteristic mass values is observed. It connected with surface modification of the graphite furnace by zirconium carbide and optimal temperature conditions of analysis.

To check the influence of zirconium matrix on measurement results the method of standard additions was applied. All results, obtained by this method agree with results, which presented in the table 2. Identity of results leads one to conclude that the zirconium matrix doesn't block atomization of the analyzed elements and allows using the electrothermal atomic absorption spectrometry method for the determination of the impurity content in zirconium materials.

Conclusions

Surface modification of the graphite furnace by the zirconium matrix doesn't prevent a reliable analysis of

Table 2. Content of impurities in zirconium materials, %

Element	Iodide method		Calcium thermal method		Magnesium thermal method	
	Standard TC 95.46-82	Measured	Standard TC 95.166-83	Measured	Standard ASTM-B-350	Measured
Al	$5\cdot10^{-3}$	$0.2\cdot10^{-3}$	$5\cdot10^{-3}$	$0.2\cdot10^{-3}$	$7.5\cdot10^{-3}$	$3.4\cdot10^{-3}$
Cd	$5\cdot10^{-5}$	$2\cdot10^{-5}$	$3\cdot10^{-5}$	$1\cdot10^{-5}$	$5\cdot10^{-5}$	$5\cdot10^{-5}$
Co	—	0.8	—	0.5	$2\cdot10^{-3}$	$2\cdot10^{-5}$
Cr	$2\cdot10^{-2}$	$0.2\cdot10^{-2}$	$5\cdot10^{-3}$	$1\cdot10^{-3}$	$2\cdot10^{-2}$	$9\cdot10^{-3}$
Cu	$3\cdot10^{-3}$	$0.2\cdot10^{-3}$	$5\cdot10^{-3}$	$0.5\cdot10^{-3}$	$5\cdot10^{-3}$	$3\cdot10^{-3}$
Fe	$3\cdot10^{-2}$	$0.7\cdot10^{-3}$	$5\cdot10^{-2}$	$1\cdot10^{-2}$	$1.5\cdot10^{-1}$	$1.3\cdot10^{-2}$
Li	$2\cdot10^{-4}$	$0.5\cdot10^{-4}$	$2\cdot10^{-4}$	$0.4\cdot10^{-3}$	—	$8\cdot10^{-5}$
Mg	—	$6\cdot10^{-4}$	—	$7\cdot10^{-4}$	$2\cdot10^{-3}$	$7\cdot10^{-4}$
Mn	$1\cdot10^{-3}$	$0.2\cdot10^{-3}$	$2\cdot10^{-3}$	$0.2\cdot10^{-3}$	$5\cdot10^{-3}$	$1\cdot10^{-3}$
Ni	$2\cdot10^{-2}$	$0.2\cdot10^{-2}$	$1\cdot10^{-2}$	$0.3\cdot10^{-2}$	$7\cdot10^{-3}$	$8\cdot10^{-4}$
Pb	$5\cdot10^{-3}$	$0.3\cdot10^{-3}$	$5\cdot10^{-3}$	$0.3\cdot10^{-3}$	—	$4\cdot10^{-3}$
Si	$8\cdot10^{-3}$	$5\cdot10^{-3}$	$1\cdot10^{-2}$	$0.3\cdot10^{-2}$	$1\cdot10^{-2}$	—
Sn	—	$8\cdot10^{-4}$	—	$6\cdot10^{-4}$	$5\cdot10^{-3}$	$4\cdot10^{-3}$

Note: Table lists results averaged over three parallel measurements. Standard deviation does not exceed 15%.

Table 3. The values of characteristic mass for different matrices

Element	Characteristic mass, pg	
	Pure water solution	Zirconium matrix
Al	10.0	8.0
Cd	0.4	0.1
Co	9.6	2.0
Cr	2.0	0.6
Cu	6.4	2.6
Fe	3.0	0.5
Li	–	0.5
Mg	–	0.7
Mn	2.4	1.1
Ni	17.0	1.0
Pb	8.0	5.0
Si	–	45.0
Sn	140	10.0

impurities in metal zirconium. Therefore the atomic absorption spectrometry method with electrothermal atomization in graphite furnaces can be successfully used for reliable determination of the metal impurity content in zirconium materials.

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