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**INFLUENCE OF MATRIX EFFECTS ON DETERMINATION OF THE
TRACE ELEMENT CONTENT IN ZIRCONIUM BY THE
ATOMIC ABSORPTION SPECTROMETRY**

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The influence of sample matrix prepared on the basis of hydrofluoric acid on the measured content of trace elements in zirconium was studied. The accuracy of determination of the trace element content was verified by the "introduced-found" method. Based on verification results the temperature regime of electrothermal atomizer was optimized.

Keywords: MATRIX EFFECTS, ZIRCONIUM, TRACE ELEMENTS, ATOMIC ABSORPTION SPECTROMETRY, "INTRODUCED-FOUND" METHOD.

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1. INTRODUCTION

Development prospects of nuclear power, its effectiveness and safety depend on quality of structural materials of the core active zone. And zirconium is one of the most in-demand materials recently [1-3].

To produce the metal zirconium of "reactor purity" it is necessary to control the content of trace element in materials both during the whole manufacturing process and in the final product. To solve this problem there is a need to correctly analyze the zirconium materials using proven scientific methods [4-8].

In publications devoted to use of the spectrum analysis methods for zirconium-containing materials the authors notice on the presence of essential matrix noise and the superposition of zirconium spectral lines onto lines of many determined elements (analyte) [9-11]. Because of exceptional selectivity and high sensitivity the atomic absorption spectrometry (AAS) is the most appropriate method for determination the "trace" element concentrations [12-15]. But analysis of the cited publications showed almost the total lack of information about AAS applications for determination of the trace element content in the metal zirconium. And the majority of available techniques are developed for the nitric-acid matrix while the measured zirconium solutions have the fluoride matrix mainly.

Trying to determine the metal traces in accordance to the known techniques the quite acceptable results were obtained, which correspond to the defined standards at all parameters, that is the trace concentrations were lower than the allowable ones in technical conditions (TC) [16]. But the absence of absorption signals of some elements can be the result of a sample

matrix, which interacting with the given analyte forms either gaseous or hardly-atomized compounds.

The aim of the present paper is to test the analysis techniques of zirconium traces by the "introduced-found" method for the purpose of the influence of matrix effects and their further optimization.

2. EXPERIMENT AND RESULTS

Measurements were carried out using the double-beam atomic absorption spectrometer C115-M1 equipped by the add-on for electrothermal analysis "Grafit-2" (complex KAS-120.1 [17] by OAO "SELMI", Ukraine).

This complex contains the electrothermal atomizer A-5, which is an analogue of the Massmann oven. Sample atomization takes place in the graphite tube furnace (the length is 28 mm, the internal diameter is 6 mm). The temperature range of an oven operation is 290-3340 K, the heating rate in the standard mode is up to 2000 K/sec, the error of temperature setting is ± 20 K, and the sample volume is 5-50 μ l.

We used ovens by the companies "LEG" (Kharkov, Ukraine) and "Karl Zeiss Jenna" [18]. The lamps with hollow cathode LT-2 and Lt-6 were the source of characteristic radiation of measured elements. The influence of non-selective light absorption was removed using the deuterium background corrector.

We investigated the sample of metal zirconium, which was obtained by the thermal-magnesium (ASTM-B-350) technological method, developed by the National Science Center "Kharkov Institute of Physics and Technology". The sample was pre-washed by bi-distilled water, aquafortis, and then re-washed by bi-distilled water with mixing in ultrasonic disperser (UZDN-A ("SELMI")) to get rid of a pollution. Further probe preparation consisted in zirconium dissolution by the hydrofluoric acid.

Zirconium sample of the mass 3,723 g was placed into fluoroplastic beaker of the volume 100 ml filled by bi-distilled water up to 40 ml. Acid was periodically added by doser in 1 ml while metal completely reacted. When sediment appeared the solution was diluted by bi-distilled water until its dissolution and resumption of the reaction. Finally, the solution volume was 100 ml, and the obtained zirconium concentration was 37,23 g/l. The "idle" solution was prepared in another beaker. To decrease the non-selective absorption the basic solution was diluted by the factor of 10 (or 100 to measure Cr) before measurements.

To prepare the calibration solutions we used the standard samples of aqueous metal salts: PK-1(Al, Cu); GSORM-3 (Sn); GSORM-23 (Cd, Mn, Pb); GSORM-24 (Co, Fe, Ni); GSORM-25 (Mg); GSORM-26 (Cr); GSORM-27 (Li); GSORM-29 (Be), and the standard of Si solution prepared according to the all-Union State Standard 84212-76.

The essence of the "introduced-found" experiment was in the following: based on analysis results, which were carried out in accordance with the generally accepted methodical recommendations [15], for each measured element the "introduced" was appointed – such amount, which was used to obtain the intermediate concentration while plotting the calibration diagram; in the presence of "introduced" the solutions based on nitrate ("idle") and fluoride ("idle" and "zirconium") matrixes were prepared; and the analyte content in solutions was determined – "found".

Elements Al, Be, Cd, Co, Cr, Cu, Li, Mg, Mn, Ni, Pb, and Si were defined using the main, most sensitive (1:1), resonance lines on the wavelengths 309,3; 234,9; 228,8; 240,7; 357,9; 324,7; 670,8; 285,2; 279,5; 232,0; 283,3; and 251,6 nm, respectively. Stable alternative lines 372,0 (1:3) nm and 286,3 (1:2) nm were chosen for Fe and Sn. The spectral aperture width was 0,4 nm except of the cases of Be, Cd, Fe, K, Li, Mn, Na, where it was 1,0 nm, and of Co and Ni, for which it was equal 0,1 nm.

Calibration was carried out over three solutions with concentrations (in mg/l): 0 – 0,025 – 0,05 (Be, Cd, Li, Mg, Mn); 0 – 0,05 – 0,1 (Al, Co, Cr, Cu, Fe, Ni, Pb, Sn); 0 – 2 – 4 (Si). Solutions were placed into oven by the microdoser MD-10 except of the cases with Li, Ni, and Sn (MD-20) that corresponded to the sample volumes of 10 and 20 μ l.

If concentrations of “introduced” and “found” coincided we concluded about the absence of matrix influence when analyzed the given element, and if concentrations did not coincide the correction of thermal program was performed toward the increase of the temperature and the duration of pyrolysis or atomization, in order to manage the hardly-atomized compounds. Signals obtained from the samples with nitrate and fluoride matrixes were intercompared. Parameters of the thermal program, for which the squares under peaks were the most closed ones, were used as the basis.

Equality between “introduced” and “found” for some elements (Al, Be, Si) was not achieved. The total absence of Si in a sample is explained by its interaction with the hydrofluoric acid and by formation of the gaseous fluorides, and the losses of Al and Be are explained by specific conditions of atomization (inert atmosphere and high temperature), through which the gaseous fluorine compounds can be formed [19]. Correct measurement of the given elements is possible in the presence of other chemical matrix only, for example, the sulphuric one [1].

Optimized programs of electrothermal atomizer for fluoride sample have consisted of the following steps: drying of a liquid at 360-380 K during 60 sec and pyrolysis at 770 K (Cd, Pb – 10 sec; Ni – 5 sec), 870 K (Cu – 10 sec), 1070 K (Co, Cr, Fe, Sn – 10 sec), 1270 K (Be – 20 sec; Li, Mg, Mn – 10 sec), 1470 K (Al – 20 sec) with argon blow of 0,007 m³/h; atomization at 2070 K (Cd), 2270 K (Pb), 2570 K (Mg), 2670 K (Be), 2770 K (Co, Cr, Cu, Mn, Sn), 2870 K (Al, Fe, Cr, Ni), 3070 K (Li) during 5 sec in the “gas-stop” mode (except of Mg, where the air-cooling was not switched off), and the further annealing (~ 3000 K) with the protective gas flow.

Atomic absorption signal was scanned with the step 0,016 sec and was processed by a computer. Results were calculated by averaging of at least three parallel measured values.

Since samples were produced in the polyethylene tubes of the volume 10 ml from the basic solution, containing 50 mg/l of analyte, and the input dose was 10 μ l, after reaching by the solution with chosen matrix the necessary volume in a tube the analyte concentration should be 50 μ g/l. Obtained results are represented in Table 1.

We have to note, that the fluoride matrix insignificantly decreases the sensitivity of determination over the most elements, but it does not essentially influence on the final result of measurements. Zirconium sample differs from the idle ones since it contains some number of traces. The reason of Si absence in Table 1 is the predicted loss of gaseous fluoride. Concentration of Al in the fluoride sample was on the background-level

due to formation in specific conditions of high temperature and inert atmosphere of volatile compound AlF. It is possible to suggest, that Be losses occur on the pre-atomization stages as well, but this question requires the additional study.

Table 1 – Found concentrations of the introduced elements in samples with different matrixes

Element	Nitrate		Fluoride			
	idle		idle		zirconium	
	concentr., µg/l	OSKO, %	concentr., µg/l	OSKO, %	concentr., µg/l	OSKO, %
Al	50,4	8,1	–	–	–	–
Be	51,1	5,3	17,7	9,8	18,3	12,2
Cd	48,9	5,6	47,5	7,3	50,1	1,6
Co	50,2	4,1	49,3	6,4	51,7	2,6
Cr	49,5	7,8	48,1	6,1	165,4	4,8
Cu	49,1	6,2	48,8	5,3	63,1	2,8
Fe	52,5	4,9	52,2	9,2	239,5	8,4
Li	49,8	10,2	49,2	8,5	50,6	9,9
Mg	49,6	9,0	48,8	7,6	233,2	10,5
Mn	51,6	3,5	50,9	5,5	128,8	7,1
Ni	49,7	6,5	48,6	7,0	92,7	6,9
Pb	48,8	6,0	47,8	6,3	71, 5	7,3
Sn	49,5	9,9	49,1	9,6	75,9	8,1

3. CONCLUSIONS

Thus, the fluoride sample using can be applied for determination of the trace element content in zirconium by the AAS method. Modification of the surface of graphite furnace by zirconium influences on the form of absorption signal only and does not impede to the reliable analysis of metals Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Sn, and that is why the AAS method can be successfully applied for determination of the mentioned traces.

REFERENCES

1. W.B. Blumenthal, *The Chemical Behavior of Zirconium* (Princeton: van Nostrand: 1958).
2. S.V. Elinson, K.I. Petrov, *Analiticheskaya khimiya tsirkoniya i grafniya* (M.: Nauka: 1965).
3. I.V. Shahno, Z.N. Shevtsova et al., *Khimiya i tehnologiya redkih i rasseyannyh elementov. Chast' 2* (M.: Vysshaya shkola: 1978).
4. Z.S. Muhina, E.I. Nikitina, L.M. Budanova et al., *Metody analiza metallov i splavov* (M.: Gosudarstvennoe izdatel'stvo oboronnoi promyshlennosti: 1959).

5. S.V. Elinson, K.I. Petrov, *Tsirkoniy. Khimicheskie i fizicheskie metody analiza* (M.: Izdatel'stvo glavnogo upravleniya po ispol'zovaniyu atomnoi energii pri Sovete ministrov SSSR: 1960).
6. M.M. Godneva, D.L. Motov, *Khimiya ftoristyh soedineniy tsirkoniya i grafniya* (L.: Nauka: 1971).
7. T.M. Malyutina, O.V. Kon'kova, *Analiticheskii kontrol' v metallurgii tsevnnykh i redkikh metallov* (M.: Metallurgiya: 1988).
8. A.N. Zelikman, B.G. Korshunov, *Metallurgiya redkikh metallov* (M.: Metallurgiya: 1991).
9. Jr.N.E. Gordon, R.M. Jacobs, *Anal. Chem.* **25** No11, 1605 (1953).
10. G. Schneider, V. Krivan, *Spectrochim. Acta* **50B**, 1557 (1995).
11. A.V. Grigorova, Yu.V. Sirobaba, *VI Vseukrains'ka konferentsiya molodykh vchenykh, studentiv ta aspirantiv z aktual'nykh pytan' khimii*, 12 (2008).
12. I. Khavezov, D. Tsalev, *Atomno-absorbtsionnaya spektroskopiya* (L.: Khimiya: 1983).
13. *Atomno-absorbtsionnaya spektroskopiya: Metodicheskie rekomendacii* (Sumy: PO "Elektron", TsZL: 1994).
14. A.V. Garmash, *Vvedenie v spektroskopicheskie metody analiza. Opticheskie metody analiza* (M.: Vysshii khimicheskii kolledzh RAN: 1995).
15. A.N. Kulik, A.N. Buhay, Yu.V. Rogulsky, O.B. Lysenko, *Visnyk SumDU. Seriya Fizyka, matematyka, mehanika* No2, 91 (2007).
16. A.N. Kulik, A.N. Buhay, Yu.V. Rogulsky, O.B. Lysenko, *Visnyk SumDU. Seriya Fizyka, matematyka, mehanika* No2, 200 (2008).
17. *Ind. Lab.-USSR +* **59** No11, 65 (1993).
18. A.N. Kulik, A.N. Buhay, Yu.V. Rogulsky, O.B. Lysenko, *Visnyk SumDU. Seriya Fizyka, matematyka, mehanika* No8, 89 (2004).
19. B.M. Rosen, Ya.B. Rosen, *Metall osoboy tsennosti* (M.: Metallurgiya: 1975).