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DETERMINATION OF HAFNIUM IN ZIRCONIUM COMPOUNDS USING FLAME ATOMIC ABSORPTION SPECTROMETRY (FAAS)

The optimum conditions for determination of hafnium in zirconium matrix by FAAS were established (1 % HF, 0,1 % Al, max. 1 % $ZrOCl_2$). The effect of various inorganic acids (HF, HCl, $HClO_4$, HNO_3, H_2SO_4) as well as influence of comparable amounts of Fe, Ca and Mg on Hf signal was also studied. ICP-AES was used as comparative method.

Определены оптимальные условия определения гафния в циркониевой матрице методом пламенной атомно-абсорбционной спектрометрии (1 % HF, 0,1 % Al, max. 1 % $ZrOCl_2$). Также изучено воздействие различных неорганических кислот (HF, HCl, $HClO_4$, HNO_3, $H2SO_4$) и влияние аналогичных количеств железа, кальция и магния на сигнал гафния. В качестве сопоставительного метода использовался метод спектрометрии индуктивно связанной плазмой - спектрометрии атомным излучением (ICP-AES).

Hafnium does not occur as the primary compound of ore but always is included in zirconium minerals, usually in the range of 2-3 %. Both of these metals are used in nuclear industry, what requires their separation. However it is very difficult, because of a large similarity of their chemical properties and analytical problems concerning determination of hafnium in zirconium matrix. The techniques like: inductively coupled plasma atomic emission spectrometry (ICP-AES), radiometric and neutron activation analysis (NNA) are the most often used for determination of Hf in Zr compounds [1]. However the techniques mentioned above are not always available. More available and the most popular for determination of metals is atomic absorption spectrometry, but there is no information in REFERENCES about determination of Hf in zirconium compounds using AAS method.

The aim of our work was to settle the conditions of hafnium determination in zirconium matrix by means of FAAS.

Experimental.

Reagents and solutions. High purity $ZrOCl_2 \cdot 8H_2O$ 99,9 % metal basis (~100 ppm Hf), $HfOCl_2 \cdot 8H_2O$ 98+ % were obtained from Alfa Aesar and used as received. Reagent grade HF, HCl, $HClO_4$, HNO_3, H_2SO_4, NH_3aq, $Al(NO_3)_3$, $Fe(NO_3)_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, D, L – mandelic acid, and "pure" $ZrOCl_2 \cdot 8H_2O$ (~2 % Hf), all from POCh (Gliwice, Poland) were used without further purification. Water was distilled and purified using a Millipore Elix 10 system.

Concentrated solutions of studied metals (~0,15 g of metal/ml) were prepared and stored in 2M HCl. The solutions were standardized by gravimetric procedure utilizing mandelic acid [2].

Apparatus. Determination of Hf by flame atomic absorption spectrometry (FAAS) was performed using Perkin-Elmer 3300 spectrometer with hollow cathode Hf lamp (PHOTRON PERKIN ELMER). Following conditions were used: wavelength 286,6 nm; slit 0,2 nm; current intensity 25 mA; flame C_2H_2 – N_2O. IRIS II ADVANTAGE RAD HR (serial no 7063) Thermo Jarrell Ash (USA) inductively coupled plasma emission spectrometer was also used under conditions from previous work [3].

Procedure. Hf absorption lines 286,6 nm as one of relatively high sensitivity and free from coincidence with absorption lines of Zr was selected. First the effect of various inorganic acids on results of Hf determination was investigated. Next the effect of additions of aluminum salt (which improves some signals in FAAS measurements) on Hf excitation was studied. After selection of acid (HF) and proper

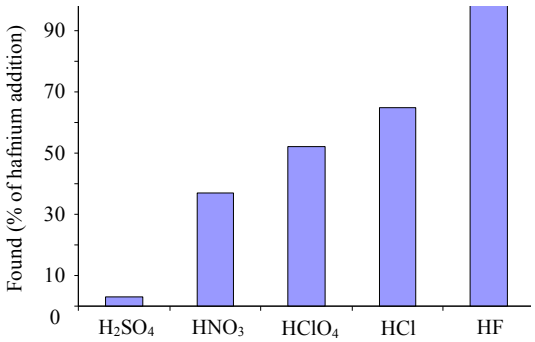


Fig.1.The effect of various acids on determination of Hf. Hf addition 300 g/ml

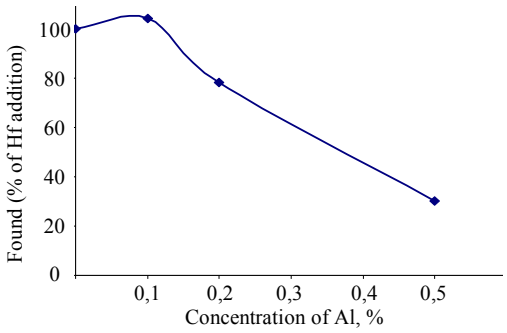


Fig.2. The effect of Al concentration on determination of Hf. Hf addition 300 g/ml, 1 % $ZrOCl_2$, 1 % HF

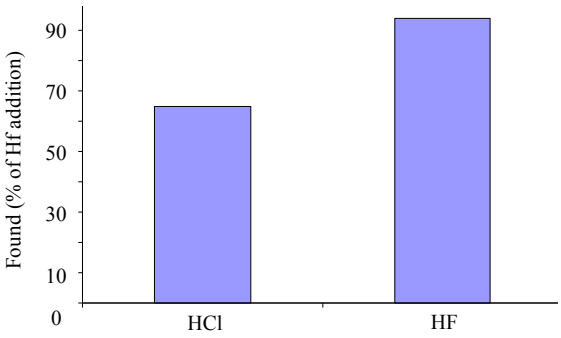


Fig.3. The effect of HF and HCl on determination of Hf in 1 % $ZrOCl_2$ matrix. Hf addition 300 g/ml

concentration of aluminum salt (0,1 %), standard curves containing 0,1 % of Al, 1 % of HF and various concentrations of matrix: 0; 0,5; 1,0 and 2,5 % $ZrOCl_2$ in the range 0-450 μgHf/ml were prepared to check the possibility of hafnium determination in zirconium compounds. Additionally, the effect of some metals (Fe, Mg, Ca), which commonly occur in zirconium ores, on Hf analysis was examined.

Inductively coupled plasma atomic emission spectrometry was used as comparative method of Hf(IV) determination applying solutions containing 2M HCl in the presence of 1 % $ZrOCl_2$ matrix.

Results and Discussion. The best conditions of hafnium excitation are obtained in HF acid (Fig.1) with addition of 0,1 % of Al salt (higher concentration significantly decrease Hf absorbance – Fig.2). In the case of using other inorganic acids, measured signal decreases in given order $HCl > HClO_4 > HNO_3 > H_2SO_4$ (Fig.1) Comparison of effect of two acids (HF and HCl) on determination of hafnium in 1 % $ZrOCl_2$ matrix (Fig.3) proves HF to be the best acid for this analysis.

The results presented in Fig.4 indicate that 0,5 and 1,0 % $ZrOCl_2$ matrix has very little effect on Hf signal, in opposite to 2,5 % $ZrOCl_2$ matrix, which significantly reduces the sensitivity of investigated method. The addition of other metals (Fe, Mg, Ca), which occur in zirconium ores in the same range as Hf, results in decreasing hafnium absorbance by about 20 % (Fig.5). Therefore utilizing the FAAS method for determination of Hf in the presence of comparable amounts of Fe, Ca and Mg is possible after introduction of proper corrections.

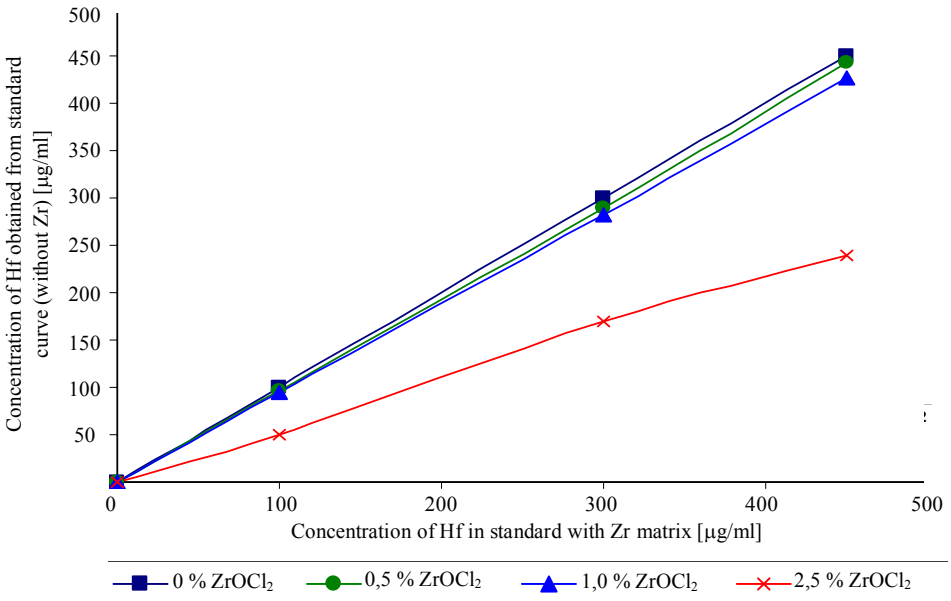


Fig.4. The effect of $ZrOCl_2$ concentration on determination of Hf

Accuracy of the investigated method was verified by determination of the precise added amounts of hafnium, employing FAAS and ICP-AES methods.

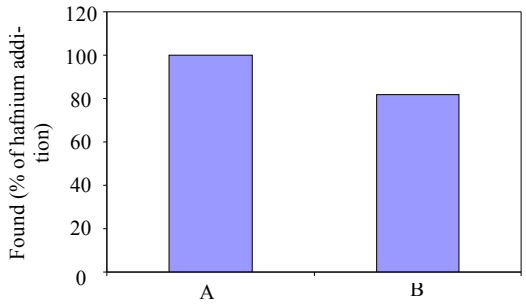


Fig.5. The effect of Fe, Ca and Mg addition on determination of Hf. 300 gHf/ml, 1 % $ZrOCl_2$, 1 %HF, 0,1 % Al. A – without Fe, Ca, Mg; B – in presence of 300 g/ml Fe, 100 g/ml Ca and Mg

Conclusions. The optimum composition of solution for determination of hafnium in zirconium matrix by FAAS was established (1 % HF, 0,1 % Al, max. 1 % $ZrOCl_2$). Other inorganic acids decrease Hf absorbance in the following order $HCl > HClO_4 > HNO_3 > H_2SO_4$. The analysis of Hf in the presence of comparable amounts of Fe, Ca and Mg is possible after introduction of proper corrections.

The presented method permits with good accuracy and precision to determine over 0,1 % of hafnium in zirconium matrix (in relation to $ZrOCl_2$).

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