Development of methods for determination of impurity elements in zircon-alumo-ytterbium ceramic materials for medical purpose

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Abstract. Determining the presence of impurities, carcinogenic and harmful elements in the synthesized materials is a necessary step to identify the field of application, especially for medicine. Methods have been developed for the atomic emission with inductively coupled plasma (AES-ICP) for simultaneous quantifying of impurities contents: Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, Y, Yb, Hf, V, Zn in new zircon-alumo-ytterbium ceramic materials for medical use. Various schemes for dissolving samples were offered for different types of ceramic compounds. Elements were determine with founded optimal analytical parameters. The influence and methods elimination of matrix elements (Zr, Al, Yb) were studied. It allowed to determine elements with good metrological characteristics in a wide range of concentration from 1·10⁻³ to n·10% without preliminary separation of the matrix and without using solid standard samples. The relative standard deviation (Sr) does not exceed 0.12.

1. Introduction
At present, the production of ceramic materials relies on the initial powders of high dispersion, synthesized by various methods, high-energy and low-energy, which include the methods of "soft" chemistry. The synthesized powders, especially the powders of multicomponent systems, for new ceramic materials require control over the conformity of the final composition to the specified one. In addition, the assessment of the content of impurity elements makes it possible to specify areas of application, in particular, to assess the safety of ceramics for use in medical purposes.

The development of materials for medicine is one of the most important tasks in modern material science. New zircon-alumo-ytterbium ceramic compounds are promising materials for medical purposes due to biological inertness, high biocompatibility and wear resistance [1,2]. Quantitative analysis of impurities is contained in the feedstock and introduced during the synthesis process can be very useful for practical use of functional materials. Medical materials are also subject of high purity requirements for the content of harmful impurities (As, Cr, Cd, Li, Pb), which are regulated by international standards.

The purpose of this work is to develop methods for determination of impurities in the following composition ceramic materials: ZrO₂–Al₂O₃–Yb₂O₃ of different purity.
Determination of the contents impurities in compounds of this composition is have not been adequately covered in the literature.

2. Experimental part
Lack of standard composition samples to determine the list of impurity elements Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, Y, Hf, V, Zn limits the choice of analysis method. We used atomic emission spectrometry with inductively coupled plasma (AES-ICP). This method has the following advantages: low detection limits, expressivity, reliable measurement of analytical signals, linearity of calibration in the range of 5-6 orders with high reproducibility, possibility of simultaneous determination of elements in a wide range of contents, relatively small level of influence of accompanying elements and ability to work without solid standard samples of the composition [3,4].

2.1. Sample preparation
It is necessary to transfer the analyzed samples to solution to perform elemental analysis using method AES-ICP. Zircon-alumo-ytterbium ceramic materials are rather complex objects of investigation because of difficulties transferring samples to solution and obtaining stable solutions of high concentrations of readily hydrolyzed elements of zirconium and hafnium [5,6]. Optimal schemes for sample dissolution and methods of retaining elements in solution have been found (table 1). Different temperature regimes could be used for producing ceramic compounds. Open systems were used to dissolve ceramics obtained without decrepitation. Accelerated techniques were developed, using the microwave system Mars 5 (CEM Corporation, USA) to translate difficult-to-open oxide ceramics obtained with decrepitation to 500°C into the solution. To confirm completeness of the dissolution of oxides, a classical scheme of alloy fusion with alkali metal salts was used [5]. The most effective was autoclaved microwave dissolution using the MARS 5 module. A 100 mg sample was completely dissolved for 50 minutes in a mixture of concentrated nitric, chloric and hydrofluoric acids at temperature of 210°C. Classical schemes of samples melting with alkali metal salts were used to transfer to the solution of ceramic compounds, obtained with decrepitation above 500°C. These ceramic compounds failed to dissolve in the microwave system MARS 5 for several days even using rigid regimes (P, T) (table 1). The solutions residues were transferred with 4M HCl after dissolving the samples and removing hydrofluoric acid. Such high concentration of acid is necessary for obtaining stable solutions of zirconium and hafnium [6]. Before measurement on the plasma spectrometer the solutions obtained were diluted 10 times with 1 M HCl. This method of sample preparation is not suitable to determine silicon, so the wet-fusion method was also used [5]. At the same time, blank experiments were conducted to control the purity of the reagents. All used reagents were of the high purity. Samples of ceramic compounds are the most difficult soluble compounds.

2.2. Optimal analytical parameters for the determination of elements
Atomic-emission spectrometer with inductively coupled plasma from the firm "HORIBA JOBIN YVON", the model "ULTIMA 2" (France- Japan) was used for investigation. The high optical resolution (5 pm) of spectrometer provides the best signal to the background ratio, which leads to low detection limits of elements. The following optimal analytical parameters for determination of elements were experimentally found: discharge power - 1,2 kW; cooling argon flow - 14 l/min; transporting - 0,80 l/min; plasma - 0,5 l/min; observation height - 14 mm above the top turn of the induction coil; the speed rate samples - 1,0 ml/min [7]. Analytical lengths of waves were chosen for determination of elements to provide suitable detection limits, a minimum of adjustments for background and overlapping of spectral lines [8]. Optimal analytical lengths of waves for determination are presented in table 2.

It is very important to find the concentration of the matrix elements in the solution, which is not violated the stability for the system burner - nebulizer. Total concentration of matrix elements: Zr, Al, Yb should be not more than 500 ppm.
Table 1. Methods of dissolution of zircon-alumo-ytterbium ceramic materials.

| Ceramics | Temperature regime for producing ceramic compounds | Reagents for dissolution | Dissolution conditions | Reagents for retention of matrix and determinable elements in solution | Determinable elements | Method of analysis (found impurity content) |
|----------|-------------------------------------------------|--------------------------|-----------------------|-------------------------------------------------|---------------------|--------------------------------------------|
| ZrO₂     | Ceramics, obtained without decrepitation       | HF + HNO₃ + H₂SO₄        | Open system: heating in Pt, teflon, glass-carbon dishes (from 30 minutes to 5 hours) | HF NH₄F H₂O₂ H₂SO₄ (1-4M) HCl (2-6M) HNO₃ (2-9M) HClO₄ (2-4M) | Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Ti, Y, Yb, Hf, V, Zn | AES-ICP (10⁻³-n%) AAS-Flaming option (10⁻²-n%) |
| ZrO₂-Yb₂O₃ | Ceramics, obtained with decrepitation to 500°C | HF + HNO₃ + HClO₄ | Autoclaved dissolution in the microwave oven MARS 5 (from 15 to 50 minutes) | H₂C₂O₄ (oxalic) H₆C₆O₆ (lemon) H₆C₄O₆ (wine) | Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Ti, Y, Yb, Hf, V, Zn | AES-ICP (10⁻²-n%) AAS-Flaming option (10⁻³-n%) |
| ZrO₂-Al₂O₃-Yb₂O₃ | Ceramics, obtained with decrepitation above 500°C | Melting with: LiBO₂ Na₂B₂O₇ Na₂CO₃ Na₂B₄O₇ NaOH KOH Na₂O₃ KHF₂ K₂S₂O₇ | Pt crucible Pt crucible Pt crucible Ni crucible Ni crucible Pt crucible Pt crucible | Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, Y, Yb, Hf, V, Zn | AES-ICP (10⁻²-n%) AAS-Flaming option (10⁻³-n%) |
were prepared from high purity metals \[6\]) were used as the zero calibration solutions. The second calibration solutions were prepared for the background solution of zirconium 500 ppm (or aluminum, or ytterbium, or sum elements). The possibility to determine low concentrations of impurity elements on the background of zirconium was established by studying of the spectral interference from the base element at the scan-out of the spectrum from 190 to 800 nm. Solutions of pure zirconium (500 or 1000 ppm) and impurity elements (5, 10, or 100 ppb) were introduced in the plasma. The detection limits of elements were estimated using the formula [9]:

\[
\text{LOD} = k \cdot \text{BEC} \cdot \text{RSD}_0
\]

LOD - limit of detection; k - coefficient equal to 3 for detection 3σ limits; BEC - the concentration of noise; RSD0 - relative standard deviation at zero standard.

Calibration curve was built for two points 0 and 5 ppm to evaluate detection limits. Calibration was used to determine the concentration of the noise BEC. The relative standard deviation RSD0 was determined as results of the zero standard analysis for 5 minutes. The standard solutions 500 ppm of zirconium (or aluminum, or ytterbium, or sum elements), prepared from high purity metals [6]) were used as the zero calibration solutions. The second calibration solutions were prepared for the background solution of zirconium 500 ppm (or aluminum, or ytterbium, or sum elements).

| Element | Analytical length wave \(\lambda\), nm | Detection limit, ppb | 500 ppm Zr in pure solution (2M HCl) | 500 ppm Al | 100 ppm Yb + 500 ppm Al + 100 ppm Yb |
|---------|-------------------------------|---------------------|-----------------------------------|--------------|----------------------------------|
| Al      | 396.152                       | 0.2                 | 2.5                               | 1.2          | 5.4                              |
| As      | 193.695                       | 1.2                 | 2.2                               | 2.8          | 1.3                              |
| Ba      | 433.527                       | 0.2                 | 1.1                               | 2.1          | 0.8                              |
| Be      | 313.042                       | 0.1                 | 1.1                               | 1.8          | 0.5                              |
| Bi      | 206.170                       | 1.5                 | 2.9                               | 3.5          | 1.7                              |
| Ca      | 317.933                       | 0.03                | 0.9                               | 2.1          | 0.8                              |
| Cd      | 226.502                       | 0.02                | 0.4                               | 0.9          | 0.3                              |
| Cd      | 228.802                       | 0.1                 | 0.8                               | 1.9          | 0.6                              |
| Ce      | 413.765                       | 0.3                 | 1.9                               | 2.6          | 0.9                              |
| Co      | 228.616                       | 0.1                 | 1.5                               | 2.0          | 1.0                              |
| Cr      | 267.716                       | 0.2                 | 1.2                               | 1.8          | 0.4                              |
| Cu      | 324.754                       | 0.15                | 1.0                               | 1.9          | 0.5                              |
| Fe      | 259.940                       | 0.1                 | 1.2                               | 1.8          | 1.0                              |
| Hf      | 282.022                       | 0.2                 | 1.2                               | 1.9          | 0.4                              |
| K       | 766.490                       | 1.5                 | 3.3                               | 3.5          | 1.8                              |
| Li      | 670.784                       | 1.0                 | 1.8                               | 2.2          | 1.6                              |
| Mg      | 279.553                       | 0.01                | 0.5                               | 1.9          | 0.1                              |
| Mn      | 257.810                       | 0.05                | 1.2                               | 1.5          | 0.4                              |
| Mo      | 203.844                       | 0.2                 | 2.8                               | 2.9          | 1.2                              |
| Na      | 589.592                       | 0.6                 | 3.0                               | 4.0          | 1.6                              |
| Ni      | 231.604                       | 0.2                 | 2.3                               | 2.5          | 0.6                              |
| Pb      | 220.355                       | 0.8                 | 2.6                               | 2.9          | 1.4                              |
| Si      | 251.611                       | 1.3                 | 2.0                               | 3.0          | 1.6                              |
| Ti      | 334.941                       | 0.1                 | 1.8                               | 2.5          | 0.9                              |
| V       | 292.402                       | 0.2                 | 1.9                               | 2.4          | 1.8                              |
| Y       | 371.029                       | 0.04                | 0.6                               | 2.8          | 0.4                              |
| Yb      | 328.927                       | 0.4                 | 3.2                               | 4.8          |                                  |
| Zn      | 213.856                       | 0.1                 | 2.2                               | 2.8          | 1.6                              |
| Zr      | 343.823                       | 1.0                 | 3.0                               | 2.0          |                                  |

2.3. The influence of the matrix and methods of it removal

The possibility to determine low concentrations of impurity elements on the background of zirconium was established by studying of the spectral interference from the base element at the scan-out of the spectrum from 190 to 800 nm. Solutions of pure zirconium (500 or 1000 ppm) and impurity elements (5, 10, or 100 ppb) were introduced in the plasma. The detection limits of elements were estimated using the formula [9]:

\[
\text{LOD} = k \cdot \text{BEC} \cdot \text{RSD}_0
\]

LOD - limit of detection; k - coefficient equal to 3 for detection 3σ limits; BEC - the concentration of noise; RSD0 - relative standard deviation at zero standard.

Calibration curve was built for two points 0 and 5 ppm to evaluate detection limits. Calibration was used to determine the concentration of the noise BEC. The relative standard deviation RSD0 was determined as results of the zero standard analysis for 5 minutes. The standard solutions 500 ppm of zirconium (or aluminum, or ytterbium, or sum elements), prepared from high purity metals [6]) were used as the zero calibration solutions. The second calibration solutions were prepared for the background solution of zirconium 500 ppm (or aluminum, or ytterbium, or sum elements).
Concentrations of the determined elements (Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, Y, Yb, Hf, V, Zn) were 5 ppm.

Calculated detection limits for the impurities in the presence of matrix elements are presented in table 2. The detection limits against the background of 500 ppm zirconium (or aluminum, or ytterbium, or sum elements) are significantly different from those in pure solutions and not for the better.

The mutual influences of the determined elements were studied. It has been established that no mutual effects occur when the content of the elements up to 10 ppm.

The main problem of the emission analysis is to find and eliminate the matrix influence. Zirconium-alumino-ytterbium ceramic is very complex matrix. Determination of trace elements is especially difficult because of temporal drift of the background, sophisticated form of background in area of analytical lines and weak signal intensity. Increasing integration time reduces the detection limits but does not solve the problem of the influence matrix [4].

**Table 3.** Allowable ratios of the matrix elements: zirconium, aluminum, ytterbium to the determined elements.

| Element | Analytical length wave, nm | Allowable relationships | The optimal concentration interval of the determined element (ppm) | Relative standard deviation (S<sub>r</sub>) |
|---------|-----------------------------|-------------------------|---------------------------------------------------------------|------------------------------------------|
| Al      | 396.152                     | 1:10<sup>5</sup>        | [Zr]/[Э] 1:10<sup>5</sup> [Al]/[Э] 1:10<sup>5</sup> [Yb]/[Э] 1:10<sup>5</sup> [Zr+Al+Yb]/[Э] 1:10<sup>5</sup> | 0.10-100                                 | 0.15-0.001 |
| As      | 193.695                     | 2:10<sup>5</sup>        | 2:10<sup>4</sup> 2:10<sup>5</sup> 1:10<sup>4</sup> 5:10<sup>4</sup> | 0.15-10                                 | 0.20-0.02 |
| Ba      | 433.527                     | 1:10<sup>6</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.05-10                                 | 0.15-0.05 |
| Be      | 313.042                     | 1:10<sup>6</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.10-10                                 | 0.10-0.004 |
| Bi      | 206.170                     | 2:10<sup>5</sup>        | 3:10<sup>5</sup> 4:10<sup>5</sup> 2:10<sup>5</sup> | 0.10-10                                 | 0.18-0.02 |
| Ca      | 317.933                     | 1:10<sup>6</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.05-10                                 | 0.15-0.005 |
| Cd      | 226.502                     | 2:10<sup>6</sup>        | 2:10<sup>6</sup> 2:10<sup>6</sup> 1:10<sup>6</sup> | 0.005-10                                | 0.15-0.06 |
| Cd      | 228.802                     | 1:10<sup>6</sup>        | 1:10<sup>6</sup> 1:10<sup>6</sup> 5:10<sup>5</sup> | 0.010-10                                | 0.12-0.005 |
| Ce      | 413.765                     | 2:10<sup>5</sup>        | 2:10<sup>5</sup> 1:10<sup>4</sup> 1:10<sup>4</sup> | 0.20-10                                 | 0.15-0.01 |
| Co      | 228.616                     | 1:10<sup>5</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.15-10                                 | 0.18-0.02 |
| Cr      | 267.716                     | 2:10<sup>6</sup>        | 1:10<sup>6</sup> 1:10<sup>6</sup> 1:10<sup>6</sup> | 0.05-10                                 | 0.12-0.005 |
| Cu      | 324.754                     | 6:10<sup>5</sup>        | 3:10<sup>5</sup> 4:10<sup>5</sup> 2:10<sup>5</sup> | 0.10-10                                 | 0.15-0.01 |
| Fe      | 259.940                     | 1:10<sup>5</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.10-10                                 | 0.14-0.01 |
| Hf      | 282.022                     | 3:10<sup>5</sup>        | 2:10<sup>5</sup> 2:10<sup>5</sup> 1:10<sup>5</sup> | 0.25-10                                 | 0.15-0.01 |
| K       | 766.490                     | 1:10<sup>4</sup>        | 1:10<sup>4</sup> 1:10<sup>4</sup> 4:10<sup>3</sup> | 0.50-10                                 | 0.20-0.02 |
| Li      | 670.784                     | 1:10<sup>5</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 4:10<sup>4</sup> | 0.25-10                                 | 0.18-0.01 |
| Mg      | 279.553                     | 3:10<sup>5</sup>        | 2:10<sup>5</sup> 1:10<sup>5</sup> 1:10<sup>5</sup> | 0.10-10                                 | 0.15-0.009 |
| Mn      | 257.810                     | 2:10<sup>6</sup>        | 1:10<sup>6</sup> 1:10<sup>6</sup> 5:10<sup>5</sup> | 0.005-10                                | 0.12-0.008 |
| Mo      | 202.030                     | 1:10<sup>6</sup>        | 1:10<sup>6</sup> 1:10<sup>6</sup> 4:10<sup>5</sup> | 0.10-10                                 | 0.15-0.01 |
| Na      | 589.592                     | 1:10<sup>5</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 4:10<sup>4</sup> | 0.50-10                                 | 0.15-0.01 |
| Ni      | 231.604                     | 1:10<sup>5</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.50-10                                 | 0.15-0.02 |
| Pb      | 220.353                     | 2:10<sup>5</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.50-10                                 | 0.15-0.03 |
| Si      | 251.611                     | 1:10<sup>5</sup>        | 4:10<sup>4</sup> 3:10<sup>5</sup> 2:10<sup>5</sup> | 0.40-10                                 | 0.15-0.02 |
| Y       | 371.029                     | 2:10<sup>5</sup>        | 2:10<sup>5</sup> 2:10<sup>5</sup> 9:10<sup>4</sup> | 0.05-10                                 | 0.12-0.005 |
| Yb      | 328.927                     | 2:10<sup>6</sup>        | 2:10<sup>6</sup> 2:10<sup>6</sup> | 0.10-10                                 | 0.12-0.005 |
| V       | 310.230                     | 2:10<sup>5</sup>        | 2:10<sup>5</sup> 1:10<sup>5</sup> 8:10<sup>4</sup> | 0.20-10                                 | 0.12-0.008 |
| Zn      | 213.856                     | 1:10<sup>6</sup>        | 1:10<sup>5</sup> 1:10<sup>5</sup> 5:10<sup>4</sup> | 0.15-10                                 | 0.14-0.009 |
The influence of the matrix elements (Zr, Al, Yb) was studied. Allowable ratios of zirconium aluminum and ytterbium to determined elements are presented in Table 3. It was determined effect of Zr, Al, Yb for different elements. Such effect is especially significant for high contents of matrix elements and low concentrations of the impurities. It was observed that the slope and shift of the calibration curve depend from nature and concentration of matrix element in the solution. The concentration of the matrix elements (Zr, Al, Yb) up to 100 ppm did not affect the analytic signals of the impurity elements (more than 10 ppb). Concentration increase of Zr (Al, Yb) in the solution from 100 ppm to 500 ppm leads to change in the slope and a shift of the calibration curves. Such changes are particularly noticeable for high matrix contents (500 ppm) and low concentrations of the detectable elements (less than 5 ppb). The method of interactive concordance of matrix [4] was applied to eliminate the matrix interference due to the changing concentration of the matrix element. It is particularly difficult to determine the elements near the limits of their detection on the level of the background of complex matrices. On figures 1-3 are presented the calibration graphs of As, Pb and Cr for pure solutions and containing 500 ppm Al or 500 ppm Al plus 500 ppm Zr. There is a distortion (see figures 1-3) of the calibration curves and, consequently, a deterioration in metrological characteristics of the determination of elements concentration below 5 ppb. When determining the elements near detection limits (5 ppb), other impurity elements (at a content of more than 10 ppm) begin to affect analytical signals. There are many publications regarding calibration functions for the analysis of high concentrations but practically no work on reducing errors of determination low concentrations [10]. We used the orthorecursive expansions method (ORE) in overcomplete systems, which bases on embedded spaces [11] to construct gauge functions with various sets of matrix effects. Due to orthorecursive expansions in overcrowded systems withstand any finite number of computational errors, the application of this method in the construction of gauge functions provides the following possibilities: significantly reducing errors of calculations, taking into consideration the influence of many matrices, accelerate the conduct of analytical measurements, and determinate elements from $1 \cdot 10^{-3}\%$ without separation of the zircon-alumo-ytterbium matrix. In the case of smaller concentrations should be provided a preliminary separation of the matrix or should be used methods of mathematical modeling.

![Figure 1. Calibration curves As for pure solutions (1), containing 500 ppm Al (2), 500 ppm Al plus 500 ppm Zr (3).](image1)

![Figure 2. Calibration curves Pb for pure solutions (1) and containing 500 ppm Al (2).](image2)
2.4. The influence of acids

The influence of the concentration effect of HCl, HNO₃, H₂SO₄ acids on the analytical signals of elements were studied. The dependence curves of analytical Al signals from the nature and concentration of acids in the analyzed solution are shown on figure 4. Changes in the acid concentration of the analyzed solution lead to changes in analytical signal. The degree of signal change depends on the nature and concentration of acid. The solution of 2M HCl decreases the analytical signal Al and the sulfuric acid of the same concentration accordingly on 3% and 11%. When HCL and HNO₃ concentration increases from 0.01 M to 1 M, analytical signals of the elements change not more than 3%. Analytical signals of the elements depend significantly on concentrations of sulfuric acid in solution. Depressing action of acids is due to changes in the spray or the sample introduction systems. Change in the acid concentration leads to alteration in the effectiveness of spraying and, consequently, sensitivity. However, the methodical error can be avoided by maintaining adequate acid content in tests and standard solutions. Uncontrolled fluctuations in the concentration of acids, especially sulphuric, can lead to significantly greater errors than instrumental.

3. The results

Samples were analyzed according to developed programs. In the solutions obtained the contents of the impurity elements were determined: Al, As, Yb, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Sr, Ti, Hf, V, Y, Yb, Zn. To reduce the error in determining elements, calibration solutions were prepared for the same composition and content of acids as solutions of the analyzed samples. The of the analysis of the samples are shown in tables 4-5. Due to the lack of solid reference samples for the composition of new ceramics, the findings were compared with the data of gravimetric (Al, Zr), atomic absorption methods of analysis and inductively coupled plasma mass spectrometry to confirm correctness of the obtained results. Good convergence of the results received using different methods of analysis was obtained.

New methods allowed carry out the rapid chemical control of harmful (As, Cr, Cd, Li, Pb), "coloring" (Co, Cu, Fe, Mn, Ni), and functional (Al, Ba, Ca, Ce, Hf, K, Mg, Na, Y, Yb, Zn) impurities in zircon-alumo-ytterbium ceramic materials. Analytical control has been used during research and development of new generation ceramic biomaterials, in particular, medical composite materials, for bone repair.
Table 4. Results of determination of the elements contents in zircon-alumo-ytterbium ceramic materials, obtained by various methods of analysis (n = 10, P = 0.95).

| № | Determined elements | № sample | Found AES-ICP | Found AAS (MS-ICP) |
|---|---------------------|----------|---------------|-------------------|
|   |                     |          | Mass content, % | S_r               | Mass content, % | S_r               |
| 1 | As                  | 1        | <1·10^{-3}     | 0.15              | <1·10^{-3}     | 0.18              |
|   |                     | 2        | 0.0046         | 0.08              | 0.0043         | 0.07              |
| 2 | Ba                  | 1        | <1·10^{-3}     | 0.20              | <1·10^{-3}     | 0.18              |
|   |                     | 2        | 0.10           | 0.05              | 0.11           | 0.06              |
| 3 | Be                  | 1        | <1·10^{-3}     | 0.13              | <1·10^{-3}     | 0.15              |
|   |                     | 2        | 0.092          | 0.08              | 0.095          | 0.08              |
| 4 | Bi                  | 1        | <1·10^{-3}     | 0.20              | <1·10^{-3}     | 0.15              |
|   |                     | 2        | 0.046          | 0.06              | 0.048          | 0.08              |
| 5 | Ca                  | 1        | 0.21           | 0.015             | 0.22           | 0.018             |
|   |                     | 2        | 0.021          | 0.06              | 0.022          | 0.04              |
| 6 | Cd                  | 1        | <1·10^{-3}     | 0.15              | <1·10^{-3}     | 0.15              |
|   |                     | 2        | 0.012          | 0.07              | 0.010          | 0.08              |
| 7 | Ce                  | 1        | <2·10^{-3}     | 0.20              | <1·10^{-3}     | 0.25              |
|   |                     | 2        | 0.042          | 0.07              | 0.045          | 0.09              |
| 8 | Co                  | 1        | 0.001          | 0.12              | 0.001          | 0.15              |
|   |                     | 2        | 0.012          | 0.10              | 0.013          | 0.10              |
| 9 | Cr                  | 1        | <1·10^{-3}     | 0.16              | <1·10^{-3}     | 0.20              |
|   |                     | 2        | 0.032          | 0.08              | 0.035          | 0.07              |
| 10| Cu                  | 1        | <1·10^{-3}     | 0.20              | <1·10^{-3}     | 0.15              |
|   |                     | 2        | 0.004          | 0.12              | 0.003          | 0.13              |
| 11| Fe                  | 1        | 0.001          | 0.12              | 0.001          | 0.15              |
|   |                     | 2        | 0.012          | 0.10              | 0.013          | 0.10              |
| 12| Hf                  | 1        | 0.032          | 0.08              | 0.035          | 0.07              |
|   |                     | 2        | 1.03           | 0.01              | 1.04           | 0.008             |
| 13| Li                  | 1        | <1·10^{-3}     | 0.20              | <1·10^{-3}     | 0.20              |
|   |                     | 2        | 0.009          | 0.12              | 0.010          | 0.10              |
| 14| Mg                  | 1        | 0.005          | 0.10              | 0.006          | 0.15              |
|   |                     | 2        | 0.016          | 0.07              | 0.014          | 0.09              |
| 15| Mn                  | 1        | <5·10^{-4}     | 0.20              | <5·10^{-4}     | 0.15              |
|   |                     | 2        | 0.041          | 0.08              | 0.042          | 0.17              |
| 16| Ni                  | 1        | <1·10^{-3}     | 0.20              | <5·10^{-4}     | 0.20              |
|   |                     | 2        | 0.012          | 0.10              | 0.013          | 0.10              |
| 17| Pb                  | 1        | 0.012          | 0.10              | 0.013          | 0.10              |
|   |                     | 2        | 0.012          | 0.10              | 0.013          | 0.10              |
| 18| Ti                  | 1        | <1·10^{-3}     | 0.15              | <1·10^{-3}     | 0.15              |
|   |                     | 2        | 0.010          | 0.12              | 0.012          | 0.10              |
| 19| V                   | 1        | <1·10^{-3}     | 0.18              | <1·10^{-3}     | 0.16              |
|   |                     | 2        | 0.015          | 0.12              | 0.013          | 0.10              |
| 20| Y                   | 1        | 0.010          | 0.12              | 0.009          | 0.10              |
|   |                     | 2        | 0.12           | 0.12              | 0.13           | 0.10              |
| 21| Yb                  | 1        | 9.56           | 0.009             | 9.56           | 0.009             |
|   |                     | 2        | 5.87           | 0.012             | 5.82           | 0.01              |
| 22| Zn                  | 1        | <1·10^{-3}     | 0.20              | <1·10^{-3}     | 0.16              |
|   |                     | 2        | 0.015          | 0.12              | 0.013          | 0.10              |
The source of ceramic compounds contamination with harmful impurities (As, Cr, Cd, Li, Pb), obtained in the IMET RAS by the sol-gel synthesis method, was found. Recommendations were given to reduce the content of these elements in obtained samples.

**Table 5.** Results of determination of the elements contents in zircon-alumo-ytterbium ceramic materials, obtained by various methods of analysis (n = 10; P = 0.95).

| Determined elements | Sample №100 | | | Sample №101 | | |
|---------------------|-------------|-------------|-------------|-------------|-------------|
|                     | AES-ICP     | Other methods of analysis | AES-ICP     | Other methods of analysis |
|                     | Mass content, % | S_r | Mass content, % | S_r | Mass content, % | S_r | Mass content, % | S_r |
| Zr                  | 54.4        | 0.005 | 54.6        | 0.005 | 34.9        | 0.005 | 34.6        | 0.005 |
| Al                  | 0.34        | 0.07 | 0.34        | 0.07 | 23.7        | 0.007 | 23.5        | 0.007 |
| Yb                  | 8.42        | 0.010 | 8.47        | 0.008 | 7.14        | 0.010 | 7.19        | 0.009 |
| Ce                  | 0.72        | 0.02 | 0.68        | 0.015 | 0.002        | 0.20 | 0.002        | 0.15 |
| Y                   | 0.018       | 0.04 | 0.018       | 0.04 | 0.0031       | 0.12 | 0.0034       | 0.10 |
| Hf                  | 0.66        | 0.05 | 0.69        | 0.05 | 0.30         | 0.05 | 0.29         | 0.05 |
| As                  | <0.001      | 0.15 | <0.001      | 0.15 | <0.001       | 0.15 | <0.001       | 0.15 |
| Ba                  | 0.051       | 0.10 | 0.050       | 0.10 | 0.047        | 0.10 | 0.049        | 0.10 |
| Be                  | <0.001      | 0.13 | <0.001      | 0.13 | <0.001       | 0.13 | <0.001       | 0.13 |
| Bi                  | <0.001      | 0.15 | <0.001      | 0.15 | <0.001       | 0.15 | <0.001       | 0.15 |
| Ca                  | 0.29        | 0.08 | 0.28        | 0.08 | 0.0040       | 0.08 | 0.0044       | 0.08 |
| Cd                  | <0.001      | 0.13 | <0.001      | 0.13 | <0.001       | 0.13 | <0.001       | 0.13 |
| Co                  | <0.001      | 0.13 | <0.001      | 0.13 | <0.001       | 0.13 | <0.001       | 0.13 |
| Cr                  | <0.001      | 0.13 | <0.001      | 0.13 | <0.001       | 0.13 | <0.001       | 0.13 |
| Cu                  | 0.013       | 0.10 | 0.015       | 0.10 | 0.0083       | 0.10 | 0.0080       | 0.10 |
| Fe                  | <0.001      | 0.13 | <0.001      | 0.13 | <0.001       | 0.13 | <0.001       | 0.13 |
| K                   | 0.0049      | 0.12 | 0.0042      | 0.13 | 0.019        | 0.12 | 0.021        | 0.12 |
| Li                  | <0.001      | 0.13 | <0.001      | 0.13 | <0.001       | 0.13 | <0.001       | 0.13 |
| Mg                  | 0.051       | 0.09 | 0.056       | 0.09 | 0.024        | 0.09 | 0.020        | 0.09 |
| Mn                  | <0.001      | 0.13 | <0.001      | 0.13 | 0.0017       | 0.13 | 0.0015       | 0.13 |
| Mo                  | <0.001      | 0.13 | <0.001      | 0.13 | <0.001       | 0.13 | <0.001       | 0.13 |
| Na                  | 0.055       | 0.10 | 0.059       | 0.13 | 0.089        | 0.10 | 0.086        | 0.10 |
| Ni                  | <0.001      | 0.15 | <0.001      | 0.15 | <0.001       | 0.15 | <0.001       | 0.15 |
| Pb                  | <0.001      | 0.15 | <0.001      | 0.15 | 0.0041       | 0.15 | 0.0045       | 0.15 |
| Si                  | 0.15        | 0.10 | 0.14        | 0.10 | 0.098        | 0.10 | 0.10         | 0.10 |
| Ti                  | <0.001      | 0.15 | <0.001      | 0.15 | <0.001       | 0.15 | <0.001       | 0.15 |
| V                   | <0.001      | 0.15 | <0.001      | 0.15 | <0.001       | 0.15 | <0.001       | 0.15 |
| Zn                  | <0.001      | 0.15 | <0.001      | 0.15 | <0.001       | 0.15 | <0.001       | 0.15 |
4. Conclusion
Using of atomic-emission spectrometry with inductively coupled plasma the methods have been developed for simultaneous quantifying of impurities contents: Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, Y, Yb, Hf, V, Zn in new zircon-alumo-ytterbium ceramic materials, allowing to express determine these elements in a wide range of concentrations from \(1 \times 10^{-3}\) to \(10^{-n}\%\), using limited amount of samples (from 1 mg), without preliminary separation of the matrix and without using solid standard samples. Various schemes for dissolving samples were offered for different types of ceramic compounds. Elements were determinate with founded optimal analytical parameters. The influence and methods elimination of matrix elements (Zr, Al, Yb) were studied. The algorithms for mathematical accounting of the matrix effects when AES–ICP determining low concentrations of impurity elements in the studied compounds were proposed. The relative standard deviation (S) is 0.05-0.005 at the content of elements from 1 to 50% and does not exceed 0.12 at the elements content from 0.001 to 0.1%.

This work allows us to assess the compliance of the developed ceramics with the requirements of international standards for medical materials.

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