

# SEPARATION OF IRON AND CHROMIUM IN THE FORM OF INSOLUBLE FLUORIDES FOR ICP-AES DETERMINATION OF TRACE ARSENIC IN NICKEL HEAT-RESISTANT ALLOYS

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In critical applications alloys and high purity metals content of impurity elements having a negative impact on their quality (including arsenic [1]) is strictly controlled. Despite progress in the field of instrument design and mathematical processing of analytical signals in determining the content of the trace elements with the help of modern instrumental techniques including inductively coupled plasma atomic emission (ICP-AES) often pre-separation of trace analytes from matrix having a negative influence on the chemical analysis results is necessary in order to achieve the required detection limits. In materials with a high content of chromium and iron ICP-AES determination of arsenic trace levels without their separation from the matrix is impossible because spectral overlays [2].

The development of a simple and rapid method of arsenic separation from the main elements of superalloys is an actual problem, as it will allow the unhindered conduct of the analyte determination almost any instrumental methods.

The most common express and therefore the most preferred for use in routine chemical analysis method of arsenic concentration is the co-precipitation with metal hydroxides [3]. However, the method often is not applicable for the samples preparation to trace elements determination in heat-resistant alloys because they constitute the metal giving hydroxides which during the process may also play a role of collectors. When the determination of arsenic in the alloys it would be preferable to choose such conditions that exclude trace elements co-precipitation with hydroxides formed by components of the matrix.

In the first half of the XX century academician I.V. Tananaev and coworker in Institute of General and Inorganic Chemistry of the USSR Academy of Sciences (Moscow) conducted investigation of opportunities of separation of small amounts of zinc, cobalt, nickel, manganese, etc. from large quantities of iron by using sodium or potassium fluoride as a precipitating agent [4-5]. Whereas comfortable in terms of analytical chemist properties of the resulting hardly soluble fluoride complexes

(crystallinity and low volume), the authors of [4-5] have predicted the prospects of this method of separation of iron and trace elements when used in analytical practice.

Taking into account the data presented in [5], we can conclude that iron can be separated from the arsenic by reaction of the insoluble fluoride complex formation. Such information on the separation of arsenic and chromium are not found, although there are published data on the formation of  $\text{Na}_3\text{CrF}_6$  precipitate in the processing of solution Cr (III) by sodium fluoride, for example, in [6].

The aim of the present work is to test perspective of separation of the heat-resistant nickel-based alloys main components in the form of insoluble fluoride-containing compounds with a view to subsequent determination of arsenic by ICP-AES.

### **Experimental**

All experimental studies were performed on the model solutions simulating composition of nickel-based heat resistant alloy solution containing small amounts of arsenic: Fe = 40 wt%, Cr = 30 wt%, Ni = 30 wt%, As = 0.01 wt%. The solutions were prepared by dissolving of metals in a mixture of «aqua regia» and hydrofluoric acid with adding of certified arsenic aqueous solution.

#### ***Equipment***

X-ray examination of samples was carried out on a Shimadzu XRD-7000 diffractometer in Cu Ka-radiation using certified silicon powder as an internal standard. Measurement conditions: I = 30 mA, V = 40 kV, the angle range from 20° to 70° in 2 $\Theta$ , a step size of 0.02° and a step scan of 2 s.

At all stages of experimental investigations the chemical composition of the liquid phase after precipitation was determined by ICP-AES method using Optima 2100 DV spectrometer (Perkin Elmer) with a quartz burner. The chemical composition of the precipitate after dissolving it in concentrated hydrochloric acid was also determined by ICP-AES. The solutions for the calibration of the spectrometer and study of interfering matrix influences was prepared by diluting a certified solution of arsenic, iron, chromium and nickel ions. In these solutions was added as a blank certain quantity of reagents used to prepare the analyzed model solutions.

The following operational parameters were employing: RF power – 1300 W; Ar gas flow rate– 15 l/min; gas flow rates for auxiliary – 0.20 l/min; gas flow rates for nebulizer – 0.80 l/min; pump flow rate – 1.5 ml/min; observation mode – radial; delay time – 40 sec, the number of replicas - 2. The analytical spectral lines: As I 193.696 nm, Fe II 358.119 nm, Ni 231.604 nm, Cr II 359.348 nm.

### ***Procedure of iron separation***

The procedure was performed at room temperature. The required amount of the solution containing the Fe (III) was placed in PTFE beakers, and NaF was added by portions with constant stirring in amount necessary to produce the molar ratio NaF/Fe 3.3, 6.7, 12.1, 13.3, 26.7, 33.1. The precipitate was allowed to stand for 15 minutes, filtered through a “white ribbon” filter and washed. The filtrate was transferred to a polypropylene flask, diluted to the mark with distilled water and mixed.

To study the effect of temperature iron precipitation was carried out from model solutions by sodium fluoride (NaF / Fe  $\geq$  13.3) at 25, 80, 100 °C and the precipitate was kept for 15 min at pH = 0.

To investigate the effect of contact time of formed precipitate with liquid phase on iron precipitation was carried out by NaF / Fe  $\geq$  13.3, at T = 100 °C, pH = 0, then the precipitate was kept for 5, 10, 15, 20 min.

To study the effect of pH on precipitation process to model solutions precipitator was added (NaF / Fe  $\geq$  13.3) at T = 100 °C Then, using the ionometer pH value was adjusted to the desired in the range from 0 to 7 by 1 M NaOH solution. The precipitate was kept for 15 min.

### **Results and discussion**

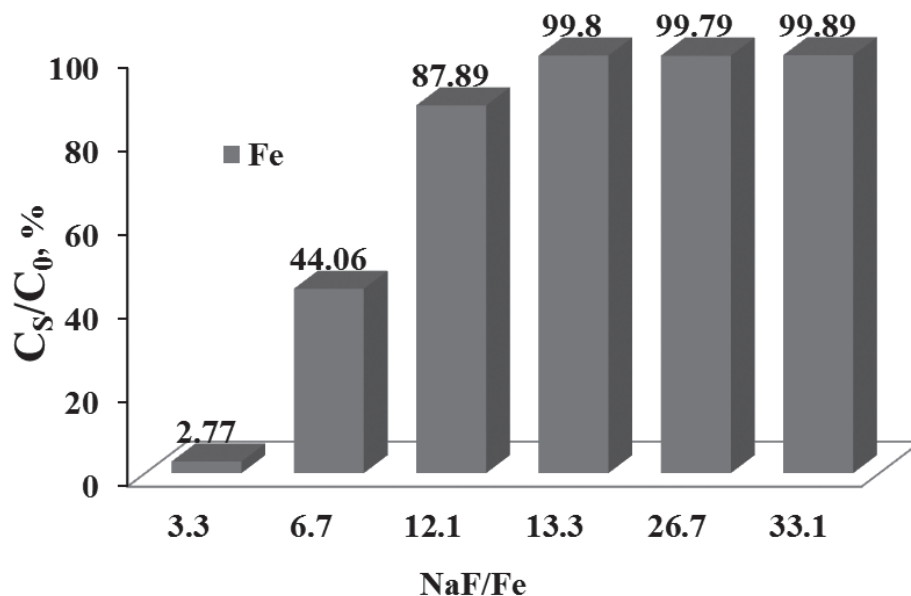
Optimization of separation of heat-resistant nickel alloys macro-components conditions from arsenic using NaF previously have not been conducted, and experiments required to find the optimal amount of precipitant. Selection was carried out on an example of iron. It has previously been established [5] that the iron is not fully precipitated by the addition of an equivalent amount of precipitant, so the excess of NaF is necessary.

In this paper, to quantify the distribution of elements in liquid and solid phases, we will use the so-called relative content of  $C_L/C_0$  ( $C_S/C_0$ ), calculated using equation:

$$C_L / C_0(C_S / C_0) = \frac{\text{mass in solution(precipite)}}{\text{initial mass}} \cdot 100\%.$$

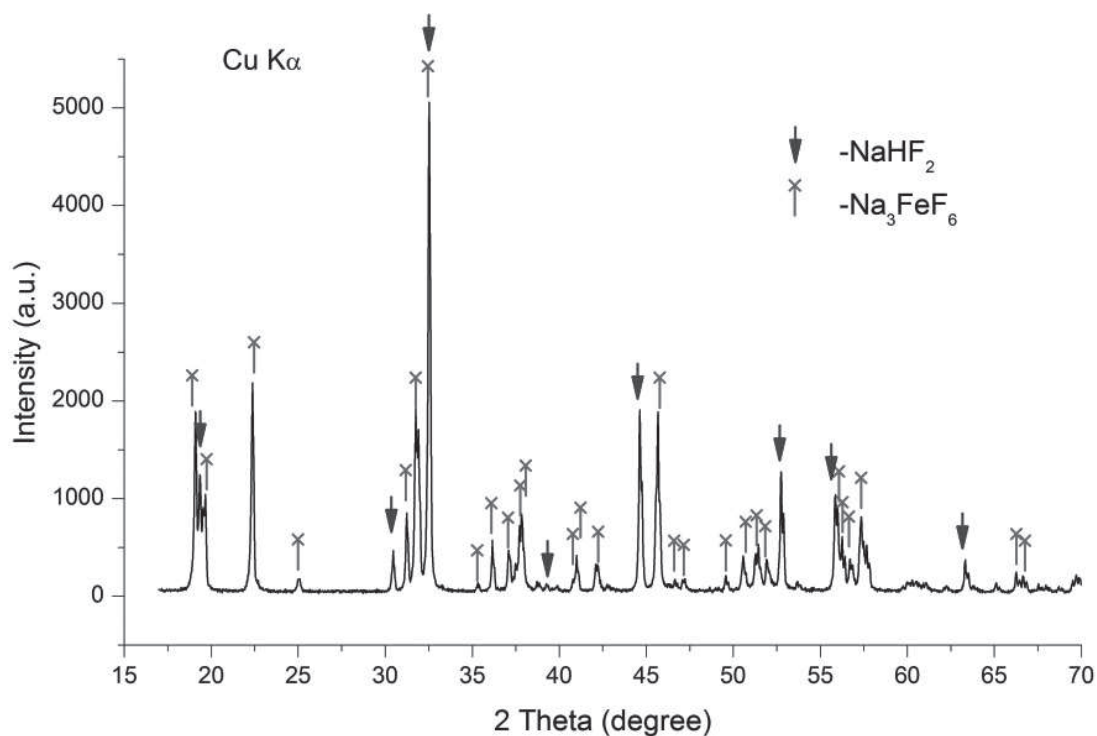
Fig. 1 shows the results of determining the molar excess of precipitant (NaF) required for complete precipitation of iron.

Fig. 1 shows that nearly complete iron precipitation is observed when the molar excess of precipitant is 13.3 (corresponding to 10 mass excess). Further increase of precipitant quantity leads to a slight change in the results.

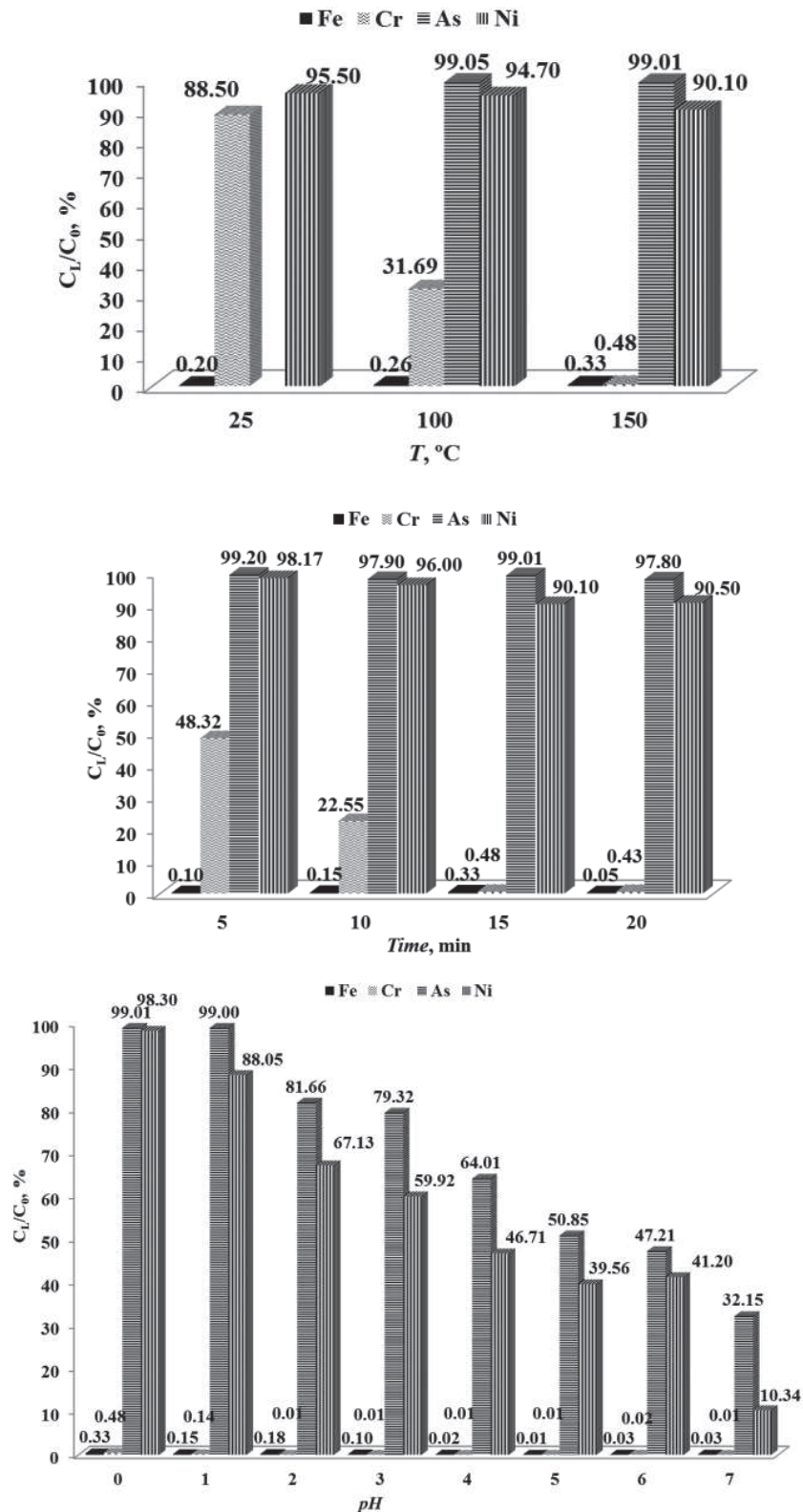


**Fig. 1.** Iron content in the solid phase vs molar excess of precipitant (NaF); pH = 0; room temperature, contact time of precipitate and liquid - 5 min

The phase composition of the precipitate (NaF/Fe = 13.3) was determined by X-ray diffraction (see fig. 2). Fig. 2 shows that the precipitation of iron from the acidic solutions using NaF formed only one iron-containing compound, corresponding to the composition  $\text{Na}_3\text{FeF}_6$ .



**Fig. 2.** X-ray diffraction pattern of the iron-containing precipitate

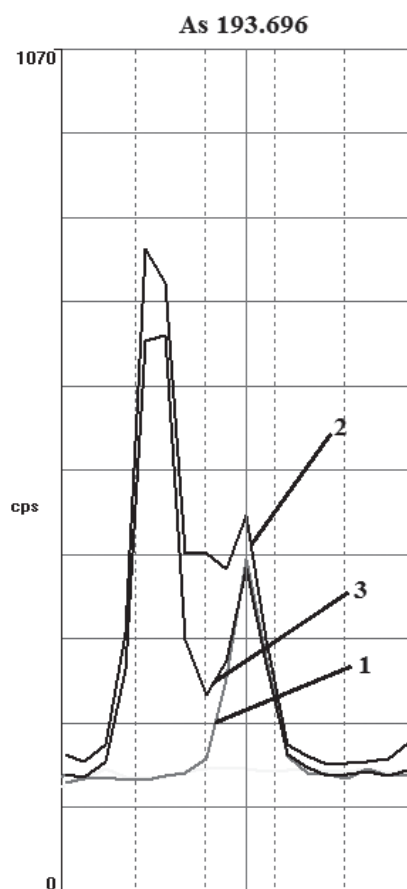


**Fig. 3.** Relative content of Fe, Cr, Ni, As in solution after precipitation by NaF, vs: a) temperature (contact time of precipitate and liquid - 15 min, pH = 0), at 25 °C arsenic content can not be determined correctly; b) contact time of precipitate and liquid (T = 80 °C, pH = 0); c) pH (contact time of precipitate and liquid - 15 min, T = 100 °C); NaF / Fe > 13.3

Then, studies of the simultaneous precipitation of all macrocomponents of heat resisting nickel alloys - chromium, nickel, iron - were carried out using the found optimum amount of precipitant ( $\text{NaF} / \text{Fe} \geq 13.3$ , which corresponds to a molar ratio  $\text{NaF} / \text{Cr} \geq 18.3$ ), as well as their separation from arsenic. During the studies pH, temperature and contact time of the solution with precipitate were varied. The results are shown in Fig. 3 (a) - (c). Fig. 3 (a) shows that after precipitation at room temperature, chromium and nickel are in solution at the concentrations close to the introduced.

In these conditions there is a complete precipitation of iron only. Due to spectral overlapping of chromium and arsenic analytical lines it is not possible to determine exact concentration of As in the model solution. Increasing the heating temperature leads to a sharp reduction of chromium concentration in the liquid phase, wherein the nickel concentration decreases slightly - i.e., sodium fluoride precipitated chromium but not nickel.

As an example, Fig. 4 shows the emission spectra of the model solutions containing arsenic, nickel, iron and chromium: the solutions obtained in the separation macrocomponents (their initial concentration:  $\text{Cr} - 1.60 \text{ gL}^{-1}$ ;  $\text{Fe} - 2.20 \text{ gL}^{-1}$ ,  $\text{Ni} - 1.6 \text{ gL}^{-1}$ ) at different temperature ( $\text{NaF} / \text{Fe} \geq 13.3$ , contact time of precipitate and liquid - 15 min).

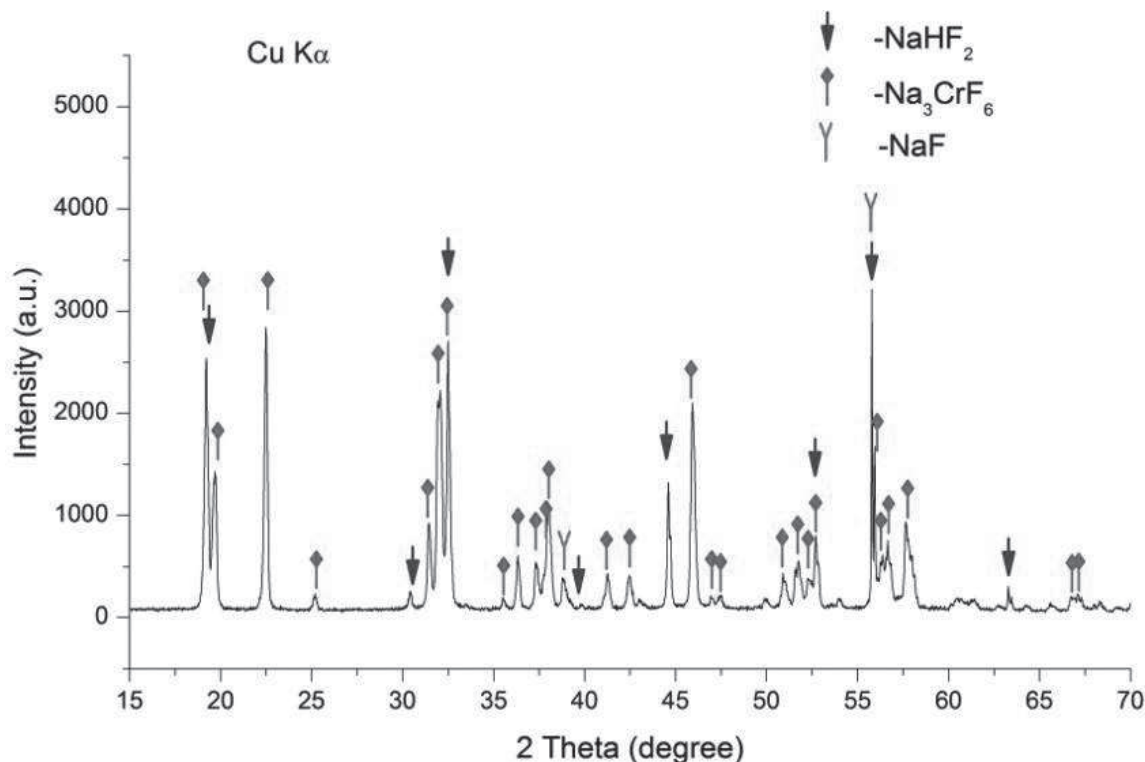


**Fig. 4.** The spectra of arsenic solution ( $C_{\text{AS}} = 0.500 \text{ mgL}^{-1}$ ) obtained by separation of macrocomponents from model solutions with a concentration of  $\text{Cr} - 1.60 \text{ gL}^{-1}$ ;  $\text{Fe} - 2.20 \text{ gL}^{-1}$ ,  $\text{Ni} - 1.6 \text{ gL}^{-1}$ , at different temperatures ( $\text{NaF} / \text{Fe} \geq 13.3$ , contact time of precipitate and liquid - 15 min): 1 - aqueous solution of As of the same concentration; 2 - model solution after precipitation at  $80 \text{ }^\circ\text{C}$ , 3 - at  $100 \text{ }^\circ\text{C}$

When comparing Fig. 4 and Fig. 3 (a) it can be seen that the partial chromium separation (at 80 °C) leads to strong matrix effect on analytical spectral arsenic line. The spectrum of model solution (Fig. 4, the spectrum 2) differs significantly from that of the aqueous calibration solution (Fig. 4, spectrum 1). Increasing the temperature to 100 °C (the temperature of rapid boiling) resulted in an almost complete separation of chromium and iron from the arsenic, which allowed practically eliminate the overlapping of matrix and the spectral line of arsenic (Fig. 4, spectrum 3).

Study of the influence of contact time of the precipitate and liquid phase and the pH (Fig. 3 (b-c)) discovered that the optimum conditions are contact time 15 min and pH = 0 – 1. With a further increase of pH and the contact time arsenic partially transits in the solid phase. This behavior is likely to be explained by the occurrence of his co-precipitation process. The observed changes in the concentration of chromium in the liquid phase, depending on varying the contact time (Fig. 3. (b)), probably due features of formation its soluble compounds with fluorine.

The phase composition of the precipitate, obtained from the model chromium-contained solution in the established optimal condition was determined by X-ray diffraction (see. Fig. 5). From Fig. 5 it is seen that using NaF under selected conditions chromium-containing compound is formed, corresponding to the composition  $\text{Na}_3\text{CrF}_6$ .



**Fig. 5.** X-ray diffraction pattern of the chromium-containing precipitate

It is found that high nickel concentrations do not have influence on the analytical spectral line of arsenic, so the processing temperature of 100 °C, can be considered optimal, since there is a complete separation of interfering macro components - iron and chromium, and arsenic loss does not occur.

### **Conclusions**

In this study we found that in the processing of solutions of heat-resistant nickel alloys samples by sodium fluoride we can separate their macro quantity of chromium and iron from the target analyte (arsenic). Nickel remains in solution, but does not interfere ICP-AES determination of arsenic. The procedure for separating arsenic from the chromium and iron proved to be effective and can be recommended for the development of procedure of its ICP-AES determination. The optimum separation conditions: molar ratio NaF / Fe  $\geq$  13.3 (NaF / Cr  $\geq$  18.3), pH = 0-1, temperature 100 ° C, contact time of precipitate and solution - 15 minutes. Considered in this paper, a method for separating arsenic from the sample matrix of superalloys is express, inexpensive, there is no need for pH control (precipitation can be carried out immediately after acid dissolution of the sample), what is its advantage over methods of separation used in the standardized methods.

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### **References**

1. Kopylov N.I., Kaminskiy Yu.D. *Arsenic*. Novosibirsk, Siberian University Press, 2004. 363 p. (in Russian)
2. Maiorova A.V., Belozerova A.A., Pechishcheva N.V., Shunyaev K.Yu. *Optimization of the sample preparation procedure for arsenic and antimony determination in steel and cast iron // Proceedings of the Fourteenth Israeli - Russian Bi-National Workshop "The optimization of the composition, structure and properties of metals, oxides, composites, nano and amorphous materials" Ariel, 2015. P. 131-137.*
3. A.A. Belozerova, A.V. Maiorova, N.V. Pechischceva, N.G. Boyarnikova, K.Yu. Shunyaev. *Development of the ICP-AES technique for determination of arsenic, antimony and bismuth in the materials with high content of tungsten and copper.// Industrial laboratory. Diagnostics of materials (Zavodskaya Laboratoriya. Diagnostika materialov) 2016. V. 82. №6. P. 10-17 (in Russian).*



4. *I.V. Tananaev, E.N. Deichman. Physico-chemical study of systems that are important in analytical chemistry // Industrial laboratory. V.11.1945. P. 763- 767 (in Russian).*
5. *I.V. Tananaev, E.N. Deichman. A new method for separating small quantities of Zn, Ni, Co, Mn, Cd, Cu and Ti from the large amounts of iron // Industrial laboratory. V. 12. 1946. P. 30-37.*
6. *Z. Zhou, P. Li, H. Xu, Yi. Zhang. A Chemical Precipitation Method to Synthesize  $\text{Na}_3\text{CrF}_6$  Crystal with Unique Shapes // J. Inorg. Organomet. Polym. 2013. V. 23. P. 1529-1533.*