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SPECTROFLUORIMETRIC DETERMINATION OF ALUMINIUM (III) WITH THE USE 8-OXYHINOLIN

The procedure of aluminium (III) spectrofluorimetric determination in foodstuffs with the use of 8-oxyhinolin is developed. The promising use of 8-oxyhinolin is shown for aluminium (III) determination.

At the development procedure the conditions of photometric reaction realization were optimized. The optimal medium creation method, analytical reagent concentration, conditions of steady aluminium complexes with reagent formation (time of color development, pH value, temperature-temporal parameters of solutions pretreatment, conditions of extraction) were investigated.

The research of analytical signal measuring choice (intensities of luminescence) was conducted. The values of initial and eventual wavelengths of registration and excitation monochromators are set, the excitation and emitting spectrums of 8-oxyhinolin and its complex with aluminium (III) are measured.

Studies of possibility of eliminating mixing ions are undertaken when analysing the real objects. 8-oxyhinolin forms complexes with many metals, therefore they must be preliminary separated on the stage tests preparation or in the process of realization of complex extraction.

Dependence of analytical signal is studied on the concentration of analyzable complex in the range of concentrations $(1-10)\cdot10^{-5}$ mol/l. Chloroform solution of 8-oxyhinolin is used as solution of comparison.

The worked out methodology can be applied in analytical laboratories to certify the quality of foodstuff.

Key words: spectrofluorimetry, fluorescent spectroscopy, photoluminescence, aluminium (III), extraction, 8-oxyhinolin, spectrums of emitting.

Introduction. The main source of aluminum (Al (III)) in the human body is the food. Other sources are of water, air, medicinal drugs, aluminum cookware, deodorants and others. Water provides no more than 5–8% of the total ingested amount of aluminum. The Expert Joint Committee FAO/WHO on Food Additives set a tolerable daily intake value (CAP) at the level of 1 mg/kg body weight. Daily aluminum consumption for adults can reach 60–90 mg, but in practice rarely exceeds 35–49 mg, and strongly depends on the individual features of organism and on diets.

Al (III) metabolism in humans has not been studied sufficiently, but it is known that the inorganic Al (III) is poorly absorbed and much of it is removed from the body. Nevertheless, the Al (III) accumulation in the organism may occur as a side process on a background of an underlying disease.

Al (III) can cause disorders in children psychomotor reactions, anemia, headache, hepatic and kidney diseases, dementia in elderly patients, neurological changes. Techniques for determination of Al (III) trace amounts in foods lack [1]

The main disadvantage of the existing methods of analysis concerning the aluminum content in the environmental objects is the impossibility of aluminum trace amounts defining, and the duration of the analysis. The main existing methods on this issue are basically devoted to the analysis of alloys [1].

Thus, the problem of determination of Al (III) trace amounts in food is very important. Ordering existing methods of analysis, selection of the most promising areas on the issue and further development of the methodology for determining the Al (III) will solve these problems.

Along with the spectrophotometric methods of analysis [2, 3], today, particular attention is paid to spectrofluorimetric methods of analysis or fluorescence spectroscopy [2–5]. These methods have extremely high sensitivity and provide universal opportunities for study: excited states of molecules, photochemical reactions, the fast dynamics of molecular processes, structure and properties of complex chemical and biological objects.

For aluminum spectrofluorimetric-definition it was proposed a large number of organic reagents, which form stable complexes with Al (III) [1, 4–6]. One of them is an 8-hydroxyquinoline (hydroxyquinoline, oxine) (OX) – heterocyclic

At interaction of 8-hydroxyquinoline with Al(III), the metal atom is substituted by the hydrogen atom of the phenol group and, furthermore, coordinately is bound with the nitrogen. This leads to the formation of very stable complexes with Al(III).

Furthermore, OX is widely used both in the spectrophotometric and the fluorescence analysis, and has low cost, so it was chosen as the complexing agent for the development of determining methods for Al (III) by spectrofluorimetric method.

Main part. The spectrofluorimetric methods for Al (III) determining in the form of complex with OX are developed predominantly for the analysis of metals and alloys, technological solutions [1, 4–6]. For the foodstuff analysis they were not used. We were to modify the methodology and adapt it to the new object of analysis. In this con-

nection, in the course of this study the following problems were solved:

– the condition optimization of the photometric reaction. It has been studied the influence of some factors on the photometric reaction – a method of creating an optimal environment, analytical reagent concentration, the conditions of Al (III) stable complexes' formation with a reagent (color development time, pH, temperature and time parameters of the solution pretreatment, the extraction conditions);

– optimization of the measurement conditions. The investigation has been conducted concerning the justification of the choice of the excitation and emission wavelength when removing excitation and emission spectra of the complexes Al (III) with a reagent, and the area concentration determining in which the dependence of the luminescence intensity on the Al (III) concentration is linear;

– the elimination of interfering ions. Quinolinol forms complexes not only with Al (III), but also with many other metals. Often, foodstuff contains salts of metals such as Fe (III) and Cu (II). It was necessary to find a rational way to eliminate the influence of ions Fe^{3+} and Cu^{2+} and on the basis of existing masking methods [1, 4–6];

– selection of the most rational method of the unknown concentration finding according to the largest analytical signal. It was decided to carry out the analysis using the additives' method, which eliminates the influence of the sample composition on the test results. In this case, the analysis methodology becomes more versatile. The main condition of the additives' method applicability is a strict adherence to the linear dependence of the analytical signal on the Al (III) concentration.

The studies were conducted on model solutions Al (III) in the concentration range $1 \cdot 10^{-5}$mol/l. The following reagents and solutions were used in the work: standard solutions of Al (III): 0.01 mol/l, prepared by accurately join hinge $AlCl_3 \cdot 6H_2O$ according to [7]; solutions of 8-hydroxyquinoline: 1%, prepared according to [6]; acetate buffer solution with pH values of 3.0 to 6.5, prepared from glacial acetic acid and CH_3COONa [7]. To adjust the pH of 2M the solution of CH_3COON was used. All the reagents had qualification a. r. g.

The control of pH was carried out with the ionomer Hanna 18314 (indicator electrode – the glass ECL 43-07; comparison electrode – silver chlorid EVL-1M3).

The determination method was as follows: 1 liter of mineral water was treated according to the sample preparation procedure [8], further a diluted solution was prepared from a Al (III) standard solution and then from this, – a series of Al (III) standard solutions. To a certain volume of treated sample being analyzed, aliquots of Al (III), standard solution were added, the extraction with 8-oxyquinoline in chloroform was conducted, and the luminescence intensity of obtained extracts with an emission of wavelength $\lambda = 430$ nm was measured with spectrofluorimeter brand SOLAR SM2203.

The pH of the solution was adjusted with acetate buffer solution at pH 5.0. Small aluminum concentrations have been removed almost completely in a single extraction. However, to increase the Al extraction degree the reextraction was performed. The extracts were combined, stirred and measured as standard solutions. As a comparison solution the 8-hydroxyquinoline dissolved in chloroform was used. From the value of the analytical signal the Al (III) concentration in the test solution was determined using a graphical method of additive series [9]. All test results are calculated as the average according to the results of five parallel definitions for the same sample under the same conditions.

To form stable complexes of Al (III) with 8-hydroxyquinoline is necessary to choose the optimum reaction conditions and extracting the formed complex. In aqueous solution at the pH content from 4.8 to 5.2 a hydroxyquinolate Al (III) residue is formed [1, 4–6]. However, this compound is well soluble in organic solvents such as benzene, carbon tetrachloride, chloroform and isoamyl alcohol. These substances are used as hydroxylquinolate Al (III) extractants. According to [1, 5, 6], extraction with benzene is fuller than with chloroform. The layer separation occurs more rapidly. Furthermore, according to the source [6], the benzene extract has a greater optical density than the chloroform one under identical hydroxyquinolate aluminum amounts. Most authors [1, 4–6] make a choice in favoure of chloroform because it has a number of advantages; particularly its use increases the analysis technique sensitivity. Therefore, we chose chloroform as the extracted substance.

Yellow Al (III) oxyquinolate coloration is formed quickly enough after the draining of the solutions and their extraction in a separatory funnels. The extraction takes about five minutes. To maintain the pH, an acetate buffer solution at pH 5.0 was used.

According to the source [4], the Al (III) hydroxyquinolate colour of the solution is constant over time.

We found that in 15 min, 1 h and 5 h colour of the complex remains constant and the luminescence intensity does not change (Fig. 1).

However, Al (III) hydroxyquinolate chloroform solution begins to darken in the light acquiring brown colour, thereby causing an increase in the optical density and the luminescence intensity change. Based on materials from publications [1, 6], the complex is partially decomposed in the dark and light and oxygen intensify its decomposition.

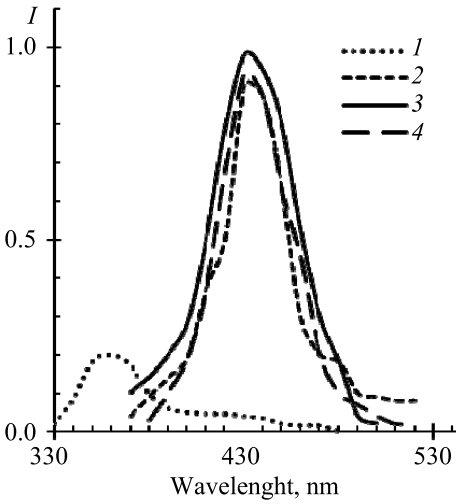

Fig. 1. The emission spectra of 8-hydroxyquinoline hydroxyquinolate and Al (III):
1 – cloroform solution 8-oxiquinoline;
2 – in 15 min; *3* – in 1 h; *4* – in 5 h
after preparation of the solution

When stored in a dark glass container, the complex is stable for 2 days.

The heating does not accelerate the complex formation. There are indications [4, 6], that the complex heating to 60–70°C improves extraction. We have found that heating does not lead to any changes in the magnitude of the analytical signal.

When heated in a boiling bath for 10 min, a maximum colour is reached that matches the colour of the solution prepared without temperature influence for the same time.

As a result of studies it was found that a solution of 8-hydroxyquinoline at pH 3.0–6.5 absorbs in the ultraviolet wavelength region (at 250–370 nm) (Fig. 2).

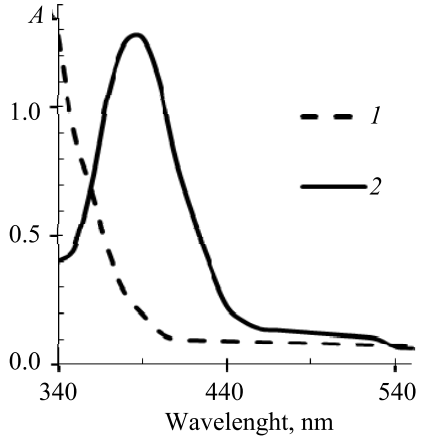

Fig. 2. The absorption spectra
of 8-hydroxyquinoline and Al (III) complex solution
in chloroform at pH 3.0–6.5:
1 – 8-hydroxyquinoline solution in chloroform;
2 – Al (III) complex with 8-hydroxyquinoline

To the aluminum complex with 8-hydroxyquinoline the value of the maximum absorption wavelength (λ_{max}) is dependent on pH and does not depend on the magnitude of the excess reagent.

If administered stoichiometric amount (for the complex composition of 1 : 3) or a slight excess of the reagent with respect to aluminum (~2-fold), then irrespective of the pH value (from 3.0 to 6.5) λ_{max}= 385nm (Fig. 1, dependence 2). With increasing excess reagent (up to 5-fold) the configuration of spectra does not change, indicating the stability of the composition complex 1 : 3.

Based on the obtained absorption spectra the excitation and emission of Al (III) with 8-hydroxyquinoline complex were taken off (Fig. 3).

The plats in Fig. 3 show, the luminescence excitation and emission spectra are broad structureless bands located in the range of 340–420 and 390–470 nm with peaks at 385 and 430 nm, respectively.

When studying the pH solution effect on extraction completeness of Al (III) with 8-hydroxyquinoline complex, the dependence of complex optical density on the pH values of the medium in the range from 4.0 to 6.5 was determined (Fig. 4).

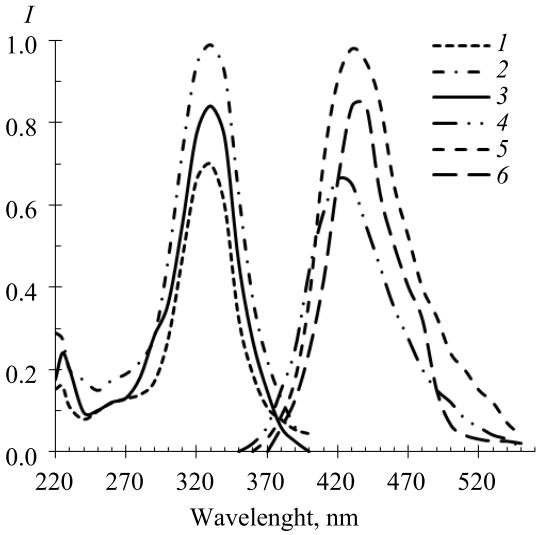

Fig. 3. The excitation (*1–3*)
and emission (*4–6*) spectra of the complex Al (III)
with 8-hydroxyquinoline at pH 4.5–5.5:
1, *4* – complex Al (III)
with 8-hydroxyquinoline (pH = 4.5);
2, *5* – complex Al (III)
with 8-hydroxyquinoline (pH = 5.0);
3, *6* – complex Al (III)
with 8-hydroxyquinoline (pH = 5.5)

Virtually complete extraction is observed in the pH range from 4.8 to 6.2 (99.9%). The value 5.0 is the most optimal in terms of the graphic dependence in Fig. 4, which is consistent with the literature [1, 3–6]. Therefore, it is advisable to measure

the luminescence intensity at the maximum emission wavelength of 430 nm (at that the excitation maximum wavelength is 385 nm), and to consider the optimal pH for the extraction of Al (III) with an 8-hydroxyquinoline complex equal to pH 5.0 (most complete extraction of complex occurs).

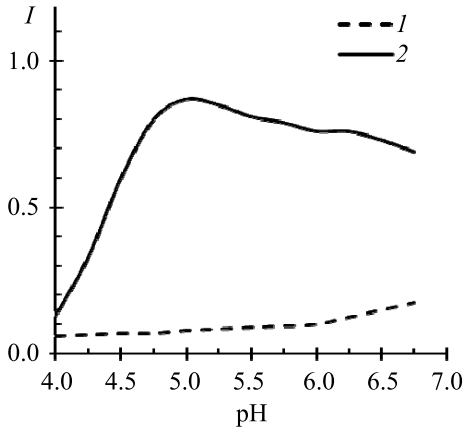

Fig. 4. PH medium effect on extraction of hydroxyquinolate Al (III) (at the wavelength 385 nm): *1* – 8-hydroxyquinoline dissolved in chloroform (blanks); *2* – complex Al (III) with 8-hydroxyquinoline

Wet or dry ashing is most often used for sample preparation of food. However, when calcinating of the product in order to remove the organic template (dry ashing) the loss of Al (III) volatile salts is possible. Wet ashing is not appropriate due to the large operation harmfulness, as well as to the complexity of the follow-up work with the sample, stipulated by high residual acid concentrations [8].

Since the developed methodology was tested using drinking and mineral water, the sample preparation was carried out in accordance with the procedure [8]. The analyzed samples were evaporated on an electric hotplate at a temperature 90°C to total residue, i. e. they were exposed to concentration. Thereafter, the obtained samples were treated by 0.1 mol/l HCl solution. These solutions were used to obtain Al (III) hydroxyquinolate complexes and their successive, extraction with chloroform. What concerns the interfering ions, at this stage it was investigated the ability to remove ions Fe (III) and Cu (II). It is found that the Fe (III), effect as well as Cu (II), can be eliminated by adjusting the pH medium. The extraction of hydroxyquinolate Fe (III) and Cu (II) with chloroform is carried out at pH 2.8 according to [1, 4, 6]. Thus, in a more acidic environment the transition of interfering elements' complexes into the chloroform layer occurs, butthe aluminum complex with 8-hydroxyquinoline remains in the aqueous phase, from which it is then extracted with a fresh chloroform portion at pH 5.0. The dependence of the luminescence intensity at an emission wavelength of 430 nm in a range of concentrations $(1–15) \cdot 10^{-5}$ mol/l has been studied. As a comparison solution is used as 8-hydroxyquinoline solution in chloroform at pH 5.0. It has been found that the linearity is observed in the range of $(1–10) \cdot 10^{-5}$ mol/l of Al (III). With further increase of the concentration there is a sharp decrease in the analytical signal.

The determination method was as follows: 1 liter of mineral water was treated according to the sample preparation procedure [8]. The dry residue after dissolution in 10 ml of 0.1 mol/l HCl solution was transferred into a volumetric flask of 100.0 ml and brought up with distilled water to the mark (solution 1).

An Al (III) solution for the additives introduction was prepared from a stock solution Al (III) at a concentration of 0.01 mol/l by hundred fold dilution. This solution had a concentration of 0.0001 mol/l (solution 2). Further, 10.0 ml of solution 1, 5.0 ml of a 1% solution of 8-hydroxyquinoline in chloroform and the measured volume of solution 2 were poured into volumetric flasks of 50 ml.

Accordingly, into the first separating funnel 0 ml of solution 2 (test solution without additive) was added; in each subsequent funnel – 2; 4; 6; 8, 10 ml of solution 2. Then solutions were brought up to the mark with acetate buffer at pH 5.0. Solutions in funnels have vigorously been shaken for 5 min exactly. As a result of extraction yellow hydroxyquinolate Al (III) was obtained. In order to achieve the equilibrium state, the emulsions have been kept at rest for 10 min. Control of pH was performed with the ionomer Hanna 18314. After separation of the layers the lower coloured chloroform layer was transferred to a quartz cuvette with a layer thickness of 1 mm and the luminescence intensity was measured using a spectrofluorometer SOLAR SM2203 at emission wavelength $\lambda = 430$ nm. As a comparison solution, a 8-hydroxyquinolate solution in chloroform at pH 5.0 was used. Then, according to the measurement results, the dependence of the luminescence intensity (I) on the additive concentration (C_{add}) was developed. The value of the desired concentration Cx corresponds to the segment being intercepted by a straight line on the absciss-axis [9]. The concentration of Al (III) in the sample was calculated using obtained data.

The technique has been tested on mineral and drinking artesian water.

Conclusion. Based on the studies, the selected optimal conditions for photometric reaction (colour development time, pH, temperature and time parameters of the solution processing) were chosen, methodology conditions were optimized: the choice of excitation and emission wavelength was

grounded, the concentration area was found in which the dependence of the luminescence intensity on the concentration is linear. In addition, the most rational method of finding the unknown concentration according to the largest analytical signal – method of additives was selected.

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