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### RESEARCH OF FLUORIDE IONS WITH THE ELECTRODE "ECOM-F"

The influence of pH and series of interfering ions on the fluoride-selective electrode "ECOM-F" function have been investigated. The optimal composition of background solution including the citric buffer, strong indifferent electrolyte and masking agent for interfering ions has been selected.

**Introduction.** Recently the quality of the food and especially drinking water are made especially stringent requirements. They are regulated by requirements documents. Control of certain elements in the water and food is dictated by the need to create balance in the human body some content of nutrients. One of these elements is fluorine. Unfortunately, most of the existing methods of its determining in various objects do not match the capabilities of modern equipment to carry out the analysis at higher and more qualitative level. It's necessary to carry out further research especially in the development of methods of analysis concerning complex compounds.

One of the most selective and fastest methods of the determination of fluoride ions is a method of direct ionometry [1]. For laboratory investigation manufacturers are offering fluoride-selective electrode "ECOM-F" with a solid membrane [2].

The object of this work was the study of the fluoride determination in complex compounds. This article is a reflection of a detailed investigation of the conditions of operation of this electrode (in particular the influence of the buffer solution and foreign ions on the type and characteristics of the electrode function).

**Main part.** There are some investigation of composition of background solutions to analyze the use of fluoride-selective electrodes with different types of membranes in scientific literature [1, 3, 4]. But the composition of the majority of background solutions designed for lanthanum fluoride electrode [3], in some other cases the composition of background solutions is not concretized [4].

As a result of previous studies of the characteristics of the electrode "ECOM-F" it was found out that in the process of using as a background the acetate buffer the linear range of the electrode function was  $10^{-1}$ – $10^{-4}$  mol/l and the slope of the electrode function and range of pH values are insufficient [2].

It should be noted that in the process of the analysis is very important to consider the effect of pH, because the effect may be different even for electrodes designed to determine the same ions but with different type of the membrane (solid or liquid plasticized with different active electrode substances) [5, 6].

To solve the problem of choosing the optimal composition of background solution the following tasks were set:

1) to determinate the possible uses of citrate buffer solution with a large buffer capacity as part of the background solution and regulator of pH environment;

2) to establish the composition of the background electrolyte to maintain a constant ionic strength and choose the best way to eliminate the interference of hydrogen ions, aluminum (III) and ferrum (III).

To conduct research on the influence of the buffer solution to the dependence of the electrode potential on the concentration of fluoride ions were prepared citrate buffer pH range 3.0–6.5 increments of 0.25 pH units. The control of pH produced potentiometrically using a pH meter HANNA, equipped with a glass indicator electrode and the reference chlorosilver electrode.

To carry out research referred to the influence of the buffer solution on the dependence of the electrode potential depending on the concentration of fluoride ions the citrate buffer with pH range 3.0–6.5 increments of 0.25 pH units were prepared. The pH control was potentiometrically realized with using of pH meter HANNA equipped with a glass indicator electrode and the chloride argentian electrode for the reference.

On the back of citrate buffer solution several series of standard solutions containing fluoride ions  $10^{-5}$ – $10^{-1}$  mol/l and the corresponding pH meaning were prepared. The measurements of fluoride-selective electrode "ECOM-F" potential were carried out in the prepared solutions and after that the curves of the potential from the concentration of fluoride ions at different pH values was created (Fig. 1). These curves (1) were compared with the analogical ones (2) previously created on the back of acetate buffer solutions [2] with the same pH.

The analysis of the curves 2 showed that in the presence of acetate buffer solution with a pH from 3.5 to 4.5 electrode function is linear in the range of pF = 1–3, at pH = 4.5 electrode function is linear in the range of pF = 1–4; at higher pH values the linear range is narrowed, at pH = 6 the electrode generally loses sensitivity.

When using a citrate buffer solution (curve 1) the electrode function is linear over a wider range of fluoride concentrations (pF = 1.4) at pH from 3.5 to 5.0, and the restriction of the linear range (at concentrations of  $10^{-4}$  mol/l or less) in notated only at pH = 6.

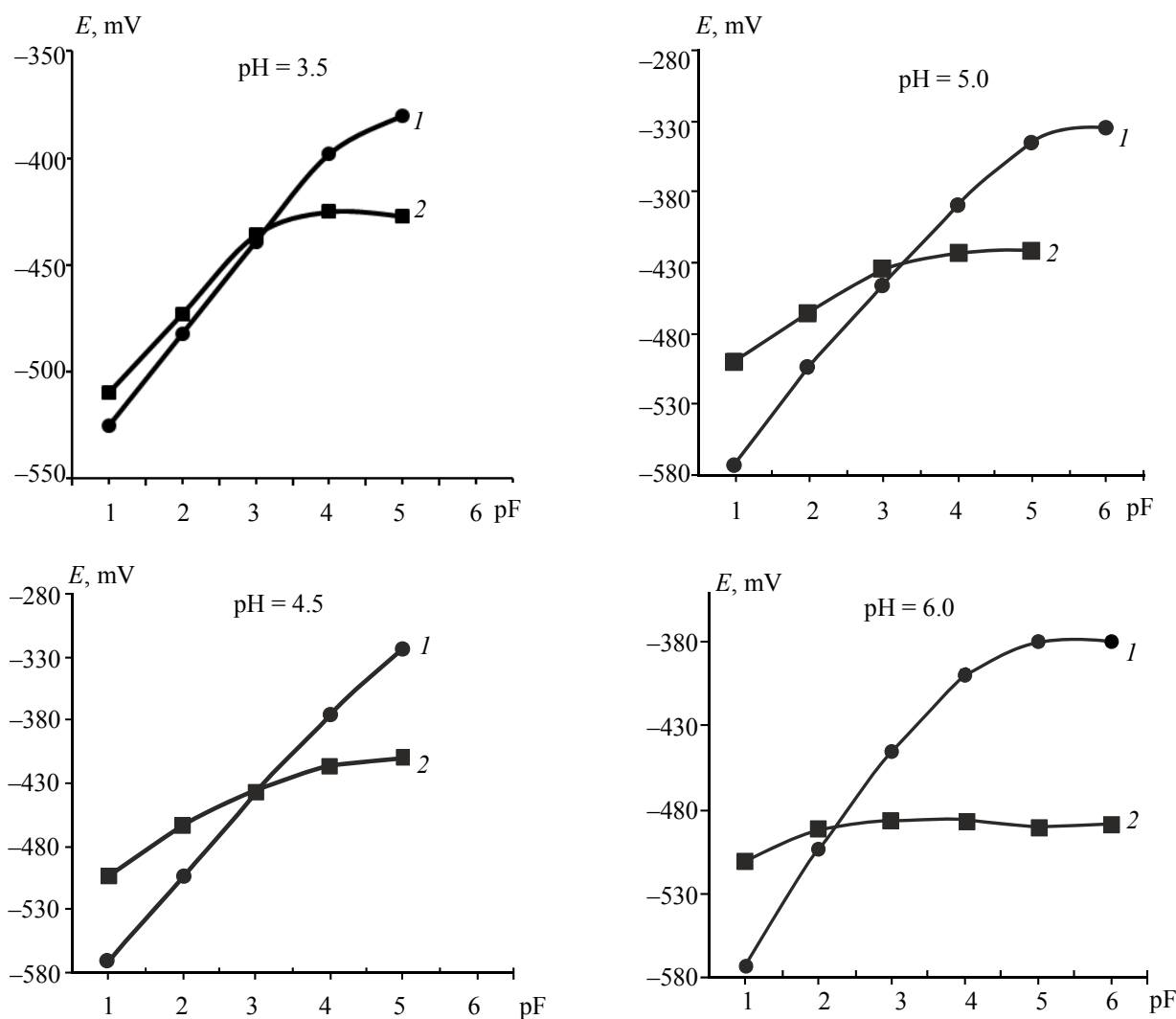


Fig. 1. Influence of pH on the electrode function to measure:  
 1 – on the back of citrate buffer solution;  
 2 – on the back of acetate buffer solutions

The influence of hydroxide ions is beginning to affect in the range of  $\text{pH} > 4-5$ . The extent of the nuisance of hydroxide ions increases with decreasing concentration of fluoride ions in the solution. With decreasing  $\text{pH} < 3.5$  the potentials is increasing. It can be explained by the decrease of free fluoride ions due to the formation of HF molecules and ions  $\text{HF}_2^-$  [3].

Comparing the values of the potential solutions with the same content of fluoride ions but at different pH values (Fig. 2) it was concluded that the stability of the potential is observed in a wider pH range at the presence of citrate buffer solutions rather than acetate buffer solutions. And the expansion of the range is as in the region of more acidic solutions as in alkaline region. But as in the case of measurements on the background of the acetate buffer solutions the impact of hydroxide ions increases with decreasing of fluoride ions concentration. And the best for measurements in citrate buffer pH range is 3.0–4.75.

The calculated values of the slope of the linear region of the electrode function measured in citrate buffer solutions are bigger than the volumes measured in acetate buffer solutions (for example, at a pH of from 3.5 to 4.75 the values of slope of the dependencies 1 more than the corresponding values for the dependencies 2 for 5–10 units, and at  $\text{pH} = 5$  the increase in the slope is up to 20 units). It indicates a higher sensitivity of the electrode in citrate buffer solutions.

As in the case of citrate buffer solutions pH operating range is much wider than in the case of acetate ones, and the sensitivity of the electrode is higher, it seems appropriate to use the citrate buffer solution as a component of the background solution.

To study the effect of foreign ions influence on the operation of fluoride-selective electrode potential measurements were carried out in a series of standard solutions containing fluoride

ions  $10^{-6}$ – $10^{-1}$  M on the back of the citrate buffer solution with the addition of the following salts: 0.1–1 M NaCl, 0.1–0.5 M NaI, 0.1–0.5 M NaBr and 0.1–0.5 M  $\text{Na}_2\text{SO}_4$ .

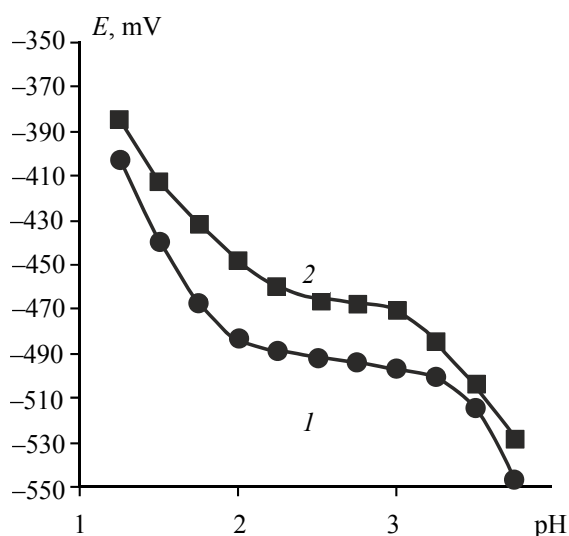


Fig. 2. Functioning of the electrode in 0.01 M NaF with various meanings pH to be measured:

1 – on the back of citrate buffer solution;  
2 – on the back of acetate buffer solutions

According to the measurements the lowest limits of detection were determined, the selectivity coefficients were calculated and the slope of the electrode function was worked out (see on the table).

It can be concluded that most harmful influence on the electrode from the studied ions have chloride ions, especially at high concentrations. In their turn the sulfate ions are characterized by the most minimal harmful influence.

According to [3–6], the definition of  $\text{F}^-$  ions is greatly troubled by the cations  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , as well as  $\text{OH}^-$  ions. The influence of  $\text{OH}^-$  is eliminated by introducing into the background electrolyte citrate buffer mixture. And to eliminate the harmful influence of ions  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  is suggested to use EDTA which forms some stable complex compounds with these cations preventing the formation of complexes containing  $\text{F}^-$  ions.

To specify these data and to establish the necessary concentration of EDTA in the background solution some investigations of the effect of different concentrations of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions on the electrode function of the electrode “ECOM-F” in the absence and in the presence of EDTA were carried out. The controlling of pH content was realized with using of citrate buffer solution. Fig. 3 shows the results reflecting the experiments carried out with  $\text{Fe}^{3+}$  ions. They completely coincide with the results of the experiments carried out with  $\text{Al}^{3+}$  ions. As Fig. 3 shows  $\text{Fe}^{3+}$  cations have a significant effect on the electrode function of the fluoride-selective electrode. Potential values increase, the slope of the linear portion of the electrode function decreases. It indicates a decline in the activity of fluoride ions as a result of their binding in complexes with interfering ions. And with the introduction of EDTA into the background solution the characteristics of the electrode function of ion-selective electrode are improving. Thus the optimum concentration of the concealing reagent EDTA for these measurement conditions to eliminate interference of ions  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  is 0.01 M. At lower concentrations the capture of interfering ions is not so strong, and the increasing the concentration does not lead to significant improvements, but causes increase in ionic solution strength.

#### Characteristics of fluoride-selective electrode in the presence of interfering ions

Background electrolyte	Selectivity factor $K_{A/B}$	The lowest detection limit, mol/l	$E = a \cdot \text{pF} + b$	Determination factor $R^2$
0.1 mol/l NaCl	$8.0 \cdot 10^{-4}$	$7.94 \cdot 10^{-5}$	$E = 57.8 \text{ pF} - 577.0$	0.9965
0.5 mol/l NaCl	$3.0 \cdot 10^{-4}$	$2.51 \cdot 10^{-5}$	$E = 57.1 \text{ pF} - 608.0$	1.000
1.0 mol/l NaCl	$1.0 \cdot 10^{-2}$	$1.26 \cdot 10^{-3}$	$E = 69.0 \text{ pF} - 544.0$	0.9845
0.1 mol/l NaBr	$2.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$E = 36.9 \text{ pF} - 555.5$	0.9978
0.25 mol/l NaBr	$3.0 \cdot 10^{-4}$	$2.95 \cdot 10^{-5}$	$E = 62.4 \text{ pF} - 604.0$	0.9975
0.5 mol/l NaBr	$6.0 \cdot 10^{-3}$	$5.62 \cdot 10^{-4}$	$E = 51.8 \text{ pF} - 519.5$	0.9347
0.1 mol/l NaI	$1.0 \cdot 10^{-4}$	$1.26 \cdot 10^{-5}$	$E = 43.5 \text{ pF} - 546.0$	0.9998
0.25 mol/l NaI	$3.0 \cdot 10^{-4}$	$2.51 \cdot 10^{-5}$	$E = 60.7 \text{ pF} - 593.5$	0.9999
0.5 mol/l NaI	$1.0 \cdot 10^{-2}$	$1.05 \cdot 10^{-3}$	$E = 59.0 \text{ pF} - 515.3$	0.9985
0.1 mol/l $\text{Na}_2\text{SO}_4$	$1.5 \cdot 10^{-5}$	$4.68 \cdot 10^{-6}$	$E = 33.5 \text{ pF} - 550.0$	0.9987
0.25 mol/l $\text{Na}_2\text{SO}_4$	$1.5 \cdot 10^{-4}$	$4.68 \cdot 10^{-5}$	$E = 49.7 \text{ pF} - 547.5$	0.9985
0.5 mol/l $\text{Na}_2\text{SO}_4$	$3.0 \cdot 10^{-5}$	$9.33 \cdot 10^{-6}$	$E = 39.2 \text{ pF} - 529.0$	0.9996

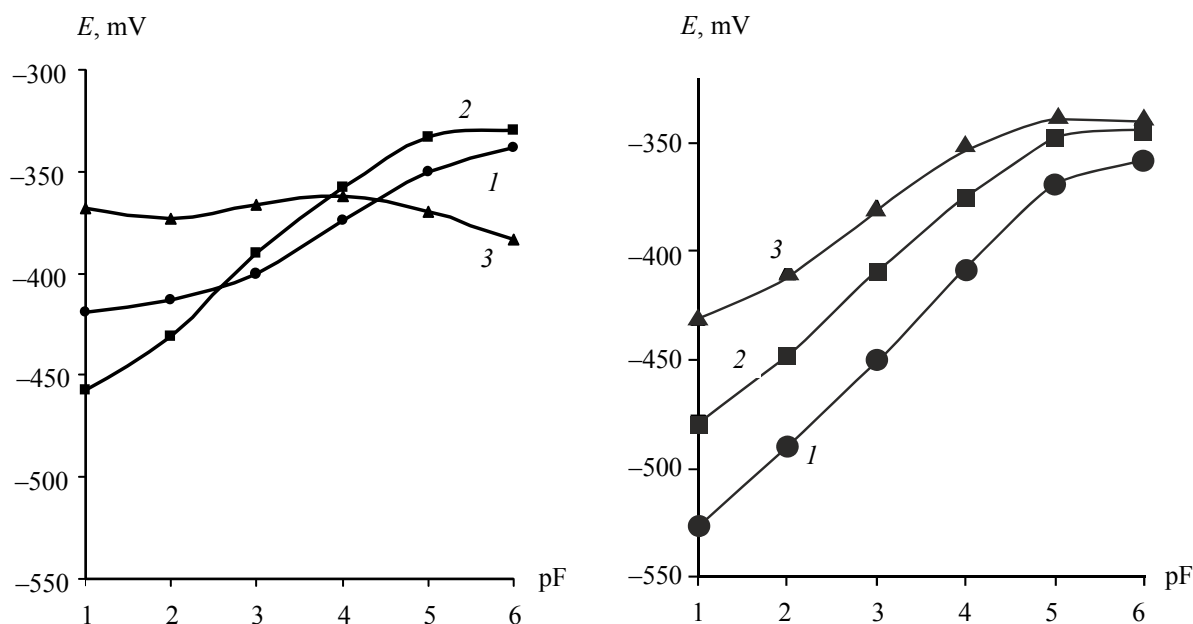


Fig. 3. Harmful influence of ions  $\text{Fe}^{3+}$  on the electrode function:  
 1 – 0.001 M  $\text{Fe}^{3+}$ ; 2 – 0.01 M  $\text{Fe}^{3+}$ ; 3 – 0.1 M  $\text{Fe}^{3+}$

**Conclusion.** The results of the carried out researches allow to conclude that the background solution for the determination of fluoride ions should be a citrate buffer solution with pH = 3.5–4.75 and should contain a concentration of 0.1 mol/l of  $\text{Na}_2\text{SO}_4$  (to maintain a constant ionic strength) and EDTA in a concentration of 0.01 mol/l (as a masking agent of interfering ions  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ).

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