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FEATURES OF SODIUM DETERMINATION IN DILUTE MIXED SOLUTIONS WITH PHENYLALANINE BY FLAME PHOTOMETRY

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Flame spectrophotometry is one of the main methods for determining alkali and alkaline earth metals in solutions. Chemical analysis by the flame photometric method have become of great importance for estimation of trace elements content and for work on small quantities of sample. The most important disadvantages of flame spectrophotometry are different types of interference (spectral, chemical, and physical). The paper considers mainly the physical interference which directly relates to the state of the sample itself and includes solution temperature, viscosity, surface tension, and vapor pressure. These effects are interdependent and not easily isolated for study. The addition of a substance increases the viscosity of the solution, which affects aerosol formation, transport, droplet size distribution, evaporation rate and flame temperature. All that leads to a decrease in the intensity of light emission. In the present article, the effect of phenylalanine on the sodium determination by the flame photometric method in the field of dilute solutions was studied. A decrease in the photocurrent emission of sodium in its joint determination with phenylalanine was found. The main reason is the increase in viscosity. It leads to a reduction in the spraying rate in the analyzer and a diminution in the analytical response of the device. The systematic type of errors in determining the concentration of sodium in the presence of phenylalanine is proved.

Keywords: flame emission spectroscopy; sodium; organic substances; solution viscosity; phenylalanine; spray rate; atomization.

Introduction

In the microbiological synthesis of amino acids, the resulting mixtures contain, in addition to the target component, mineral components and sugars. To solve the problem of amino acids separation from a mixture with sugars and mineral electrolytes, ion-exchange and membrane technologies are used. During dialysis of water-salt solutions of phenylalanine, amino acids are transferred together with sodium ions through a cation exchange membrane, which reduces the efficiency of the separation process [1, 2]. To develop rational demineralization regimes for mixed solutions, the problem of quantifying the amino acid and salt in dilute solutions arises.

The traditional method for determining alkali and alkaline earth metals is flame emission photometry. This method is based on measuring the intensity of light emitted by excited particles (atoms or molecules) when a substance is introduced into a flame. The advantages of the method are expressivity; high selectivity and accuracy (2 – 4%); high sensitivity ($C_{\min}$ — up to 10^{-7} mol/dm^3) [3]. Currently, this method finds its application not only in conducting local laboratory analyzes [4], but is also used in various important modern branches of technical research [5, 6], determination of alkali and alkaline-earth metals in food products [7, 8] and in studies of geochemical samples [9]. The possibilities of using a digital flame image to determine the sodium content in samples of sports drinks are discussed [10]. The disadvantage of the flame photometric method is the possibility of a significant overlapping of adjacent spectral lines belonging to different chemical elements. This effect leads to influence of other elements, which are in the analyzed solution, on the results of the target element determinination.

Many authors have studied the role of the influence of various kinds of interference in metals determination in a solution [6]. However, the influence of interference caused by the so-called inert materials has been given little or no consideration. Errors that occur in the presence of not only nitrogen-containing organic (urea), but also inorganic (nitric acid and ammonium chloride) substances were evaluated [11, 12]. It was established that the presence of nitrogen-containing organic substances in the solution lowers the photocurrent of sodium or potassium emission. The introduction of 0.04 mole of urea per 1 dm^3 (4% approximately) into NaCl solution (100 ppm) results in an absolute reading for sodium which is some 11% lower than the true value. The author explains this by changing viscosity of the solution and the spray rate of the sample in the flame. Many organic substances, such as glycerin, sugars, proteins, etc., increase viscosity; this reduces the spraying efficiency, which leads to a decrease in the brightness of the radiation of the element in the flame [11]. For example [11], sucrose was added to a sodium salt solution to increase the viscosity. In an extreme case where 40% sucrose was added to the sample, the results for sodium were 40% below the true value. In [12], the degree of quenching of the radiation intensity of sodium atoms (sodium content in acid-containing solutions of 0.1 g/L) in a flame in the presence of inorganic acids was studied. In case of nitric acid at a concentration 4.0 M, the decrease in optical density is 18% (decrease in consumption for the same solution — 19 – 20%), hydrochloric acid — 34% (decrease in consumption — 18 – 25%), sulfuric acid — 34% (reduction in consumption — 35%). The author assumes that the main factor in influence of inorganic acids in the flame photometry is the change in the flow rate of the analyzed solution in view of the increase in kinematic viscosity with increasing acidity of the studied solutions. Thus, the authors of [11, 12] agree that the change in the solutions viscosity has a practical importance in the analysis.

The effect of sucrose, glucose, urea, and gelatin on determination of sodium, potassium, and calcium by flame photometry was studied in detail [11]. It was found that each organic contaminant produces a progressively greater decrease in flame intensity for each of the alkali and alkaline earth metals as the concentration of contaminant in increased. In the case of the introduction of 0.05 mole of urea per 1 dm^3 into sodium chloride solution (100 ppm), the absolute reading of the device decreases by 3% relative to the true value, while the introduction of 1 mole — by 21%. The aerosol particles size of sucrose, glucose, urea and gelatin solutions was measured. It was found that with an increase in concentration of organic solutes, the viscosity increases and the aerosol particles size increases, and, accordingly, the intensity of analytical lines decreases. It was revealed that the depressing effect on the lines intensity of each studied element is almost the same per gram of sucrose as per gram of glucose. This indicates that for similar compounds, the effect is a function of mass rather than molarity of contaminant. An increase in viscosity causes a decrease in the atomization rate of the sample; therefore, in the same time fewer atoms fall into the flame. This, in turn, leads to a decrease in emission lines intensity. The author of [13] derived a theoretical formula for calculating the decrease in the photocurrent of magnesium emission in the presence of various acids, which is confirmed by experimental data. Therefore, the authors of [14, 15], when determining alkali and alkaline earth metals in honey, to exclude the interfering effect of sugars (glucose and fructose mostly) and other organic components, had to separate them using ion-exchange membranes.

On the other hand, this interference cannot be considered only from the point of view of increasing the viscosity of solutions containing an organic “contaminant” although the time intervals required for the atomization of such samples will not differ greatly for a number of organic impurities that can cause a decrease in emission lines intensity.

The aim of this work is to study the effect of amino acid (phenylalanine) on flame photometric determination of sodium in dilute solutions.

Experimental

The object of study was diluted individual and mixed model solutions of sodium chloride and phenylalanine. Model solutions of an amino acid (Sigma-Aldrich, USA) and a mineral salt (VECTON, Russia) were prepared from reagents of the classification “chemically pure.” Concentrations of sodium chloride and phenylalanine in individual and mixed solutions were in the range of 10^{-5} – 10^{-4} mol/dm^3. Sodium chloride solutions were prepared from a standard 1.0 mmol/dm^3 solution by dilution. Amino acid solutions were prepared by weight.

The concentration of sodium in solutions was determined using a flame photometric analyzer of fluids PAZh-1 (USSR). The device is equipped with interference filters for the determination of Na, K, Ca, Li. The radiation detector is an F-9 photocell with an antimony-potassium-sodium-cesium photocathode. A double-gap burner (natural gas — air flame), turned perpendicular to the radiation flux, acts as an atomizer. The measuring instrument is a microammeter 100 μA (100 divisions). The emission photocurrent was measured at a sensitivity — 8, signal attenuation factor — 0, a time constant — 1. The flow rate of the test liquid was 0.1 cm^3/sec for both individual standard solutions of sodium chloride and phenylalanine and for standard mixed equimolar solutions. According to the obtained data, calibration graphs were plotted in the region of dilute concentrations of the studied solutions.

A statistical evaluation of significance of the differences in characteristics of the calibration curves for an individual sodium chloride solution and its mixture with an amino acid was carried out using the Student’s *t*-distribution [16]. To check significance of the difference in the sensitivity coefficients values of calibration graphs ($b_1 - b_2$), coefficient t was calculated by the expression

$$t = \frac{|b_1 - b_2|}{S_d}, \qquad (1)$$

where S_d is difference variance of quantities

$(b_1 - b_2)$ found by the expression

$$S_d^2 = S_g^2\left[\frac{1}{\sum x_{i1}^2} + \frac{1}{\sum x_{i2}^2}\right], \qquad (2)$$

where x_i is the concentration of components for calibration curves *1* and *2*.

The total dispersion S_g^2 was estimated by the expression

$$S_g^2 = \frac{S_{Q1} + S_{Q2}}{n_1 + n_2 - 2}, \qquad (3)$$

where n is the number of options for calibration curves. S_{Q1} and S_{Q2} — calculated by the expression

$$S_Q = \sum (y_i - Y_i)^2, \qquad (4)$$

where y_i are the experimental values of the microammeter readings, Y_i are the values obtained from the linear regression equations $Y_i = a + bx_i$ for calibration curves *1* and *2*, respectively.

To simultaneously determine the constant and variable systematic errors, the experimental values of the analytical signal (y_i) are investigated and compared with those calculated at the same concentrations (x_i) from the regression equation $y = a + bx$. The nonzero value of constant a that describes the background indicates a constant (systematic) error. Coefficient b is greater than 1000 — about variable error [16]. Under assumption that the given values of emission photocurrent x_i (NaCl) are error-free, and the results of y_i (NaCl + Phe) obey the Gaussian distribution, the smoothing line can be calculated using unweighted regression [17]:

$$t_a = |a|/S_a; \; t_b = |1 - b|/S_b. \qquad (5)$$

The percent error of determination of sodium in solutions with phenylalanine was calculated by the expression

$$A, \% = 100(I_{\text{NaCl + Phe}} - I_{\text{NaCl}})/I_{\text{NaCl}}, \qquad (6)$$

where $I_{\text{NaCl + Phe}}$ is the intensity of light emitted by a sodium in the flame in the presence of phenylalanine, I_{NaCl} is the intensity of light emitted by a sodium solution.

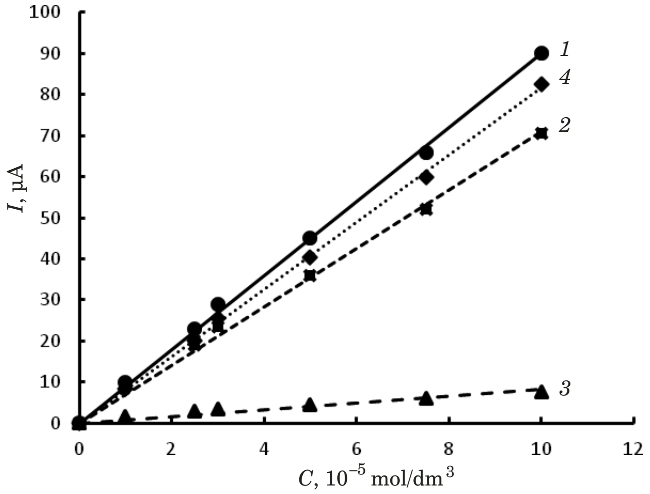


Fig. 1. The concentration dependence of the analytical response of the flame photometric analyzer in sodium chloride solutions (*1*), phenylalanine (*3*) and their experimental equimolar mixtures (*2*); curve (*4*) was calculated by additivity principle of signals

Results and discussion

Calibration curves in coordinates of the microammeter reading (I) and the molar concentration (C) of sodium (phenylalanine) in individual and mixed equimolar solutions are presented in Fig. 1. The characteristics of the flame photometry method when determining sodium and phenylalanine concentration in their individual solutions are presented in Table 1. It was established that in the spectral region in which the analytical line of the sodium element being determined is located, phenylalanine in individual solutions gives a linear response that is an order of magnitude lower than the sensitivity of the sodium response.

An analysis of the results for mixed solutions showed that when determining the sodium concentration in a mixture with an amino acid, the response of the mineral component is less than in its individual solutions. The metrological characteristics of the obtained calibration dependences are presented in Table 2.

Significance assessment of value of constant that describes the background a using the Fisher's criterion F ($F < F_{\text{tab}}$) [17] showed that all the obtained calibration curves pass through the origin and correspond to a dependence $y = bx$. Thus, instrumental and experimental background noises,

Table 1. Characteristics of the flame photometry method when determining sodium and phenylalanine concentration

Characteristics	Component	
	Na	Phe
Sensitivity coefficient dI/dC, 10^3 μA · dm^3/mol	900 ± 20	80 ± 10
Correlation coefficient of the calibration curve R^2	0.998	0.920
Minimum detectable component concentration $C_{\min}$, 10^{-5} mol/dm^3	1.2	4.1

Table 2. Correlation of flame photometer signal and component concentration

Component	Dependence type of the analytical signal					
	$y = a + bx$			$F < F_{tab}$	$y = bx$	
	$a \pm \Delta a$, μA	$b \pm \Delta b$, 10^3 μA · dm^3/mol	R^2		$b \pm \Delta b$, 10^3 μA · dm^3/mol	R^2
NaCl	0.9 ± 0.2	890 ± 30	0.999	1.17 < 4.95	900 ± 20	0.998
Phe	0.8 ± 0.1	70 ± 15	0.966	1.94 < 4.95	80 ± 10	0.921
NaCl + Phe	1.1 ± 0.3	700 ± 50	0.996	1.03 < 4.95	720 ± 30	0.995

Table 3. Statistical evaluation results of difference significance in the sensitivity coefficients of the calibration curves in individual (NaCl) and mixed with amino acid (NaCl + Phe) solutions

Parameter	NaCl	NaCl + Phe
b, 10^3 μA · dm^3/mol	900 ± 20	720 ± 30
S_g^2	2.43	
S_d, 103	45.68	
$t_{exp} > t_{tab}$ ($f = 12$, $P = 0.95$)	6.66 > 2.18	

Table 4. Statistical assessment results of presence of systematic errors when sodium determination in the presence of phenylalanine

Parameter	Value
S_a	0.15
S_b	0.019
t_a	2.88
t_b	11.05
t_{tab} ($P = 0.95, f = 5$)	2.57

as well as other possible random phenomena, did not make a significant contribution to the analytical signal.

The results of a statistical evaluation of the difference significance in sensitivity coefficients (slopes) of the calibration curves for individual and mixed with amino acid of sodium chloride solutions (Fig. 1) are presented in Table 3.

The excess of Student's coefficient t_{exp} calculated by experimental data over the tabular value t_{tab} by three times indicates that the difference between the characteristics of the calibration curves in individual and mixed sodium chloride solutions is statistically significant.

A constant deviation of the results in one direction from the true value indicates a systematic error. It is important to know type of systematic error that appears, since this will make it possible to draw a conclusion about the cause of its occurrence and to optimize the method as far as possible.

The results of checking for systematic errors are presented in Table 4.

The obtained value of t_b is greater than t_{tab}, therefore, the presence of a linearly varying systematic error when determining sodium concentration in dilute solutions in the presence of phenylalanine can be established.

Thus, phenylalanine causes a decrease in emission of sodium when determinating in dilute solutions, similar to the known influence of urea [11, 19, 20].

It is known that the main factors affecting analytical response of a flame photometer are the spray rate and the average diameter of the aerosol particles generated during operation of the pneumatic sprayer [11]. According to Poiseuille's law, the main characteristic that affects the suction rate of a solution V (cm^3/sec) is sprayed solution viscosity:

$$V = \frac{10^6 r^4 \pi \Delta P}{8 \eta L}, \tag{7}$$

where ΔP is the pressure drop along the length of the capillary; r is the radius of the capillary; η is the viscosity of the sprayed solution; L is the length of the capillary. The viscosity of amino acid solutions exceeds the viscosity of sodium chloride solutions (Fig. 2). In this case, with increasing concentration, the difference in solutions viscosity of the amino acid and the mineral component increases. In [18], it was found that phenylalanine solutions have an increased viscosity in the concentration range of more than 0.005 mol/dm^3 due to the formation of spatial associates. According to Poiseuille's law, an increase in solution viscosity decreases the spray rate [11, 12], which is one of the reasons for decrease in response of flame photometer in sodium chloride solutions in the presence of the phenylalanine amino acid.

In flame photometry, the bulk of the interference caused by dissolved organic substances is due to the increased viscosity. However, in some of the cases investigated, an increase in viscosity causes only a small part of the interference. An important characteristic of the resulting aerosol quality is the average droplet diameter [11]. The size of aerosol particles depends on viscosity, surface tension and density of the sprayed solution. The particle diame-

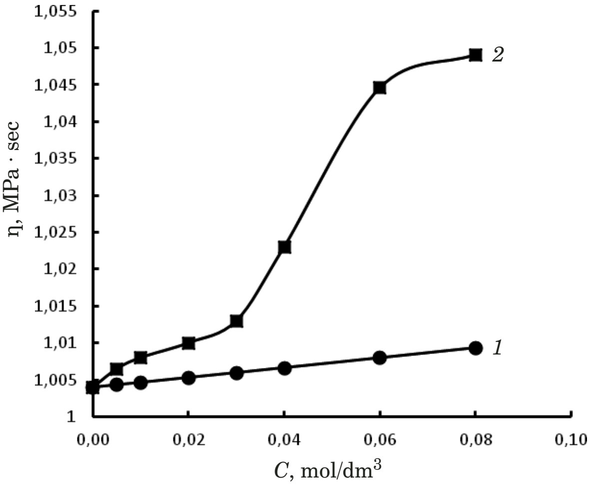


Fig. 2. The concentration dependence of the dynamic viscosity in sodium chloride (*1*) and phenylalanine (*2*) solutions

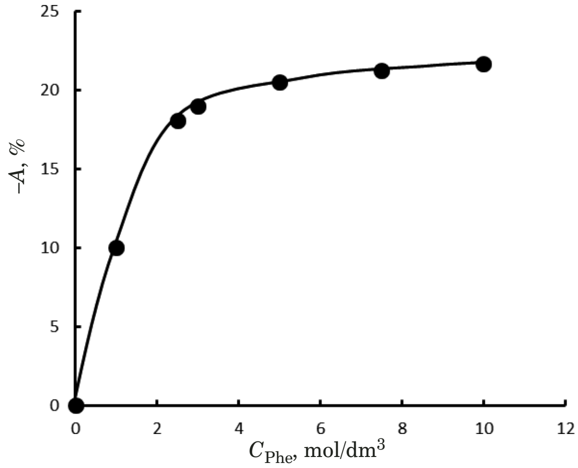


Fig. 3. The dependence of the error in sodium determination on phenylalanine concentration in equimolar mixed solutions

ter can be estimated using the empirical relation [12]

$$d = \frac{585\sqrt{\sigma}}{u\sqrt{p}} + 507\left(\frac{0.1\eta}{u\sqrt{p}}\right)^{0.45}\left(\frac{1000V}{V_1}\right)^{1.5}, \qquad (8)$$

where u is the spray gas flow rate, m/sec; σ is the surface tension, N/m; η is the viscosity coefficient of the solution, Pa · sec; ρ is the solution density, g/cm^3; V and V_1 are the flow rates of the solution and gas per unit time, cm^3/sec.

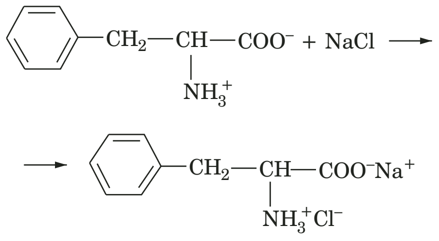
Thus, addition of an amino acid changes the atomizer operation mode, as a result of which quantity and particles size of aerosol formed change. As a result, the amount of substance introduced into the flame changes, and, consequently, the radiation intensity.

Interferences can also be caused by individual action of dissolved organic substances and are associated with their influence on the spray nature followed by an obstacle to metal activation in the flame.

The response dependence of determined sodium component on the interfering organic component concentration of phenylalanine was experimentally established. Checking the difference significance in the sensitivity coefficients of sodium chloride and phenylalanine equimolar solution (curve *1*, Fig. 1) and the difference in the sensitivity coefficients for the individual components (curve *4*, Fig. 1) allowed us to conclude that in the selected concentration range (1.0 – 10.0) × × 10^{-5} mol/dm^3 the additivity principle is not observed. The light emitted intensity by sodium in a flame decreases to a greater extent than could be expected according to the observance of the additivity rule of signals.

The intensity of the light emitted by sodium in the flame decreases as the concentration of equimolar solutions increases. The concentration dependence of sodium determination errors in solutions with phenylalanine calculated by expression (5) is presented in Fig. 3. It was found that phenylalanine at its concentration of 0.01 mmol/dm^3 reduces the radiation intensity of sodium by 10%, and in an equimolar mixed 0.1 mmol/dm^3 solution — by 21%.

This is apparently caused by an increase in size of the aerosol particles formed by the sprayer and a corresponding decrease in the substance flow into the flame. A significant increase in the aerosol particles size in mixed equimolar solutions of phenylalanine and sodium chloride can occur due to the possibility of formation of the organomineral salt particles [20]:



Formation of a similar structure about a 1:1 ratio of components is confirmed by a minimum on the concentration dependence of the electrical conductivity of aqueous mixed solutions. This fact confirms the decrease in the number of conductive particles as a result of formation of a neutral organic mineral salt. It should be noted that the organomineral structure is also formed with other ratios of components. In this case, equivalent amounts of amino acids and salts are bound, while the remaining “free” amount of components participates in other processes [21].

In addition, the organomineral salt formation can affect the processes occurring in the flame and affect the metal atoms concentration in the flame, that is, affect the evaporation of salt from aerosol particles, the dissociation of its vapor and atoms ionization. Partial absorption of radiation generated by a metal or partial dissipation of flame energy by a contaminant are other possible causes of the observed effects.

Conclusion

Influence of phenylalanine on the determination of sodium concentration by flame photometric method in the field of dilute solutions has been studied. A decrease in the photocurrent of sodium emission in the presence of phenylalanine was found. It is proved that influence of amino acids on determining the sodium concentration in dilute solutions by flame photometry is statistically significant. The main reason is that the amino acid increases the solution viscosity, which leads to a decrease in spray rate in the analyzer and reduces the analytical response. Another possible reason is due to influence of the presence of amino acids on the atomization process and the increase in particle size.

The systematic type of errors in determining sodium concentration in the presence of phenylalanine is proved. Their positive correlation with an increase in the concentration of the interfering component is established.

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