KINETIC DETERMINATION OF BERYLLIUM USING DECOMPOSITION OF ITS COMPLEX WITH CHLOROPHOSPHONAZO R

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Fast decomposition of beryllium complex with Chlorophosphonazo R in the absence of acetylacetone can be used for its kinetic determination by the tangent method. Analysis time drops from 30 min to 2 min. Optimal conditions and metrological characteristics of the procedure have been found. In the presence of EDTA selectivity, precision and sensitivity increase. The lower limit of concentration range is 0.15 μg/mL, the relative error does not exceed 2 %, while the observed errors of reproducibility are less than 3.3 %. Selectivity factors for a number of interfering cations and anions have been determined.

Keywords: kinetic analysis, tangent method, photometric analysis, beryllium, chlorophosphonazo R.

Introduction

Due to application of beryllium and its compounds in industries, toxic beryllium-containing wastewaters can contaminate natural waters, leading to a serious environmental hazard. Maximum permissible concentration of beryllium in drinking water is one of the lowest among allowable limits for various chemical elements. For example, in this country it equals 0.0002 mg/L [1], i.e. 0.2 μg/L, and the values of the same magnitude in other countries. Different national guides suggest that beryllium concentrations should not exceed a limit of 0.1 μg/L for tap water and 0.2 μg/L for surface water, to the maximum of 0.5 μg/L [2]. Obviously, these low amounts demand combination of determination methods with concentration processes.

Thus, in the State Standard currently in force, GOST 18294–2004 [3], separation and concentration of beryllium is carried out by sorption on silica gel, and then the spectrofluorimetric method of determination is used, based upon the ability of beryllium when reacting with morin in highly basic aqueous medium (pH 13) to produce a compound with green fluorescence (a non-structured band with the maximum 510-530 nm, under the emission light within the 410–450 nm range). Besides, a number of other fluorimetric reagents have been used [2, 4]. Fluorimetry is a sensitive method, but is has been shown that its sensitivity depends upon many factors, including the reagent ratio, which means a very narrow concentration range for determination proper (luminescence quenching); furthermore, in order to ensure the necessary reaction yield it is necessary to keep pH values higher than 12, it makes the choice of labware difficult and the work itself hazardous. For optical methods of beryllium determination one more difficulty to take into account touches upon instability of the complexes, their tendency to decomposition, at greater or lesser rates. In particular, the morin complex luminescence drops at 5–10 % an hour [3]. However, it has been suggested that addition of specific beryllium-binding components, such as NH_4HF_2 or acetylacetone, increases stability [4].

Among other methods of trace determination the group of photometric methods is widely used. These techniques are simple, fast, and cheap, they offer much wider optimal concentration intervals of reactants influencing the formation process of the colored compound; the reaction products are more stable, as a rule. Nowadays many organic reagents for photometric determination of beryllium are known, such as Eriochrome Cyanin R, Thorin I, Chlorophosponazo R, Calcichrome, Sulphochlorophenol S, Beryllon II, Chrome Azurol S, including determination in waters [5–7], and new reagents are suggested all the time [8, 9]. Unfortunately, almost all the reagents used for the photometric determination of beryllium are not free from shortcomings. For example, Be^{2+} complexes with polyoxyquinones are unstable and necessitate close control of analysis conditions. Sensitivity of the reaction with Thorin, Aluminon, p-Nitrobenzol-resorcine is comparatively low. The use of Eriochrome Cyanine R, Pentachrome Azurol Blue B, and Chrome Azurol S is significantly limited by high absorbance of the dye solution at the determination conditions, and for Eriochrome Cyanine R temperature greatly influences photometric intensity of the complex [2]. That's why many researches resort to one or another of modified methods of spectrophotometric determination.

A conventional method of ternary complex formation with surfactants in concentrations higher than critical micelle concentration has some application. In particular, the complex formation of beryllium with Chrome Azurol S in the presence of nonionic surfactants, and with aspartic acid for use in test-methods [10], as well as addition of a cathionic surfactant (cetyltrimethylammonium bromide or chloride) at photometric deterimination of beryllium with Chrome Azurole S [6, 7] or Xylenol Orang [11].

Other authors rely upon mathematical treatment enabling to eliminate high absorbance of the blank solution. Specifically, a method for simultaneous determination of beryllium and aluminum has been suggested, based upon the difference between their rates of reaction with Chrome Azurol S; the fixed time method is used (with measuring at 100 s and 300 s after the beginning of complex formation) [13].

The reagents of chlorophosphonazo group (such as Clorophosphonazo R, Chlorophosponazo-mA and DBC-Chlorophosphonazo) provide the sensitive and selective reaction with beryllium; selectivity becomes significantly higher in the presence of ethylenediaminetetraacetate (EDTA), though at $pH > 5$ the absorbance and the sensitivity of photometric determination decrease, which is caused mainly by EDTA properties at these conditions [5]. However, the color reaction fully develops only after a time: thus, for Chlorophosphonazo R at pH 9.4 in 30 min after the reagent is added, and even then in the presence of acetylacetone as binding agent (without it the complex quickly decomposes) [2]. Presumably, it can be used as the basis for beryllium determination with this photometric system with the kinetic method of analysis.

The present paper studies the possibilities of beryllium kinetic determination with Chlorophosphonazo R (CPR) using the tangent method, as well as to determine the optimal conditions of analysis, its metrological characteristics and selectivity.

Experimental

A standard solution of beryllium 0.01 M was prepared by dissolving 0.1771 g of analytical-reagent grade beryllium sulfate tetrahydrate $BeSO_4\cdot 4H_2O$ in distilled water with addition of 0.5 mL concentrated H_2SO_4 (chemically pure) in a 100-mL volumetric flask; the solution contains 90 μg/mL of beryllium. Working solutions were prepared daily by precise diluting in distilled water.

A stock solution of analytical-reagent grade CPR $C_{22}H_{16}Cl_2N_4O_{14}P_2S_2$ (0.1% m/v) was prepared by dissolving 0.5 g of the powder in 500 mL distilled water.

A borate buffer solution of pH 10 was prepared in the following way: 41.0 mL 0.1 M NaOH solution was brought to 100 mL by 0.05 M sodium tetraborate $Na_2B_4O_7$ solution. When various pH values were needed, the ratio of the components was changed according to the data of the handbook [14]. In several experiments more concentrated borate buffer solutions were used, prepared from 1 M NaOH and 0.5 M $Na_2B_4O_7$ solutions.

A sodium tetraborate solution of analytical-reagent grade $Na_2B_4O_7$ 0.05 M was prepared by dissolving 12.3670 g boric acid in small amount of distilled water, adding 100 mL 1 M NaOH and diluting to the mark by distilled water in 1000 mL volumetic flask. A 0.5 M solution was prepared from the same amounts in the same way, diluting to 100 mL by distilled water.

Sodium hydroxide solutions of various concentrations were prepared from samples of NaOH by dissolving in distilled water.

An EDTA solution 0.05 M was prepared by dissolving the standard titrimetric substance $Na_2H_2C_{10}H_{12}O_8N_2\cdot 2H_2O$; in several experiments 10 % EDTA solution was used, which was prepared by dissolving the calculated sample of $Na_2H_2C_{10}H_{12}O_8N_2\cdot 2H_2O$ in warm distilled water.

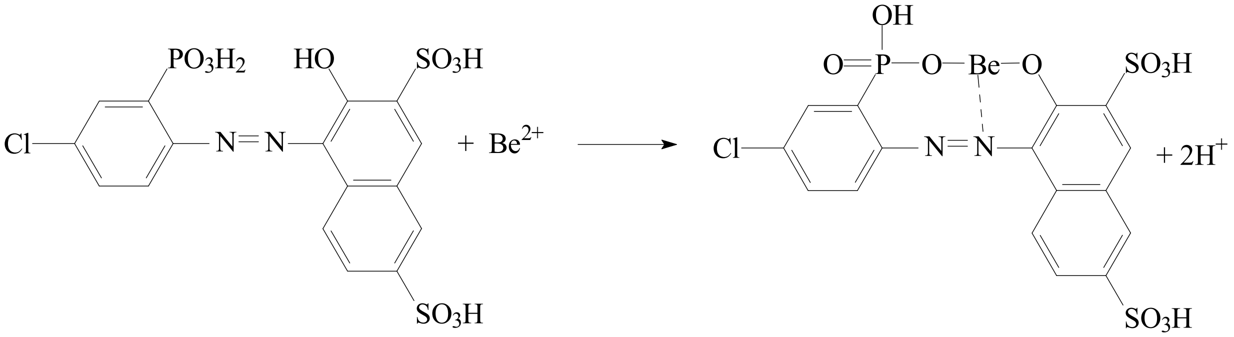
For investigation of the selectivity factor the solutions were prepared from calculated masses of water-soluble salts NaCl, KF, $BaCl_2\cdot 2H_2O$, $CuSO_4\cdot 5H_2O$, $MnSO_4\cdot 5H_2O$, KH_2PO_4; solutions of aluminum, iron (III) and zinc chlorides were prepared from calculated masses of the corresponding metals by dissolving them in HCl (1:1), at that iron was additionally oxidized by concentrated HNO_3; while $CaCl_2$ and $MgCl_2$ solutions were prepared from $CaCO_3$ and MgO by dissolving in HCl (1:1) – then the solutions were transferred into volumetric flasks and completed to the mark by distilled water.

The procedure of beryllium-CPR complex formation in the presence of acetylacetone was as following: in 50-mL volumetric flask to an aliquot of the standard solution of beryllium 10 mL of 0.05 M EDTA was added, 10 mL of triethanolamine (1:3), 1-2 drops of 0.1 % ethanol solution of thymolphtalein, the mixture was neutralized by 20% NaOH solution. Then HCl (1:1) was added dropwise until the blue solution lost its color. After addition of 1 mL acetylacetone (1:9) 2 mL of 0.1 % CPR solution was added and the mixture was diluted to the mark by the borate buffer solution of pH 9.4. The blank solution, containing all the reagents except beryllium, was submitted to the same procedure. For both analytical and blank solutions the absorbance change in time was measured at wavelength 540 nm and pathlength 1 cm in reference to distilled water.

The procedure of beryllium-CPR complex decomposition was as following: in 25-mL volumetric flask to an aliquot of the standard solution of beryllium 5 mL of 0.05 M EDTA was added, then 2.5 mL of 0.1 % CPR solution, and the mixture was diluted to the mark by the borate buffer solution of pH 10.0. The blank solution, containing all the reagents except beryllium, was submitted to the same procedure. For both analytical and blank solutions the absorbance change in time was measured in twenty-second intervals at wavelength 540 nm and pathlength 1 cm in reference to distilled water. Kinetic curves were plotted and the tangent (slope ratio) was calculated by the least-squares regression. If necessary, the pH value was controlled on pH-meter-ionometer pH-121.

Results and Discussion

Chlorophosphonazo R (4-[(4-chloro-3-oxy-2-phosphonophenyl)azo]-2,7-naphtalenedisulphoacid slowly forms beryllium complex with 1:1 ratio according to the reaction:



First of all we have studied the possibilities of kinetic beryllium determination with the use of the photometric method of the beryllium-CPR complex formation at pH 9.4 in the presence of acetylacetone. Indeed, if the complex is not formed instantly, then it is possible to compare its formation rates (slope ratios of the initial part of a kinetic curve) at various concentrations of the analyte. The experiment has been carried out according to the procedure of complex formation used in photometric determination of beryllium. The results are shown on Fig. 1.

It can be observed that the absorbance of the blank (graph 1') does not change in time, which is not surprising: CPR is stable in aqueous solution; the rest of the components contributory to the complex formation, obviously, do not influence the reagent in the absence of beryllium. The kinetic curve is parallel to the abscissa axis, accordingly, the tangent (slope ratio) of the studied curve equals zero. It gives significant advantage to the kinetic method over the photometric one. If the absolute value of the blank absorbance is measured, it has high value, higher even than the analytical signal of a beryllium-containing solution (for the given concentrations 0.495 and 0.406, respectively), so the necessity arises to work at the analytical wavelength differing from the wavelength of the maximum absorbance for the complex, therefore, at the conditions of significant decreasing of sensitivity. Besides, though the photometric color of beryllium-CPR complex in the presence of acetylacetone develops steadily and, in fact, remains stable at least for a day, the increase of the absorbance is so slow, that for the analyte, too, the slope ratio of a kinetic curve is very small and visually indistinguishable from zero (graph 1). In this case the kinetic determination won't be sensitive, either.

However, by contrast to the direct photometric determination, the kinetic method of analysis lets use not only increasing, but also decreasing, color intensity as the analytical signal – as long as there is the concentration dependence. Well, if the presence of acetylacetone is necessary for stabilization of the chromophore system, then its absence gives the chance to compare the rates of the complex decomposition.

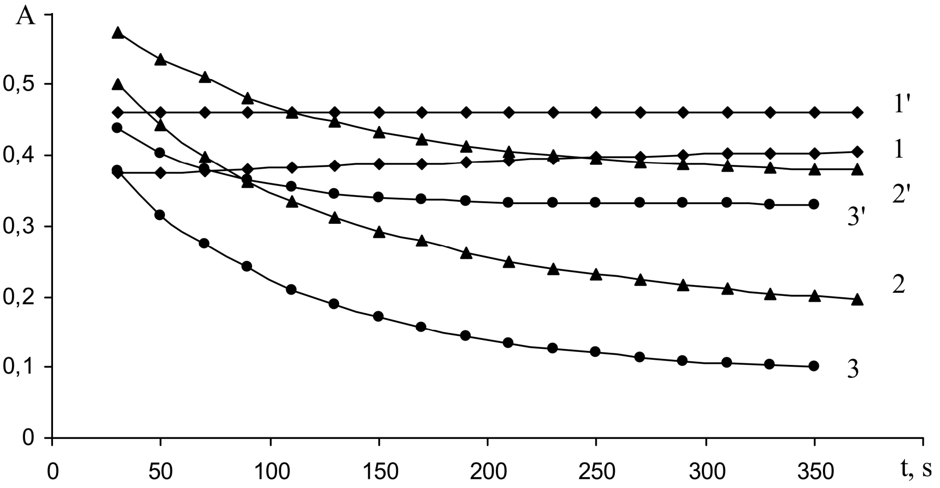


Fig. 1. Absorbance–time plots for the complex of beryllium with Chlorophosphonazo R and the blank solution (1'): 1, 1' – C_{CPR} = 1.38·10^{-4} M; C_{EDTA} = 0.005 M; C_{AA} = 4 M; pH = 9.4; λ = 450 nm; *l* = 1 cm; 2, 2';3, 3' – C_{CPR} = 1.73·10^{-4} M; pH = 10.0; λ = 450 nm; *l* = 1 cm; 2, 2' – C_{EDTA} = 0.01 M; 3, 3' – C_{EDTA} = 0; 1 – C_{Be} = 14 μg/mL; 1' – C_{Be} = 0; 2, 3 – C_{Be} = 4 μg/mL; 2', 3' – C_{Be} = 2.5 μg/mL

Appropriate experiments have been carried out according to the procedure of the complex decomposition, the results are shown on Fig.1. We have compared the behavior of the colored beryllium complex both in the presence of EDTA and in its absence, as there are data in literature that a masking agent is necessary for beryllium determination with CPR, and EDTA can influence not onl e selectivity, but also the sensitivity of a photometric determination.

Kinetic curves for the blank solution are not shown in graphical form, as they are parallel to the abscissa axis, too; that is, the tangent of the slope equals zero.

Surely, if acetylacetone is not added to the system, the absorbance of a solution decreases fast enough, and the color becomes stable in few minutes, while the interval of 2–2.5 min corresponds to the rectilinear part of kinetic curves, enough to get the tangent value. The higher is the beryllium concentration, the faster the process runs. The values of slope ratios arrived at after the treatment of the rectilinear parts by the least-squares method equal –1.60·10^{-3} and –2.58·10^{-3} (C_{EDTA} = 0.01 M), for beryllium concentration 2.5 μg/mL and 4 μg/mL, respectively; at C_{EDTA} = 0 the values are –1.43·10^{-3} and –2.57·10^{-3}. From this point on we have studied how the absolute tangent values depend on several variables.

Among other things, from the chemical reaction of complex formation and from literature sources it follows that the formation of beryllium-CPR complex should depend upon pH of the solution. The reaction takes place in basic medium; as during the reaction hydrogen ions are liberated, it is necessary to add a buffer solution to the system. We used the basic tetraborate buffer solution, prepared according to the handbook [14].

The slope ratio – pH plot is shown on Fig. 2. Both photometric and kinetic determination of beryllium with CPR requires basic media; otherwise the complex does not form and, consequently, does not decompose. When pH increases in the range 8.0–10.0, the slope ratio increases also, but decreases a little from this point on. The absorbance of the blank solution remains unchanged, therefore in the absence of beryllium the tangent of the kinetic curve slope equals zero at any pH value within the studied basicity interval.

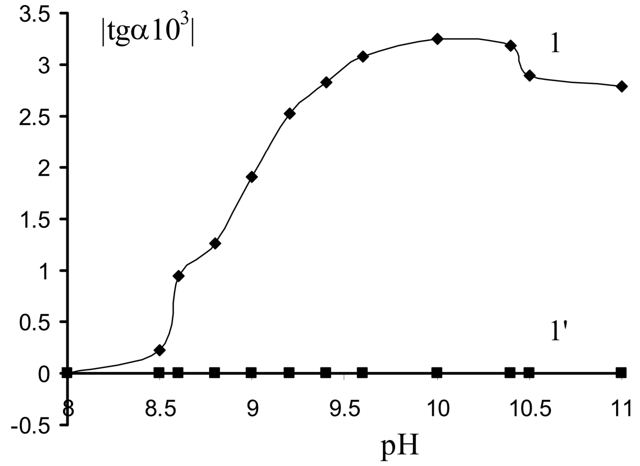


Fig. 2. Effect of the buffer solution pH value on the kinetic curve slope ratio: C_{CPR} = 1.38·10^{-4} M; C_{EDTA} = 0.01 M; λ = 450 nm; *l* = 1 cm; 1 – C_{Be} = 10 μg/mL; 1' – C_{Be} = 0

As for the optimal pH value of the added buffer solution, in the range 9.8–10.2 the slope ratio of kinetic curves does not change. In later experiments the tetraborate buffer solution of pH 10 is used. It should be stressed that we are referring to pH of the buffer solution, not of the photometric system. Buffer capacity of the solution with sodium tetraborate concentration in the 0.05 M area is not enough, so it cannot maintain the same pH value. The discrepancy is different on various parts of the plot, but the maximum is at pH 8.5–9. At the same time the efforts to get greater buffer capacity, using solutions of greater concentration (0.5 M sodium tetraborate) has not led to the desired result. The capacity is still insufficient, with discrepancy of pH values; and it is impossible to have it increased, as the solubility of sodium tetraborate is limited. Besides, the reaction itself begins to run at much greater rate, in this case the tangent calculation is awkward and imprecise.

However, decreasing sodium tetraborate concentration lower than 0.05 M is unpractical, as the discrepancy between pH values of the buffer solution and the photometric system becomes noticeably greater and the probability of ending with weakly basic or even neutral medium increases, with the attendant drastic drop of the analytical signal. We have observed such decreasing at 0.02 M sodium tetraborate concentration; for the same amount of beryllium (10 μg/mL) the tangent of the kinetic curve slope has fallen down from $3.25 \cdot 10^{-3}$ to $0.1 \cdot 10^{-3}$, which is completely unacceptable, of course.

Though the chosen method is kinetic, the measurement of the analytical signal uses absorbance of the photometric system; therefore it is bound to be affected by the concentration of the chromophore. Fig. 3 shows the dependence of reaction rate from CPR concentration. The experiment was carried out according to the procedure above, including EDTA addition, only the amount of CPR solution was changed so that its final concentration in the photometric system was within the range $(0.35–2.77) \cdot 10^{-4}$ M. It can be seen from the plot that the blank solution slope ratio is almost the same throughout, except for the lowest CPR concentrations. It is conceivable that the equilibrium shifts towards another form of the chromophore, different form its coordinated form. In the interval corresponding to the maximum analytical signal, the blank signal is equal to zero as before, though the absorbance of the chromofore reagent itself increases sharply.

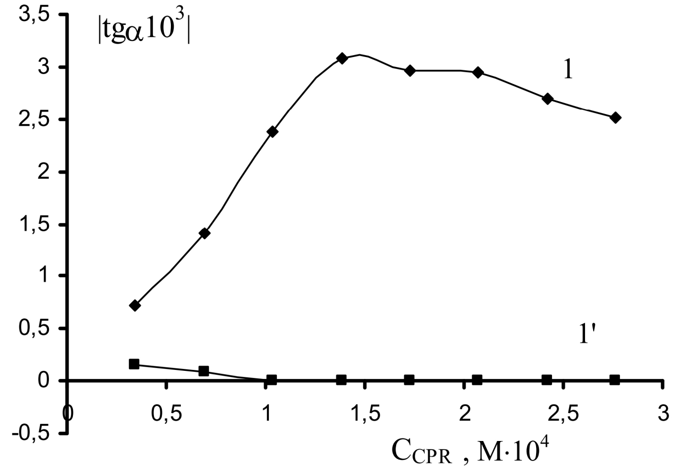


Fig. 3. Effect of Chlorophosphonazo R concentration on the kinetic curve slope ratio. C_{EDTA} = 0.01 M; pH = 10.0; ; λ = 450 nm; *l* = 1 cm; 1 – C_{Be} = 10 μg/mL; 1' – C_{Be} = 0

The CPR concentration, used by us earlier (according to the optimal conditions of the photometric determination), that is, $1.38 \cdot 10^{-4}$ M, is near the maximum sensitivity of determination in the kinetic modification of the method, too. However, we have decided to increase the working concentration of the chromophore somewhat, in this case the loss of sensitivity is insignificant, but the gain in the analytical signal stability is observed (the plateau instead of the maximum). From this point on we used the CPR concentration equaling $1.73 \cdot 10^{-4}$ M in the photometric system.

It is necessary to investigate the interference of cations and anions typically present in natural waters and waste waters, as the environmental objects are usually complex systems, they can contain many ions interfering with the beryllium determination. The experiment was carried out according to the procedure above, but in addition to beryllium in the amount near the higher limit of concentration range (3-4 μg/mL), specific water-soluble salts, intricate to the element composition of natural waters and waste waters, were introduced in various mass ratios to the analyte. The values of the kinetic curve slope ratios are shown in Table 1.

Table 1

Effect of mass ratios of beryllium to interfering components on the kinetic curve slope ratios

C_{ion}, μg/mL	$C_{Be} : C_{ion}$	b·10^3	Δ, %	C_{ion}, μg/mL	$C_{Be} : C_{ion}$	b·10^3	Δ, %
aluminum Al^{3+}				barium Ba^{2+}			
1	1: 0.3	–1.825	5.2	2	1: 0.6	1.887	2
1.5	1: 0.5	–1.600	16.9	4	1: 1	1.903	1.1
2	1: 0.7	–0.650	66.2	6	1: 2	1.815	5.7
3	1: 1	–0.175	90.9	8	1: 2.6	2.219	15
4	1: 1.35	–0.100	99.5	10	1: 3.3	2.750	43
calcium Ca^{2+}				magnesium Mg^{2+}			
2	1: 0.6	–1.940	0.8	1	1: 0.3	–1.999	3.9
4	1: 1.3	–1.860	3.4	2	1: 0.67	–1.825	5.2
5	1: 1.7	–1.575	18.2	2.5	1: 0.83	–1.675	13.0
6	1: 2	–1.100	43	3	1: 1	–1.300	32.5
8	1: 2.6	–0.050	97	4	1: 1.3	–0.100	94.8
iron (III) Fe^{3+}				copper (II) Cu^{2+}			
0.5	1: 0.17	–1.900	2.7	0.5	1: 0.17	–1.940	0.8
1	1: 0.3	–1.670	9.7	1	1: 0.3	–1.980	2.9
1.2	1: 0.4	–1.475	20.3	1.5	1: 0.5	–2.010	4.4
1.5	1: 0.5	–1.125	39.2	2	1: 0.6	–2.175	13.0
2	1: 0.7	–1.131	38.3	2.5	1: 0.8	–2.375	23.3
manganese Mn^{2+}				lead (II) Pb^{2+}			
0.2	1: 0.07	–1.825	5.2	2	1: 0.7	–2.025	5.2
0.4	1: 0.13	–2.025	5.2	2.5	1: 0.8	–1.275	33.8
0.6	1: 0.2	–2.125	10.4	3	1: 1	–1.125	41.6
0.8	1: 0.27	–2.125	10.4	4	1: 1.75	–1.175	39.0
0.1	1: 0.3	–2.300	19.5	6	1: 2	–0.575	70.0
zinc Zn^{2+}				sodium Na^{+}			
0.2	1: 0.07	–2.325	4.5	4	1: 1	–1.875	2.6
0.6	1: 0.2	–2.325	4.5	6	1: 2	–1.920	0.2
1.0	1: 0.3	–2.422	8.9	8	1: 2.6	–1.825	5.2
1.2	1: 0.4	–2.500	12.4	10	1: 3.3	–1.400	27
1.4	1: 0.47	–2.575	15.7	12	1: 4	–5.129	73
1.6	1: 0.5	–2.613	17.4	14	1: 5	–5.950	69
phosphate PO$_4^{3-}$				fluoride F^{-}			
0.02	1: 0.007	–1.925	0	2	1: 0.6	–1.985	3.1
0.04	1: 0.01	–2.100	4.7	3	1: 1	–1.840	4.4
0.06	1: 0.02	–2.035	5.7	4	1: 1.35	–1.955	1.6
0.08	1: 0.027	–2.150	11.7	5	1: 1.67	–1.950	1.3
0.1	1: 0.03	–2.175	13.0	5.5	1: 1.8	–1.995	3.6
0.12	1: 0.04	–2.251	17.0	6	1: 2	–2.150	11.7

The interference of ions manifested itself in various concentration ranges, the most characteristic selectivity factors for each of the investigated elements are shown in table 2. An ion has been taken as interfering, if its mass ratio to the analyte has changed the kinetic curve slope ratio compared to the initial value by ±10 %.

Dramatic effect of phosphate is probably due to formation of beryllium phosphorus-containing salts precipitation, which can exist in colloid form. The influence of heavy metal ions is characteristic for all methods, both photometric and kinetic ones; these have the characteristic feature of masking beryllium by hindering its interaction with the chromophore reagent. As for aluminum, beryllium and its compounds have properties that are close to those of aluminum and its compounds (diagonal relationship) in the periodic system of elements.

Table 2

Selectivity factors of some elements in beryllium determination

Element	Selectivity factor	Element	Selectivity factor	Element	Selectivity factor
Al	0.3	F	1.8	Na	2.7
Ba	2.0	Fe	0.3	P (PO_4^{3-})	0.02
Ca	1.3	Mg	0.7	Pb	0.7
Cu	0.5	Mn	0.13	Zn	0.3

Taken all in all, the investigated method is not highly selective, therefore it should be used with the masking agents, EDTA for example, or after separation of beryllium from the analyzed object, as in the procedure recommended in the State Standard GOST 18294–2004 [3].

The calibration graph for beryllium determination with Chlorophosphonazo R is shown on Fig. 4. For comparison purposes, a part of the calibration dependence corresponding to the kinetic curve slope ratios for development of beryllium-CPR complex color in the presence of acetylacetone is provided here (graph 3). It is linear in the range (1.6–10) μg/mL, though, obviously, cannot be compared in sensitivity to the graphs obtained from decomposition of beryllium-CPR complex.

The calibration graph for beryllium determination has been treated with the least-squares method, the straight line corresponds to the linear regression equation:

$$Y = (-0.13 \pm 0.07) + (0.68 \pm 0.03)\,X,$$

with correlation coefficient 0.999.

The lower limit of concentration range calculated taking into account the error of the calibration graph, has been found according to the standard formula

$$C_{\min,P} = \frac{t_{P,f}\left(S_a + \bar{C}S_b\right)}{b + t_{P,f}S_b},$$

and equals 0.15 μg/mL (at confidence level 0.95).

The linear regression equation of the calibration graph got at the same conditions without EDTA:

$$Y = (-0.6 \pm 0.5) + (0.80 \pm 0.22)X,$$

with correlation coefficient 0.989. Owing to the greater spread of points the lower limit of concentration range equals 1.1 μg/mL.

The use of acetylacetone stabilizes the beryllium-CPR complex, therefore the slope ratios of the linear parts in kinetic curves are positive in its presence. They are definitely lower in order of magnitude, the linear regression equation is $Y = (-0.8 \pm 0.3) + (0.35 \pm 0.04)\,X$, with correlation coefficient 0.998; the lower limit of concentration range equals 1.4 μg/mL.

The free terms of the linear regression equations are statistically significant, but this is a widely occurring case in kinetic analysis.

In order to evaluate the metrological characteristics of beryllium determination by the suggested method we placed the known amounts of the standard solution of beryllium into 25-mL volumetric flasks (in 6 replicate aliquots), added the necessary reagents according to the experimental procedure above, measured decreasing absorbance in time in 20-second intervals, calculated the kinetic curve slope ratios using the linear regression equation obtained in the similar conditions (in the presence and in the absence of EDTA), found the beryllium concentration in the analyzed solutions. Evaluation of metrological characteristics was carried out on the basis of conventional statistical criteria. The results are shown in Table 3.

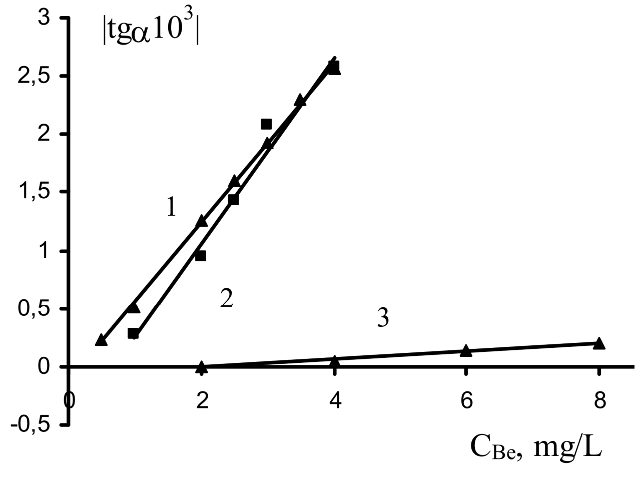


Fig. 4. Effect of beryllium concentration in the photometric system on the kinetic curve slope ratio. λ = 450 нм; *l* = 1 cm; 1, 2 – $C_{CPR} = 1.73 \cdot 10^{-4}$ M; $pH_{buf} = 10.0$; 1 – $C_{EDTA} = 0.01$ M; 2 – $C_{EDTA} = 0$; 3 – $C_{CPR} = 1.38 \cdot 10^{-4}$ M; $C_{EDTA} = 0.005$ M; $C_{AA} = 4$ M; pH = 9.4

Table 3

Evaluation of beryllium determination errors (C_{CPR} = 1.73·10^{-4} M; pH = 10; λ = 450 nm; *l* = 1 cm)

$-\text{tg}\alpha \cdot 10^3$	X_i, μg/mL	$\bar{X}$	S	ΔC	(ΔC/C)100%	δ,%
present in sample: C_{Be} = 1.5 μg/mL; C_{EDTA} = 0.01 M						
0.800; 0.800; 0.750; 0.800; 0.775; 0.850	1.50; 1.50; 1.41; 1.50; 1.43; 1.56	1.49	0.06	0.05	3.3	0.6
present in sample: C_{Be} = 3.5 μg/mL; C_{EDTA} = 0.01 M						
2.300; 2.325; 2.325; 2.375; 2.325; 2.350	3.50; 3.51; 3.51; 3.53; 3.51; 3.52	3.51	0.01	0.008	0.2	0.3
present in sample: C_{Be} = 3.0 μg/mL; C_{EDTA} = 0						
2.000; 1.987; 1.978; 1.935; 2.005; 2.075	2.99; 2.97; 2.96; 2.94; 2.99; 3.00	2.98	0.04	0.03	1.0	0.9

According to Table 3, the reproducibility of the results of beryllium determination is expressed by the relative error 3.3% for the lowest concentration, while the relative error of determination proves to be 0.6%. Increasing beryllium concentration, we get both metrological characteristics appropriately smaller, namely 0.2 % and 0.3 %, respectively. The error of beryllium determination in the absence of EDTA (for comparable concentration) increases up to 0.9 %, while reproducibility error is 1.0 %.

In waters at our disposal, sampled on Chelyabinsk territory, beryllium has not been found in concentrations over the lower limit of concentration range (0.15 μg/mL), therefore we had to carry out evaluation of accuracy of beryllium determination in the presence of interfering ions with the use of imitating mixtures. In one of them beryllium concentration equaled 1 mg/L – for determination in the presence of EDTA masking agent, while in the other, it equaled 2 mg/L, with due regard to the higher limit of concentration range determined without EDTA.

In other respects the mixtures were identical and contained the following concentrations of the interfering elements usually contained in natural waters: 4 mg/L sodium, 4 mg/L calcium, 2 mg/L barium, 2 mg/L lead, 2 mg/L magnesium, 1 mg/L aluminum, 1 mg/L copper, 0.5 mg/L iron (III), 0.2 mg/L manganese, 0.2 mg/L zinc, 0.04 mg/L phosphate.

The method of standard additions was used for determination of accuracy, that is, aliquots of the standard solution of beryllium were mixed with the sample, in such a way that the sum of the concentrations wouldn't be greater than the higher limit of the linear calibration graph. Then according to the procedure described above, the slope ratios were measured. The results are shown on Fig. 5.

The average of 5 replicate analyses equals (0.98±0.05) mg/L for the solution containing 1 mg/L beryllium (determination at 0.01 M EDTA), in other words, the true value is within the confidence interval, which means the absence of systematic error, while the error of determination amounts to 2 %. In the solution containing 2 mg/L beryllium, analyzed in the absence of EDTA, the average concentration is (2.2±0.2) mg/L, that is, reproducibility is significantly lower, though determination can still be considered accurate wit h 10% error.

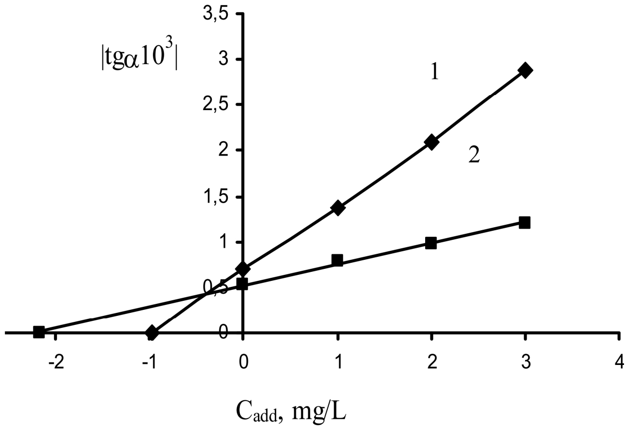


Fig. 5. Effect of beryllium standard addition concentration in the photometric system on the kinetic curve slope ratio. C_{CPR} = 1.73·10^{-4} M; pH_{buf} = 10.0; λ = 450 nm; *l* = 1 cm; 1 – C_{EDTA} = 0.01 M; 2 – C_{EDTA} = 0

Conclusion

1. Decomposition of beryllium-CPR complex can be the basis of kinetic determination, at that the time needed for one analytical measurement decreases from 30 min to 1-2 min compared to photometric determination, with the blank experiment nullified.

2. Optimal pH value of buffer solutions with 0.05 M tetraborate ion is 9.8–10.2, while pH of photometric system equals 8.5–9, insufficient buffer capacity is compensated by convenience of determination. The optimal range of the chromophore concentration is $(1.3–2.1)\cdot10^{-4}$ M.

3. At EDTA concentration 0.01 M the lower limit of concentration range equals 0.15 μg/mL beryllium, and only 1.1 μg/mL without EDTA, due to more scattered calibration graph. Comparable concentrations of beryllium are found with errors of reproducibility 0.2 % and 1.0 %, while relative errors of determination are 0.3% and 0.9%, respectively with and without EDTA (n = 6, P = 0.95).

5. Selectivity factors for a number of interfering cations and anions, typical for the composition of natural waters and wastewaters, have been found. The absence of systematic error has been proved with the use of the standard addition method, discrepancy with the beryllium concentration present in the samples equals 2 % in the presence of EDTA, and 10% in its absence.

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КИНЕТИЧЕСКОЕ ОПРЕДЕЛЕНИЕ БЕРИЛЛИЯ ПО РАЗЛОЖЕНИЮ ЕГО КОМПЛЕКСА С ХЛОРФОСФОНАЗО Р

Е.И. Данилина, Ю.В. Акатьева

Быстрое разложение комплекса Be^{2+} с хлорфосфоназо Р в отсутствие ацетилацетона может служить основой для его кинетического определения методом тангенсов. Время определения падает с 30 мин до 2 мин. Определены оптимальные условия и метрологические характеристики методики. Присутствие ЭДТА в системе позволяет увеличить селективность, точность и чувствительность определения. Нижняя граница определяемых содержаний 0,15 мкг/мл, относительная погрешность не превысила 2 %, а погрешность сходимости – 3,3 %. Найдены факторы селективности ряда мешающих катионов и анионов.

Ключевые слова: кинетический метод анализа, метод тангенсов, фотометрический анализ, бериллий, хлорфосфоназо Р.

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