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Luminescent properties of magnesium and calcium 8-hydroxyquinolinates

© D.A. Petrova, I.Yu. Tikhomirova, M.V. Puzyk ¶

Herzen State Pedagogical University of Russia, St. Petersburg, Russia

¶ e-mail: puzyk@mail.ru

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The dependence of the luminescence intensity of magnesium and calcium 8-hydroxyquinolinates obtained on the paper surface on the type of buffer solution and solvent for 8-hydroxyquinoline was studied. The detection limit of magnesium and calcium cations in an aqueous solution was established: for Mg^{2+} — 77.8 μg/ml (the highest luminescence intensity was established in an ammonia buffer solution when using a solution of 8-hydroxyquinoline in chloroform); for Ca^{2+} — 252.2 μg/ml (the highest luminescence intensity was established in a tetraborate buffer solution when using a solution of 8-hydroxyquinoline in ethanol). Regression equations were obtained that make it possible to determine the concentrations of cations (Mg^{2+}, Ca^{2+}) in the solution depending on the luminescence intensity.

Keywords: Magnesium and calcium 8-hydroxyquinolinates, luminescence, detection limit.

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Magnesium and calcium cations are an integral part of physiological fluids that need to be monitored to clarify a person's diagnosis. As can be seen from the table, the reference values of the cation content (Mg^{2+} and Ca^{2+}) in clinical and laboratory diagnostics [1–3] are different. Exceeding the concentrations of these cations can be a precursor or even a consequence of serious diseases. Hypermagnesemia (blood concentration Mg^{2+} above 1.1 mmol/l) indicates chronic kidney or adrenal insufficiency, myeloma. Hypercalcemia may indicate possible malignant tumors, sarcoidosis, hyperparathyroidism, leukemia (blood concentration Ca^{2+} 2.9−3.6 mmol/l).

The relevance of this study is due to the request for primary in-process testing of physiological fluids to check the content of magnesium and calcium cations, which reduces both the time and cost of quantitative analysis. The content of small amounts (μg/ml) of magnesium and calcium cations is estimated using atomic absorption or fluorescent spectroscopy [4,5]. The most commercially available and sensitive method is the fluorescence analysis. According to literature data, a number of nitrogen-containing heterocycles form with the metal cations the substances with fluorescent properties: magnesium cations — with 4-(*N*, *N*'-dicarboximethyl)-aminobenzyl-(1-azo-2)-1,8-dioxy-naphthalin-3,6-disulfoacid [6], 2, 2'-dihydro-xiazobenzene [7], azoxin [8], 5-pyrazolone [9], lumomagnesone [10], 8-oxychinolin [11], calcium cations — with 2,4-bis-[N,N'-di(carboximethylaminomethylfluorescein (fluorexone or calcein) [5,12], 8-oxyquinolylhydrazone 8-quinaldine aldehyde [5], 1,5-bis-(dicarboxymethylamino methyl)-2,6-dioxynaphthalene [5].

The purpose of this study is to determine the detection limit of magnesium and calcium cations in aqueous solutions by the fluorescent method using 8-hydroxyquinoline with visual detection of analytical signal and its quantitative assessment based on spectral fluorescence analysis.

Experimental part

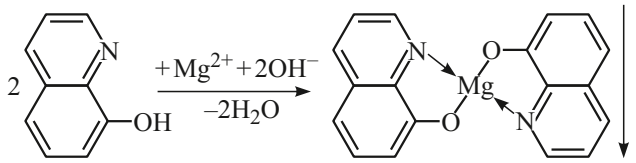
Reagents. 8-Hydroxyquinoline (h), calcium chloride and magnesium sulfate (standard titer), sodium hydroxide (standard titer), aqueous ammonia solution (AR), 10-aqueous sodium tetraborate (standard titer), sodium hydroxide (AR), ammonium chloride (AR), ethanol and chloroform (AR), decontaminated filter „blue strip" (size of pores $\sim 2.5\,\mu$m).

5% solutions of 8-hydroxyquinoline in chloroform and ethanol were prepared immediately before the experiment. It is known from jcite13 that 8-hydroxyquinoline is best soluble in chloroform (382 g/l). However, based on the low solubility of chloroform in water (8.0 g/kg [13]), it could be assumed that when mixing aqueous solutions (magnesium/calcium salts and buffer solution) with a solution of 8-hydroxyquinoline in chloroform, there would be a lowered diffusion rate of 8-hydroxyquinoline molecules to aqueous complexes of magnesium (calcium) cations across the phase interface, which will result in the declined fluorescence intensity of the reaction product. In this regard, ethanol, which mixes well with water and has a solubility of 20 g/l [14], was used as another solvent for 8-hydroxyquinoline.

To create an alkaline solution medium that ensures interaction of 8-hydroxyquinoline with magnesium (calcium) cations, buffer solutions were prepared (tetraborate (pH 9.8), ammonia (pH 9.25) in accordance with GOST 4919.2-2016 [15]) and sodium hydroxide solution (pH 12.0).

As the analyzed sample, 8-hydroxyquinolinates of calcium and magnesium were used, obtained in accordance with GOST 5847-76 [14] on filter paper as a substrate. 5 μl of aqueous solutions of calcium chloride (concentration

$CaCl_2$ from 100 to 6.3 mmol/l) or magnesium sulfate (concentration of $MgSO_4$ from 25 to 3.2 mmol/l), 5 μl of buffer solution (tetraborate, ammonia) or sodium hydroxide solution and 5 μl of solution in 8-hydroxyquinoline in chloroform or ethanol were placed on the filter paper one by one. The interaction of magnesium cations (similar for calcium) and 8-hydroxyquinoline in an alkaline medium proceeds according to the equation



The light yellow precipitate of magnesium/calcium 8-hydroxyquinolinate formed on filter paper (the diameter of the sediment spot $\sim$ 12 mm) was dried in air for $\sim$ 10 min. Thus, three batches of magnesium 8-hydroxyquinolinate samples were prepared (the first — based on an ammonia buffer solution and 8-hydroxyquinoline dissolved in chloroform, the second — based on a tetraborate buffer solution and 8-hydroxyquinoline dissolved in ethanol, the third — based on an ammonia buffer solution and 8-hydroxyquinoline dissolved in ethanol) and two batches of samples of calcium 8-hydroxyquinoline (the first — based on tetraborate buffer solution and 8-hydroxyquinoline dissolved in ethanol, the second — based on a solution of sodium hydroxide and 8-hydroxyquinoline dissolved in chloroform).

The fluorescence of magnesium and calcium 8-hydroxyquinolinates was observed when the samples were irradiated with UV light (Optimal Owlet Locator, $\lambda = 365$ nm). However, fluorescence was not detected for two cases: solutions of calcium cation in an ammonia buffer using a solution of 8-hydroxyquinoline in ethanol or chloroform.

Spectral investigations were carried out using the equipment provided by the Shared Research Facility Center at the Department of Chemistry, Herzen University: the fluorescence spectra were recorded at room temperature using spectrofluorometer Fluorat-02-Panorama (GK „Lumex“, Saint-Petersburg, Russia) using a quartz-fiber line, excitation wavelength — 370 nm, step — 0.5 nm [16].

Results and discussion

The fluorescence spectra of magnesium or calcium 8-hydroxyquinolinates have a bell-shaped shape with a maximum at 488 ± 3 nm and differ in fluorescence intensity for the front and back sides of the substrate. The fluorescence intensity of 8-hydroxyquinolinate and magnesium and calcium on the front side is lower ($\sim$ 30%) than on the back side because of different particle sizes of the dispersed phase: particles larger than 2.5 μm are trapped on the front side of the filter paper, and particles of a smaller size (there were more of them) passed through the filter pores and

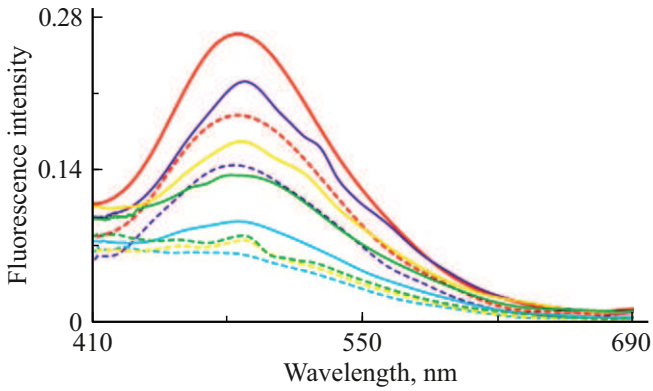


Figure 1. Fluorescence spectra of calcium 8-hydroxyquinolinate obtained in a tetraborate buffer solution for various initial concentrations of calcium cation: dashed line — fluorescence spectrum of the frontal spot, solid line — fluorescence spectrum of the spot on the reverse side, red — for a solution with a calcium cation concentration of 100 mmol/l, violet — 50 mmol/l, yellow — 25 mmol/l, green — 12.5 mmol/l, blue — 6.3 mmol/l.

were fixed on the back of the filter paper. Moreover, starting from the concentration of 25 mmol/l, there's practically no difference in the fluorescence intensity of the samples on the frontal side (Fig. 1, three lower dashed curves).

In this regard, further analysis of the obtained results was carried out using samples of 8-hydroxyquinolinates of magnesium (calcium) on the back of the filter paper. Figure 2 illustrates the fluorescence spectra of three batches of magnesium 8-hydroxyquinolinate, differing in the type of buffer solution and solvent for 8-hydroxyquinoline: $2, a$ — ammonia buffer solution and 8-hydroxyquinoline solution in chloroform, $2, b$ — tetraborate buffer solution and 8-hydroxyquinoline solution in ethanol, $2, c$ — ammonia buffer solution and 8-hydroxyquinoline solution in ethanol. Figure 3 shows a batch of fluorescence spectra of calcium 8-hydroxyquinolinate: $3, a$ — tetraborate buffer solution and 8-hydroxyquinoline solution in ethanol, $3, b$ — sodium hydroxide and 8-hydroxyquinoline solution in chloroform. The dashed line in Fig. 2 and the dotted line in Fig. 3 show the fluorescence spectra of 8-hydroxyquinoline in a buffer solution at zero concentration of magnesium (calcium) cation.

The weak fluorescence of 8-hydroxyquinoline at zero magnesium/calcium content is explained by the formation of 8-sodium hydroxyquinolinate in tetraborate buffer solution or sodium hydroxide solution or 8-ammonium hydroxyquinolinate in ammonia buffer solution. In this regard, the detection limit of magnesium cation is determined by the proximity of the fluorescence spectra with zero concentration and the concentration of magnesium sulfate solution of 3.2mmol/l. This is consistent with the concentration of 77.8 μg/ml, which greatly exceeds the concentration of magnesium cation in blood and saliva, but is lower than in urine. The detection limit of calcium cation in calcium chloride solution was 6.3 mmol/l equivalent to 252.5 μg/ml,

Concentrations of Mg^{2+} and Ca^{2+} cations in the physiological fluids of a healthy person.

Fluid	Concentration of Mg^{2+}		Concentration of Ca^{2+}	
	μg/ml	mmol/l	μg/ml	mmol/l
Blood	15.0–26.0	0.62–1.07	80.2–102.2	2.00–2.75
Saliva	2.4–10.2	0.10–0.42	30.0–120.0	0.75–3.0
Urine	195.0	8.02	113.0	2.83

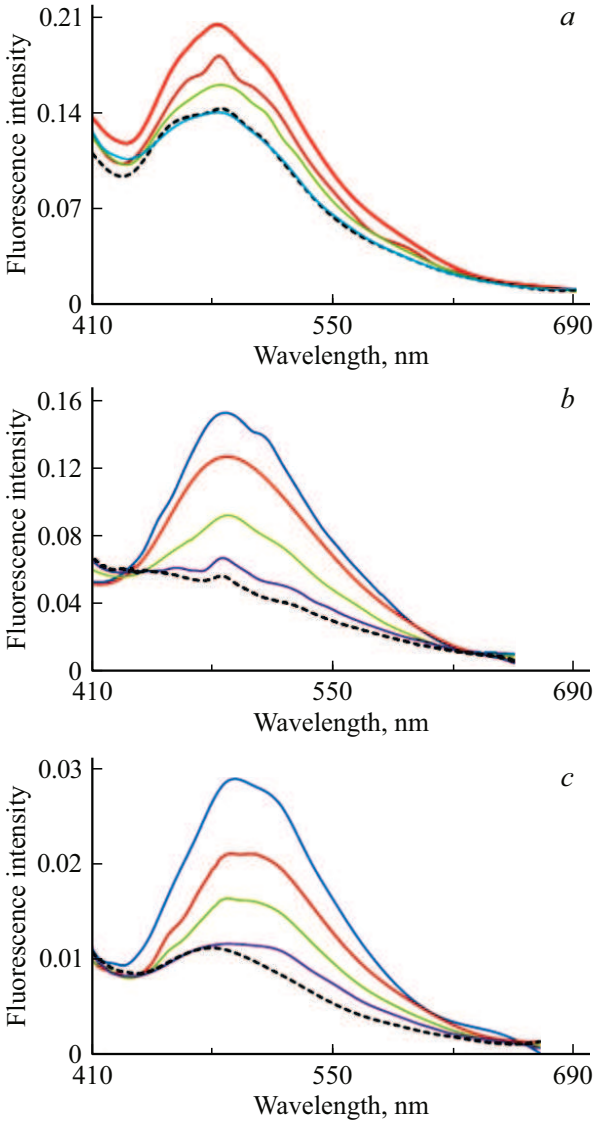


Figure 2. Fluorescence spectra of magnesium 8-hydroxyquinolinates depending on the concentration of magnesium cation, type of buffer solution and solvent of 8-hydroxyquinoline: (a) ammonia buffer solution and chloroform, (b) tetraborate buffer solution and ethanol, (c) ammonia buffer solution and ethanol.

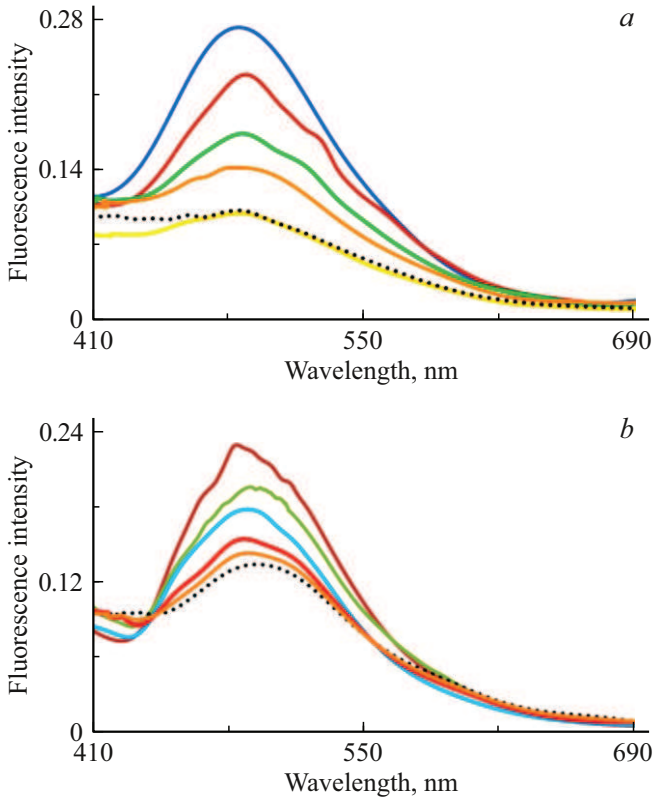


Figure 3. Fluorescence spectra of calcium 8-hydroxyquinolinate depending on the concentration of calcium cation, type of buffer solution and solvent of 8-hydroxyquinoline: (*a*) tetraborate buffer solution and ethanol, (*b*) sodium hydroxide and chloroform.

i.e. significantly exceeded the concentration of calcium in physiological fluids (see the Table).

To determine the effect of the type of buffer solution and 8-hydroxyquinoline solvent on the maximum fluorescence intensity versus magnesium sulfate (Fig. 4) and calcium chloride (Fig. 5) concentrations the graphs approximated by linear dependencies were plotted.

As can be seen from Fig. 4, the samples obtained in an ammonia buffer with a chloroform solution of 8-hydroxyquinoline have the highest fluorescence. It follows from Fig. 5 that the most intense fluorescence was recorded for calcium 8-hydroxyquinolinate obtained in a tetraborate buffer solution with an ethanol solution of 8-hydroxyquinoline. Regression equations are given next to linear approximations, which make it possible to determine the concentrations of cations (magnesium or calcium).

When irradiated with UV light (Optimal Owlet Locator), a bluish-turquoise glow of magnesium (calcium) 8-hydroxyquinoline was reliably observed regard-

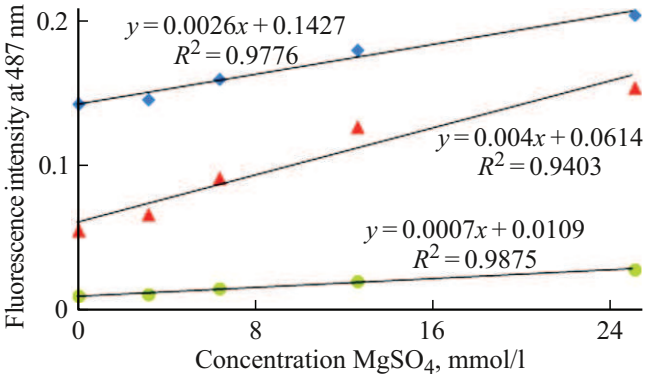


Figure 4. Fluorescence intensity at the maximum versus magnesium sulfate concentration, versus buffer solution, and versus 8-hydroxyquinoline solvent: upper dependence (marker — square) — ammonia buffer solution and chloroform, medium dependence (marker — triangle) — tetraborate buffer solution and ethanol, lower dependence (marker — circle) — ammonia buffer solution and ethanol.

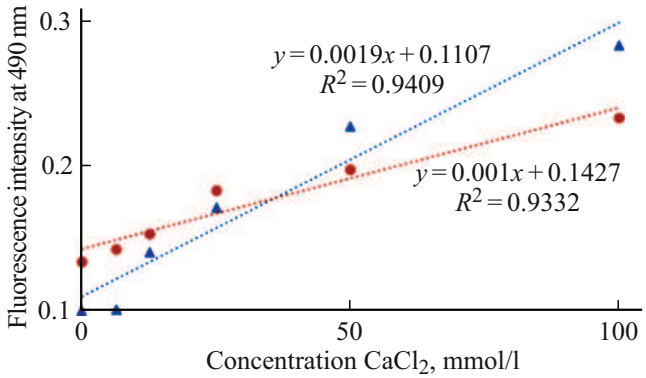


Figure 5. Fluorescence intensity at the maximum versus calcium chloride concentration, versus buffer solution, and versus 8-hydroxyquinoline solvent: upper dependence (marker — triangle) —tetraborate buffer solution and ethanol, lower dependence (marker — circle) — sodium hydroxide and chloroform.

less of the type of buffer system and solvent 8-hydroxyquinoline. For samples with zero concentration of magnesium/calcium cations, the light green-yellow color of fluorescence indicated the glow of sodium or ammonium 8-hydroxyquinolinates. At a low concentration of 8-hydroxyquinolinates of magnesium and calcium, the fluorescence had a mixed color.

The following conclusions may be drawn from the obtained results. 1. According to spectral fluorescence analysis, the detection limit of magnesium and calcium cations in aqueous solutions has been determined. For magnesium cations — 77.8 μg/ml (the highest intensity was set in an ammonia buffer solution using a solution of 8-hydroxyquinoline in chloroform), for calcium cations — 252.2 μg/ml (the highest intensity was set in tetraborate buffer solution when using a solution of 8-hydroxyquinoline in ethanol).

2. To quantify the content of calcium and magnesium cations in the analyzed sample, regression equations were obtained using spectral fluorescence method to determine the ion concentrations depending on the fluorescence intensity.

3. The visual method of fluorescence control in the low concentration region does not provide reliable determination of magnesium and calcium cations, regardless of 8-hydroxyquinoline solvent and the type of buffer system.

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Conflict of interest

The authors declare no conflict of interest.

References

[1] A.I. Ovsyannikov, S.I. Konkov, V.K. Gurkalo. Klinicheskaya laboratornaya diagnostika, **1** (16), 1999 (in Russian).
[2] N.V. Kopylov. *Razrabotka i sravnitel'naya otsenka sposobov opredeleniya magniya v farmatsevticheskom i biopharmatsevticheskom analize.* Disc.cand.farm.nauk (Kursk, 2004) (in Russian).
[3] N.V. Kanskaya, V.Yu. Serebrov, G.E. Chernogoryuk, G.E. Zhavoronok, T.V. Pozdnyakova, I.A. Romanova. *Klinicheskaya laboratornaya diagnostika. Iterpretatsiya resul'tatov laboratornykh issledovaniy*: uchebnoye posobiye; edited by N.V. Kanskoy (SibGMU, Tomsk, 2015) (in Russian). (Electronic source) URL: https://e.lanbook.com/book/105896
[4] E.A. Bozhevolnov, A.M. Lukin, G.V. Serebryakova. *Sposob kolichestvennogo luminescentnogo opredeleniya.* Patent № G01N 21/64(1995.01) C01F 5/00(1995.01). № 638298: claimed. 1959.09.07: published 1960.10.10 /– 3 p.
[5] N.S. Frumina, E.S. Kruchkova, S.P. Mushtakova. *Analytcheskaya khimiya kaltsiya.* Edited by I.M. Korenman. (M., Nauka, 1974) (in Russian).
[6] N.N. Basargin, Yu.G. Rozovsky, N.A. Tamarova, D.A. Dolgorev. *Sposob fotometricheskogo opredeleniya magniya.* USSR author's certificate №1 436 068 A1 11.07.1988.
[7] H. Duchl, R. Olsen, G. Spielhelz, R. Jensen. Anal. Chem., **35** (9), 1144 (1963). DOI: 10.1021/ac60202a054
[8] A. Badrinas. Talanta, **10** (6), 704 (1963). DOI: 10.1016/0039-9140(63)80091-0
[9] G.V. Serebryakova, A.M. Lukin, E.A. Bozhevolnov. Zhurn. analit. khimii, **18** (706), 1963 (in Russian).
[10] L.F. Fedorova, E.A. Bozhevolnov, G.S. Petrova, A.M. Lukin, O.A. Fakeeva. *Sposob kolichestvennogo opredeleniya magniya.* USSR author's certificate 566171 (25.07.1977).
[11] H. Goto, Y. Kakita. J. Chem. Soc. Japan, Pure Chem. Sec., **80** (12), 1448 (1959).
[12] M.A. Demertzis. Anal. Chim. Acta, **209**, 303 (1988). DOI: 10.1016/S0003-2670(00)84577-8
[13] A.I. Lazarev, I.P. Kharlamov, P.Ya. Yakovlev, E.F. Yakovleva. *Spravochnik khimika analytika* (Metallurgiya, M., 1976) (in Russian).

[14] GOST „*Reagents. 8-hydroxyquinoline*“ of 01.01.1977 № 5847-76 // Interstate standard (1977 with amendments revised 01.01.2021).
[15] GOST „*Reagents and superpure substances. Methods for preparation of buffer substances*“ of 01.01.2018 № 4919.2-2016 // Interstate standard. 2018.
[16] M.S. Khakhalina, I.Y. Tikhomirova, M.V. Puzyk. Opt. Spectrosc., **108** (5), 703 (2010).
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