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КОНЦЕНТРИРОВАНИЕ И ОПРЕДЕЛЕНИЕ СИНТЕТИЧЕСКОГО ПИЩЕВОГО КРАСИТЕЛЯ ЗЕЛЕНЫЙ ПРОЧНЫЙ FCF (E143) С ИСПОЛЬЗОВАНИЕМ АМИНИРОВАННОГО ОКСИДА АЛЮМИНИЯ

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Определены условия сорбционного концентрирования синтетического пищевого красителя Зеленый прочный FCF (E143) основным оксидом алюминия и оксидом алюминия, модифицированным полигексаметиленгуанидином (Al_2O_3-ПГМГ). Время установления сорбционного равновесия при извлечении красителя Е143 составляет 15 мин для обоих сорбентов. Количественное извлечение красителя сорбентом Al_2O_3-ПГМГ достигается в диапазонах рН 1,0–3,0 и рН 6,5–7,5. Максимальная степень извлечения основным оксидом алюминия не превышает 80% и достигается в диапазоне рН 2,0–5,0. Сорбционная емкость сорбентов по отношению к красителю Е143 составляет для Al_2O_3 20 мкмоль/г, для Al_2O_3-ПГМГ 35 мкмоль/г при рН 1 и 11 мкмоль/г при рН 6,5. Полученные экспериментальным путем изотермы сорбции для Al_2O_3-ПГМГ при рН 1 и рН 6,5 удовлетворительно описываются моделью Ленгмюра. Изотерма адсорбции для Al_2O_3 на отрезке роста сорбционной емкости наиболее удовлетворительно описывается моделью Фрейндлиха. При извлечении красителя Е143 поверхность сорбентов приобретает окраску, характерную для красителя в растворе. При этом в спектре диффузного отражения поверхности сорбентов наблюдается интенсивная полоса с максимумом при 620 нм. Предложена методика сорбционно-фотометрического определения красителя Е143 в варианте спектроскопии диффузного отражения с использованием Al_2O_3-ПГМГ. Предел обнаружения, рассчитанный по 3s-критерию, равен 7 мкг/л при использовании 10 мл раствора. Диапазон определяемых содержаний 0,02–3,0 мг/л. Относительное стандартное отклонение не превышает 0,08 (n=10). Селективность концентрирования и последующего определения красителя Е143 в фазе сорбента при рН 1,0 выше, чем при рН 6,5. Разработанная методика опробована при определении красителя Е143 в модельном растворе на основе безалкогольного напитка.

Ключевые слова: оксид алюминия, полигексаметиленгуанидин, синтетический пищевой краситель, Зеленый прочный (Е143), сорбционное концентрирование, определение

PRECONCENTRATION AND DETERMINATION OF SYNTHETIC FOOD DYE FAST GREEN FCF (E143) USING AMINATED ALUMINA

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The conditions for solid-phase extraction of the synthetic food dye Fast Green FCF (E 143) by basic and modified with polyhexamethylene guanidine alumina (Al_2O_3-PHMG) were determined. The equilibration time for extraction of E143 dye was 15 min for the both adsorbents. Quantitative extraction of E143 dye with Al_2O_3-PHMG was achieved in the ranges of pH 1.0–3.0 and pH 6.5–7.5. The maximum extraction of the dye by basic alumina was observed in the pH range of 2.0–5.0 and did not exceed 80%. The adsorption capacity of adsorbents for E143 dye was 20 μmol g^{-1} for Al_2O_3, 35 μmol g^{-1} for Al_2O_3-PHMG at pH 1 and 11 μmol g^{-1} at pH 6.5. The experimental adsorption isotherms for Al_2O_3-PHMG at pH 1 and pH 6.5 are best fitted the Langmuir model. The adsorption isotherm for Al_2O_3 in the segment of growth of the adsorption capacity is best fitted the Freundlich model. When extracting E143 dye, the surface of the adsorbents acquired a color characteristic for the dye in solution. In this case, an intense band with a maximum at 620 nm was observed in the diffuse reflectance spectra of the surface of the adsorbents. The procedure of adsorption-photometric determination of E143 dye in the variant of diffuse reflectance spectroscopy using Al_2O_3-PHMG was proposed. Limit of detection, calculated by the 3s-criterion, was 7 μg L^{-1} when using 10 mL of solution. The analytical range of dye concentrations was 0.02–3.0 mg L^{-1}. The relative standard deviation did not exceed 0.08 (n=10). The selectivity of preconcentration of E143 at pH 1.0 was higher than at pH 6.5. The developed procedure was used for determination of the Fast Green FCF dye in a model solution based on the soft drink.

Key words: alumina, polyhexamethylene guanidine, synthetic food dye, Fast Green FCF (E143) dye, solid-phase extraction, determination

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INTRODUCTION

Dyes are one of the most common and numerous additives used in the food industry and pharmacology. Synthetic food dyes are widely used because they are not destroyed and do not lose their bright color during heat treatment and food preservation, unlike natural food dyes. They are resistant to photo- and biodegradation and accumulate in the environment almost unchanged. The negative effect of synthetic food dyes on living organisms, including humans, requires the development of simple and rapid methods for their determination in food and drinks.

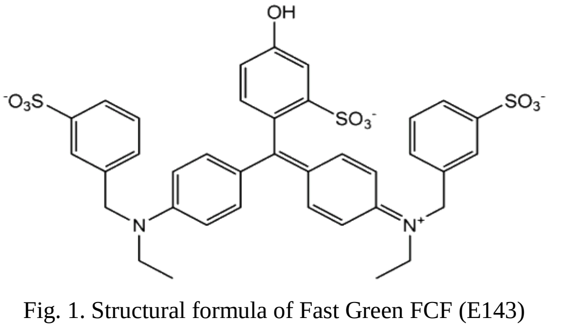


Fig. 1. Structural formula of Fast Green FCF (E143)
Рис. 1. Структурная формула красителя Зеленого прочного FCF (E143)

Synthetic food dye Fast Green FCF - E143 (Fig. 1) is approved for use in the food industry of the Russian Federation for coloring juices, desserts, sweets, lollipops, dragees, as well as jellies and sauces, and is prohibited for use in the pharmaceutical industry. In the European Union, on the contrary, the dye E 143 is allowed in the production of medical products and is strictly prohibited for use in food products [1].

When determining synthetic food dyes in the environment and food, the main task is their isolation from the matrix and separation from matrix components. Synthetic food dyes contain strongly acidic sulfonic groups; therefore, anion exchangers are mainly used for their solid-phase extraction, for example, Dowex Optipore V493 [2] and Amberlite XAD-1180, Amberlite XAD-16 [3], Chromosorb 108 [4], magnetic adsorbents [5, 6], amino silicas [7], hydrophobic silicas [8, 9], polyurethane foams [10-12]. A number of works are devoted to the preconcentration and determination of synthetic food dyes using γ-Al_2O_3 and α-Al_2O_3 [8, 9, 12-15]. It was shown that when extracting dyes in the range of 0.5 M HCl - pH 8.0, only one form of the dye was extracted, which was predominant under these conditions in an aqueous solution. The maximum extraction of food dyes by *α*-Al_2O_3 was achieved at pH < 5, because with an increase in the acidity of the medium, the number of Lewis acid sites on the surface of aluminum oxide and, accordingly, the total positive charge of the surface increased, which led to the extraction of dyes by the ion-exchange mechanism.

For their isolation and subsequent determination in food (jelly, caramel, spices, alcoholic and non-alcoholic drinks, etc.) methods using aluminum oxide as an adsorbent are recommended [16-19]. The main methods used for this are the adsorption of the studied dye, its desorption with aqueous ammonia, and evaporation using a water bath.

In this work, Al_2O_3 was chosen as the basis for the synthesis of adsorbents due to its availability, the absence of its own color, mechanical and chemical strength. The high surface concentration of hydroxyl groups makes it possible to efficiently modify the alumina surface with polymeric amines, in particular, polyhexamethylene guanidine, to create a positively charged surface [20-22]. The fixation of PHMG on the aluminum oxide surface occurs due to the formation of multicenter hydrogen bonds between the amino groups of PHMG and the surface hydroxyl groups of Al_2O_3. As we have shown earlier [20, 21], aminated aluminum oxides quantitatively extracted sulfonated complexing reagents in a wide pH range with equilibration times less than 10 min.

In the present study, basic alumina and modified with polyhexamethylene guanidine were proposed for the preconcentration of the synthetic food dye Fast Green FCF and its subsequent photometric determination directly in the phase of adsorbent using diffuse reflectance spectroscopy.

MATERIALS AND METHODS

Reagents. Fast Green FCF (E143) dye with a purity of ≥ 90% (Sigma-Aldrich, Germany) was used in the study. The stock solution of the E143 dye with a concentration of 0.1 g L^{-1} was prepared by dissolving an exact weighted portion of the reagent in distilled water. Solutions with lower concentrations were prepared by diluting the stock solution with distilled water.

Aluminum oxide 150 basic (particle size of 0.063-0.160 mm; specific surface area of 256 m^2 g^{-1}; average pore diameter of 15 nm) (Merck, Germany) was used as the matrix for the synthesis of the adsorbent. To modify the aluminum oxide surface, we used a 7.5% solution of polyhexamethylene guanidine (PHMG) prepared from a reagent produced by the Institute of Eco-technological problems (Moscow, Russia) with a purity of more than 95%. The PHMG solution was prepared by dissolving an accurate weighted portion in distilled water. The required pH was adjusted by adding of HCl and NaOH solutions of special purity grade.

Instrumentation. The diffuse reflectance (R) of the adsorbents in the range of 380-720 nm was measured using a Pulsar spectrometer (NPO Khimavtomatika, Russia). The UV-Vis spectra and optical density of solutions were registered using Cary 100 spectrometer (Varian, Australia). The pH of the solutions was measured using a SevenMulti ion meter (Mettler-Toledo, Switzerland) equipped with an InLabExpertPro combined electrode.

Experimentation. Modification of alumina with polyhexamethylene guanidine (Al_2O_3-PHMG) was carried out according to the previously described procedure [21].

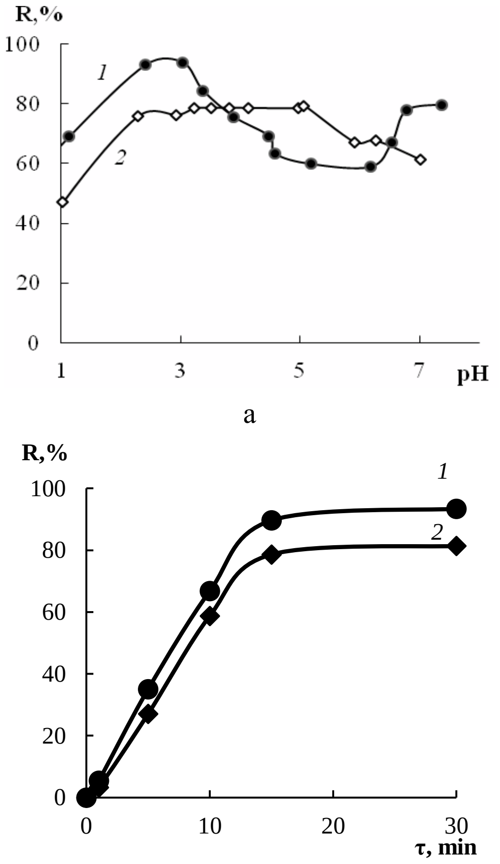
Adsorption of the dye by basic Al_2O_3 or Al_2O_3–PHMG adsorbent was carried out in a batch mode at room temperature. A dye solution (10 mL) of various concentrations was placed to graduated test-tube with a ground stopper; HCl, NaOH, or an acetate buffer solution were added to adjust the required acidity from 0.5 M HCl to pH 7.0. A weighted portion (0.1 g) of adsorbent (Al_2O_3 or Al_2O_3–PHMG) was placed into the solution, the test-tube was plugged and stirred for 1-30 min. The solution was decanted, the adsorbent was moved to fluoroplastic cell, excess liquid was removed by filter paper, than the diffuse reflectance was measured. Diffuse reflectance spectra (DRS) were plotted in coordinates F(R) – λ (nm), where F(R) – the Kubelka-Munk function calculated as $F(R) = (1-R)^2/2R$.

The distribution of Fast Green FCF between the solution and the adsorbent was monitored by analysis of aqueous phase using characteristic band of the dye at $\lambda max = 624$ nm.

RESULTS AND DISCUSSION

The maximum extraction of Fast Green FCF with basic Al_2O_3 was observed in the pH range of 2.0-5.0 and did not exceed 80% (Fig. 2a). The decrease in the degree of Fast Green FCF extraction at pH > 5 was associated with a decrease in the positive charge of the Al_2O_3 surface (the point of zero charge is 6.8 for γ-Al_2O_3 and 6.3-6.9 for α- Al_2O_3 [23, 24]). The protonization of the sulfo-groups of the dye and its transition to an uncharged molecular form occurred at pH < 1. A similar process was observed for α-Al_2O_3 by the authors of [9], where at pH < 3 and pH > 4, a sharp decrease in the recovery of Fast Green FCF was observed.

When Al_2O_3–PHMG was used as an adsorbent, a higher degree of extraction of the E143 dye was observed compared to unmodified Al_2O_3. The maximum extraction (90–93%) of the E143 dye by the Al_2O_3–PHMG adsorbent was observed in two ranges of pH 1.0-3.0 and pH 6.5-7.5. At pH > 3, a decrease in the extraction of Fast Green FCF was probably due to a change in the kind of its specie in solution (for -NH group pK_a = 2.8), as well as a change in the mechanism of PHMG fixation on the alumina surface. The equilibration time was 15 min for both adsorbents (Fig. 2b).



a

b

Fig. 2. Extraction of Fast Green FCF dye by Al_2O_3–PHMG (1) and Al_2O_3 (2) adsorbents vs. pH (a) and phase contact time (b): CE143 = 4.0 mg l^{-1}, $m_{adsorbent}$=0.1 g, $V_{solution}$=10 ml, τ=15 min (a), pH 3 (b)

Рис. 2. Зависимость степени извлечения красителя Зеленый прочный сорбентами Al_2O_3–ПГМГ (1), Al_2O_3 (2) от pH (a) и от времени контакта фаз (b): CE143 = 4,0 мг/л, $m_{сорб}$=0,1 г, $V_{р-ра}$ =10 мл, $τ_c$=15 мин (a), pH 3 (b)

In contrast to Al_2O_3, the extraction of E143 with the Al_2O_3–PHMG adsorbent increased at pH > 6. At these pH values, PHMG was firmly fixed on the alumina surface due to electrostatic interactions with surface hydroxyl groups. The strength of PHMG fixing due to multicenter electrostatic bonds was shown using the example of silica modification with PHMG [22]. At pH > 6, the concentration of a completely deprotonated dye species (for the OH group pK_a = 8.6) with a maximum negative charge increased in the solution, which also led to an increase in the extraction of the dye anions on a positively charged surface. PHMG, being a strong base (pK_a = 13.5), shifts the ionization of the hydroxyl group of the dye to a more acidic region.

During the adsorption of the E143 dye, the Al_2O_3–PHMG adsorbent turned into an intense green-blue color, which is characteristic for the anionic species of the dye. In a 0.5 M HCl solution, the UV-Vis spectrum of the dye had two bands: one of low intensity with a maximum at 450 nm and the other one, intense, with a maximum at 624 nm (Fig. 3). With an increase in pH to 10.5, the position of the long-wavelength band and its maximum remained, and the low-intensity band shifted to the short-wavelength region with a simultaneous decrease in its intensity.

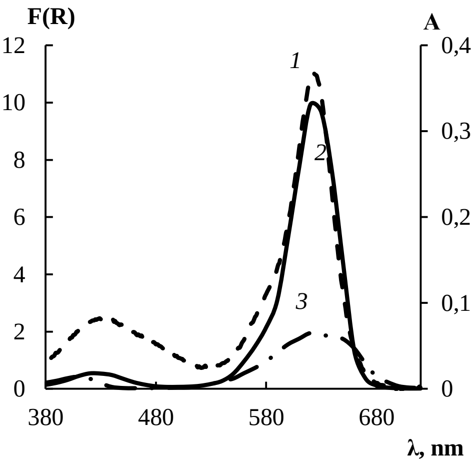


Fig. 3. UV-Vis (*1*) and diffuse reflectance (*2*, *3*) spectra of Fast Green FCF in solution (*1*) and on the surface of Al_2O_3–PHMG (*2*) and Al_2O_3 (*3*): CE143= 4.0 mg l^{-1}, $V_{solution}$=10 ml, pH 2.9, $m_{adsorbent}$=0.1 g, τ=15 min

Рис. 3. Спектры поглощения (*1*) и диффузного отражения (*2*, *3*) красителя Зеленого прочного в растворе (*1*) и на поверхности Al_2O_3–ПГМГ (*2*) и Al_2O_3 (*3*): CE143 = 4,0 мг/л, $V_{р-ра}$=10 мл, pH 2,9, $m_{сорб}$=0,1 г, $τ_c$=15 мин

The diffuse reflectance spectrum of the Fast Green FCF adsorbed on the surface of the Al_2O_3–PHMG was identical to the UV-Vis spectrum of the Fast Green FCF in solution and had maxima at 430 and 620 nm (Fig. 3). The color of Al_2O_3 after the preconcentration of E143 was less intense, and the long-wavelength absorption band was broadened and had a maximum at 630 nm.

The maximum color intensity of the surface of the adsorbents during the extraction of E143 was observed in the ranges of its maximum extraction: pH 1.0–3.0 and pH 6.5–7.5 for Al_2O_3–PHMG and pH 3–5 for Al_2O_3.

The phase contact time sufficient for the development of the maximum color intensity of the Al_2O_3 and Al_2O_3–PHMG adsorbents was equal to equilibration time (15 min).

The adsorption capacity of the adsorbents for the E143 dye, calculated from the horizontal sections of the adsorption isotherms, was 20 µmol g^{-1} for Al_2O_3 and 35 µmol g^{-1} for Al_2O_3-PHMG at pH 1. At pH 6.5, the adsorption capacity of the Al_2O_3-PHMG adsorbent was 11 µmol g^{-1} (Fig. 4). Such a difference in the capacities of the Al_2O_3-PHMG adsorbent for Fast Green FCF at pH 1.0 and 6.5 was due to different kinds of dye species on the surface and, accordingly, due to its different location on it. At pH 1, the fixation of the Fast Green FCF occurred only due to the electrostatic interaction only between the sulfo-groups of the dye and the protonated amino groups of PHMG, and in this case the dye molecules were located perpendicular to the surface. At pH 6.5, the hydroxyl group of the dye was ionized, which, along with the sulfo-groups of the dye, interacted with the protonated amino groups of PHMG, which led to a parallel arrangement of the dye molecules on the surface of the adsorbent. A similar change in the arrangement of the reagent molecules on the surface of the adsorbent was observed during the fixation of Tiron on the surface of Al_2O_3 [25].

Experimental adsorption isotherms of Fast Green FCF were analyzed according to Langmuir and Freundlich models. The parameters of the E143 dye adsorption isotherms were calculated using the Langmuir and Freundlich models by plotting the dependencies $C_e/a_e = f(C_e)$ and $\lg a_e = f(\lg C_e)$, respectively. C_e is the dye concentration in solution (µmol L^{-1}) under adsorption equilibrium conditions, a_e is the adsorption capacity (µmol g^{-1}) under equilibrium conditions.

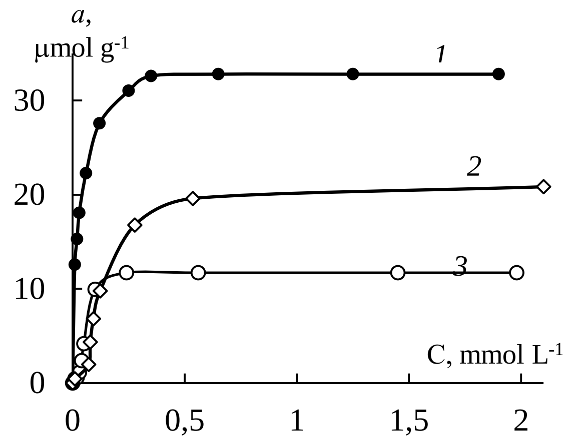


Fig. 4. Adsorption isotherms of Fast Green FCF by Al_2O_3–PHMG (*1, 3*) and Al_2O_3 (*2*): pH 1 (*1, 2*); pH 6.5 (*3*); τ = 15 min
Рис. 4. Изотермы сорбции красителя Зеленый прочный на поверхности Al_2O_3–ПГМГ (*1, 3*) и Al_2O_3 (*2*): pH 1 (*1, 2*); pH 6,5 (*3*); τ_c = 15 мин

The isotherms of Fast Green FCF adsorption by Al_2O_3-PHMG best fit the Langmuir model with a correlation coefficient of 0.98-0.999; the calculated maximum adsorption capacity (33.2 for pH 1 and 13.2 µmol g^{-1} for pH 6.5) is in good agreement with the experimental values determined from the horizontal sections of the adsorption isotherms.

The adsorption isotherms of Fast Green FCF by Al_2O_3 best fit the Freundlich model: with a calculated maximum capacity of 21.7 µmol g^{-1}. This may be due to the presence of active centers of various energies on the surface of alumina. Good consistency of the experimental adsorption isotherms of dyes and the Freundlich model was observed for membranes based on poly-m-phenylenisophthalamide [26].

Adsorption-photometric determination of food dye Fast Green FCF. With an increase in the concentration of the Fast Green FCF dye on the Al_2O_3–PHMG surface, the intensity of the band in the diffuse reflectance spectrum at λ_{max} = 620 nm increased proportionally. This effect became the basis of the method of its adsorption-photometric determination in the variant of diffuse reflectance spectroscopy using Al_2O_3–PHMG.

Construction of calibration curves. Solutions containing from 0.005 to 3.0 mg L^{-1} of Fast Green FCF at pH 1.0 and pH 6.5 were put into two rows of test tubes with ground stoppers; 0.05 g of Al_2O_3 or Al_2O_3–PHMG adsorbent was added. The tubes were tightly stoppered and stirred at room temperature for 15 min. The adsorbent was separated from the solution by decantation, moved to fluoroplastic cell, excess liquid was removed by filter paper, and the diffuse reflectance was measured at a wavelength of 620 nm. The calibration curves were plotted in the coordinates $\Delta F(R) = f(C)$, where $\Delta F(R)$ is the difference between the F(R) of the adsorbent with the dye and the F(R) of the blank adsorbent sample.

Limit of detection of E143 dye, calculated by the 3s-criterion, was 7 µg L^{-1} when using 10 mL of solution. The analytical range of dye concentrations was 0.02-3.0 mg L^{-1} and was described by the equation $\Delta F(R) = (2.6 \pm 0.1)\cdot C_{E143}$ with a correlation coefficient of 0.998, where C_{E143} was the dye concentration mg L^{-1}. The relative standard deviation did not exceed 0.08 for Fast Green FCF concentration 10 times higher than its detection limit.

Synthetic food dyes are used to maintain the color of foods. These products also contain significant amounts of other additives – sugar, preservatives, antioxidants, etc. Therefore, the interfering effect of these components on the adsorption-photometric determination of Fast Green FCF at pH 1 and pH 6.5, corresponding to the maximum degree of dye extraction, was studied.

The selectivity of the determination was studied in binary systems containing 0.2 mg of E143 and increasing amounts of related components from 0.02 to 10 g. The interfering effect of the component was recorded if the color intensity (Kubelka-Munk function) of the adsorbent changed by more than ± 5%.

The amounts of accompanying compounds that did not affect the adsorption-photometric determination of the Fast Green FCF are given in Table 1. As can be seen from the table, the selectivity of preconcentration of E143 at pH 1.0 was higher than at pH 6.5. This is due to the fact that the additives and preservatives used are organic carboxylic acids, which are protonated at pH 1.0, they are in molecular form and are not extracted by the positively charged surface of the Al_2O_3–PHMG adsorbent; at pH > 4, deprotonization of carboxyl groups occurs, preservatives acquire a negative charge and begin to be extracted by the Al_2O_3–PHMG adsorbent, interfering with the extraction of the dye. Thus, the adsorption-photometric determination of the dye E143 in real samples containing significant amounts of various additives should be carried out at pH 1.

Table 1

Additive concentrations that do not interfere with the adsorption-photometric determination of synthetic food dye Fast Green FCF using Al_2O_3–PHMG adsorbent

Таблица 1. **Концентрации добавок, не мешающие сорбционно- фотометрическому определению красителя Зеленый прочный FCF с использованием Al_2O_3–ПГМГ**

Interfering substances	Concentration, g L^{-1}	
	pH 1	pH 6.5
Citrate	15	-
Ascorbic acid	20	7
Glucose	45	12
Caffeine	4	-
Benzoic acid	3	0.5
Citric acid	40	10
Ethanol	96*	-

Note: * given in volumetric %

Примечание: * объемный процент

The developed adsorption-photometric procedure was used for determination of the E143 dye in a model solution based on the “Silver Tonic” carbonated soft drink (JSC Ayan, Abakan, Russia). The drink contains: drinking water, sugar syrup, natural flavor "Tonic", acidity regulators – citric acid, carbon dioxide. To create a model solution, a certain amount of Fast Green FCF dye (Table 2) was added to the drink.

To determine the dye, 10 mL of a model solution with pH 1.0 was placed in a graduated test-tube with a ground stopper, and 0.1 g of the Al_2O_3–PHMG adsorbent was added. The test-tube was tightly stoppered and stirred at room temperature for 15 min. The adsorbent was separated from the solution by decantation, moved to fluoroplastic cell, excess liquid was removed by filter paper, and the diffuse reflectance was measured at a wavelength of 620 nm. The dye concentration was determined from a calibration curve constructed under the same conditions.

The obtained results are shown in Table 2. The accuracy of the results was confirmed by the analysis of spiked solutions.

Table 2

Results of the adsorption-photometric determination of the Fast Green FCF dye in a model solution using the Al_2O_3–PHMG adsorbent (n=3, P=0.95)

Таблица 2. **Результаты определения красителя Зеленый прочный FCF в модельном растворе с использованием Al_2O_3–ПГМГ (n=3, P=0,95)**

Added, mg L^{-1}	Found, mg L^{-1}
0.5	0.5 ± 0.1
1	1.1 ± 0.2
2	1.9 ± 0.2

Desorption of E143 dye from the Al_2O_3–PHMG surface. One of the most important characteristics of the adsorbent is the possibility of its regeneration. Dilute solutions of inorganic acids and NaCl solution were tested as desorbing solutions for the dye. As follows from Table 3, with an increase in the concentration of acid and NaCl, desorption of the dye increased, however, quantitative desorption was achieved only when using 4 M HNO_3. The Al_2O_3–PHMG adsorbent withstood at least 5 “sorption-regeneration” cycles without loss of adsorption capacity for the Fast Green FCF dye.

Table 3

Desorption degree (R_{desorb}) of E143 dye from the adsorbent’s surface

Таблица 3. **Степень десорбции ($R_{десорб}$) красителя E143 с поверхности сорбента**

C_{HNO3}, M	R_{desorb}, %	C_{HCl}, M	R_{desorb}, %	C_{NaCl}, M	R_{desorb}, %
0.5	11	0.5	13	0.1	11
1	32	1	19	0.5	13
2	61	2	45	1	28
4	98	4	76		

CONCLUSION

Solid-phase extraction of anionic synthetic food dye Fast Green FCF from aqueous solution was more efficient when using aminated alumina compared to basic alumina. The proposed Al_2O_3–PHMG adsorbent quantitatively extracted (extraction ≥ 90%) Fast Green FCF from aqueous solutions at pH 1.0-3.0

and pH 6.5-7.5 with equilibration time not exceeding 15 min. The change in the color of the Al_2O_3–PHMG adsorbent during the adsorption of the E143 dye was included in the development of a procedure for its adsorption-photometric determination using diffuse reflectance spectroscopy.

Measurement of color intensity directly on the surface of the adsorbent eliminates the need for desorption of the dye into the solution and simplifies the procedure of its determination. The developed procedure is characterized by high selectivity and tested in the determination of the Fast Green FCF dye in a model solution based on a soft drink and is characterized by high accuracy and reproducibility.

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