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Article *in* Journal of Water Chemistry and Technology · July 2015

DOI: 10.3103/S1063455X15040049

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# Karmoazin as a Single Redox Reagent for Spectrophotometric Determination of Mn, Cr, Se, and V in Different Categories of Water

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Received April 7, 2014

**Abstract**—Karmoazin as a single redox reagent is proposed for spectrophotometric determination of Mn, Cr, Se, and V in case of their joint presence in different categories of water. It has been found out that the main parameters of complexation reactions of the specified metal ions with karmoazin determining its selectivity include the redox potential of redox pairs of metals, medium acidity and temperature. It was shown that the ions of macro-base intrinsic to water bodies did not interfere with determination of Mn, Cr, Se, and V in a wide range of concentrations.

**DOI:** 10.3103/S1063455X15040049

**Keywords:** different categories of water, manganese, chromium, selenium, vanadium, karmoazin.

## INTRODUCTION

There is a group of multivalent metals that carry out a dual function during the interaction with components of aqueous medium due to their physicochemical properties. Depending on the concentration and state of their ion-molecular forms they may play a role of vitally important bioelements or ecotoxicants [1]. In Ukraine enterprises of such branches of industry as metallurgy, coal mining, chemical, oil refining, paint-and-varnish, textile, semiconductor production and others, discharge untreated or insufficiently treated wastewater, the composition of which includes a vast array of heavy metals (M). They include manganese, chromium, selenium, and vanadium that may be found in different reactive forms depending on temperature, oxidation reduction potential (ORP), the chemical environment and acidity that are typical of industrial wastewater [2, 3]. Moreover they can exist simultaneously at different molar ratios along with metals forming the macro composition ( $M_{MC}$ ) of water bodies [4]. This leads to the need of quantitative determination of Mn, Cr, Se, and V in such multicomponent aqueous medium.

At present a large number of spectrophotometric methods for determination of the specified M is available, however, as a rule they are labor-intensive and poorly selective [5–8]. In earlier papers [9–12] a representative of the class of azo dyes, namely 4-sulfo-2(4'-sulfonaphthalene-1'-azo)-naphthol-1, under the name of karmoazin (KAN) was proposed for simple and rapid spectrophotometric determination of Mn(VII), Cr(VI), Se(VI), and V(V) as a redox reagent. KAN participates in complexation reactions with the specified M in their highest oxidation states in accordance with the mechanism of mutual oxidation—reduction that determines its selectivity. The optimal complexation conditions and peculiarities of each of the specified M with KAN were established, and main chemico-analytical characteristics of complex compounds (CC) forming an appropriate analytical signal were also calculated.

The purpose of this study is to investigate the possibility of spectrophotometric determination of one of  $M_1$  while varying the multiple molar ratios of the second  $M_2$  in a series of metals under consideration (Mn, Cr, Se, and V) in the presence of other interfering metals  $M_{ints}$  that create a salt background typical of different categories of water while using the single redox reagent karmoazin.

## EXPERIMENTAL

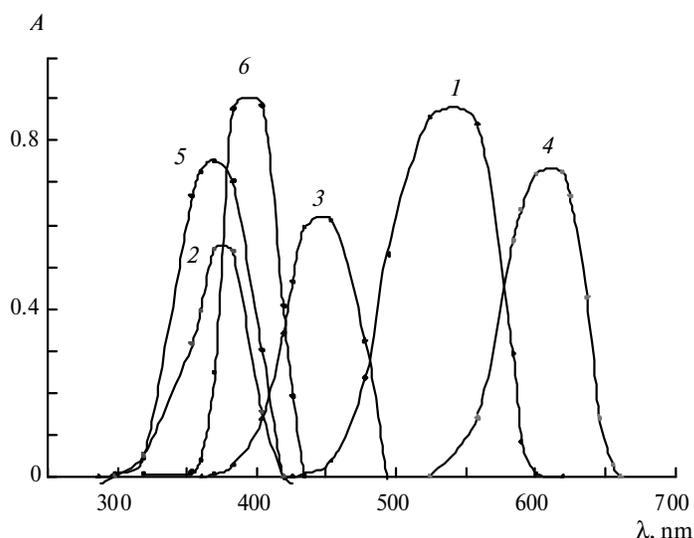
The initial solutions of Mn(VII), Cr(VI), Se(VI), and V(V) were prepared by dissolving the accurate weights of appropriate metal salts (chempure grade) in distilled water; solutions of selenium and vanadium were prepared by acidifying the distilled water with concentrated  $HNO_3$ . Water solutions of KAN at concentration  $1 \times 10^{-2}$  mol/dm<sup>3</sup> were prepared by dissolving the weight of dry reagent (chempure grade) in distilled

water. The solutions of ions of the specified metals and the reagent at lower concentrations were prepared by diluting the initial solutions directly before use.

For estimation of the selectivity of proposed reactions of M with KAN the reaction systems  $M_1-M_2-KAN$  were prepared, where  $M_1$  is the target (main) ion and  $M_2$  is the accompanying ion from the series Mn, Cr, Se, and V. These systems were obtained by successive mixing of their multiple molar ratios, such as  $M_1 : M_2 = 1 : 1, 1 : 2, 1 : 5, 1 : 10, 1 : 50, 1 : 100, 1 : 200, 1 : 500$ . The salt background simulating the micro- and macro-composition of a number of industrial wastewaters was created by addition of appropriate sum of electrolytes ( $\Sigma M_{ints}$ ) in accordance with papers [13–15]. The required value of medium acidity intrinsic to complexation of the main ion  $M_1$  was set, and the specified amount of KAN solution ( $C_{KAN} = 1 \times 10^{-1} - 1 \times 10^{-4} \text{ mol/dm}^3$ ) was added. The required temperature was specified with due regard for the kinetic parameters of the target ion reaction. After termination of the complexation reactions for all reactive systems, the electronic absorption spectra were registered on a spectrophotometer SF-56 (OKB LOMO-Spektr, St. Petersburg, Russia) in the wavelength range of the absorption band that was adopted as analytical with  $\lambda_{max}$  for each ion of  $M_1$  to be determined. The reduction of absorbance intensity of the appropriate analytical band for  $M_1$  was used to establish the molar quantity of  $M_2$ , which specifies the beginning of its detectable effect.

## RESULTS AND DISCUSSION

Figure 1 presents a set of analytical absorption bands for complexes of tested metals and their location in the wavelength range of 250–700 nm in relation to the band of free reagent KAN ( $\lambda_{max} = 530 \text{ nm}$ ).



**Fig. 1.** Absorption spectra of aqueous solution of KAN (1) and its complexes with Mn(VII) at pH 2 (2) and pH 6 (3); Cr(VI) (4); Se(VI) (5); and V(V) (6).

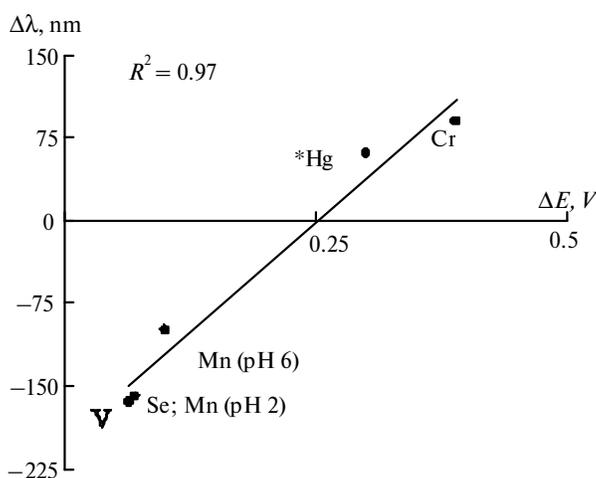
As can be seen from Fig. 1, each of the electronic spectra of absorbance of CC solutions in the wavelength range under consideration contains one characteristic intensive band with pronounced maximum. Moreover, practically for all analyzed systems, except Cr(VI)–KAN, we can observe their considerable hypsochromic shift. The peculiarity of the Mn(VII) reactivity should be noted: there are two possible analytical forms for Mn(VII) with KAN of the same composition implemented at pH 2 and 6 with different chemico-analytical characteristics that enhances the Mn(VII) capabilities of selective determination in the presence of other M. For the complete description and comparative analysis of the analytical forms in use that are determined by M, their chemico-analytical characteristics are summarized and harmonized in Table 1.

Taking into account that the complexation process in chemical systems under investigation is accompanied by oxidation reduction reaction (ORR) of reactants, the values of real ORP were calculated [16]. In order to corroborate the relationship of  $\lambda_{max}$  values for each of analytical forms and the ORP values of redox pairs of M, we calculated the appropriate deviations:  $\Delta\lambda \text{ (nm)} = \lambda_{maxKAN} - \lambda_{maxCC}$ , and also  $\Delta E \text{ (V)} = E^0 - E$ ; in addition, the functional relationship  $\Delta\lambda = f(\Delta E)$  was also plotted (Fig. 2). For better clarity and reliability of

the presented relationship we used the chemico-analytical characteristics of CC ions  $\text{Hg}^{2+}$  with KAN [17]. The obtained coefficient of approximation reliability  $R^2$  unequivocally indicates the direct relationship of quantities under consideration.

**Table 1.** Optimal conditions and chemico-analytical characteristics of complexes of Mn, Cr, Se, and V with karmoazin

Indicator	Mn(VII)–KAN		Cr(VI)–KAN	Se(VI)–KAN	V(V)–KAN
	$\text{MnO}^-/\text{Mn}^{2+}$	$\text{MnO}_4^-/\text{Mn}^{4+}$	$\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$	$\text{SeO}_4^{2-}/\text{SeO}_3^{2-}$	$\text{VO}^{3+}/\text{V}^{3+}$
$E^0$ , V (standard)	1.51	1.69	1.33	1.15	1.26
$\Delta$ , V (real)	1.44	1.59	0.97	1.08	1.20
$\text{pH}_{\text{comp}}$	2.0	6.0	2.0	-0.5 (1.5M $\text{H}_2\text{SO}_4$ )	0.0 (0.5M $\text{H}_2\text{SO}_4$ )
Structure of complex (M : KAN)	1 : 1	1 : 1	1 : 3	1 : 4	1 : 3
$T_{\text{comp}}$ , °C	20	20	80	80	80
$\lambda_{\text{max}}$ , nm	380	430	620	370	365
$\epsilon\lambda_{\text{max}}$	7500	9500	11000	10000	16000
$C_{\text{range}}$ , $\mu\text{g}/\text{cm}^3$	0.9–6.3	0.3–9.0	0.4–4.5	1.6–12.6	0.3–1.8



**Fig. 2.** The relationship between the values of absorption maximum shift and the potential variation in chemical systems: M–KAN ( $\text{pH}_{\text{comp}} = 6-7$ ;  $\lambda_{\text{max}} = 590$  nm;  $\text{Hg(II)} : \text{KAN} = 1 : 1$ ;  $E^0 2\text{Hg}^{2+}/\text{Hg}_2^{2+} = 0.91$  V;  $E = 0.61$  V).

From data in Fig. 2 it follows that hypsochromic shifts of analytical bands for Mn(VII), Se(VI) and V(V) correspond to small values of  $\Delta E$  (0.06–0.10) of chemical systems M : KAN. The closeness of  $E^0$  and  $E$  for these redox pairs of metals indicates that KAN enters into reaction in oxidized form with disturbed system of  $\pi$ -bonds that determines the hypsochromic shift of the main absorption band. Bathochromic shift of the analytical CC absorption band is observed in the case where the calculated real ORP of chemical system is much lower than the corresponding standard potential of redox pair  $\text{M}_{\text{oxid}}/\text{M}_{\text{red}}$  similar to the case of systems Cr(VI)–KAN ( $\Delta E = 0.36$  V) and Hg(II)–KAN ( $\Delta E = 0.30$  V). During their interaction with reagent the conjugation of  $\pi$ -bonds is enhanced that is corroborated by the bathochromic shift of the absorption band in electronic spectrum. All tested redox pairs of metals are characterized by a considerable proper value of ORP that determines their capability to enter into ORR with KAN under specific conditions (see Table 1). In turn, it completely rules out the possibility of KAN reaction with many ions of metals determining macro- and micro-compositions of different categories of water: Fe, Zn, Cd, Pb, Sn, Al, Mg, Ca, Cu, Co, Ni, Ti, Mo, W, etc. The necessary and important condition of mutual oxidation-reduction of M ion with KAN, along with sufficiently large value of ORP of their redox pair, is the existence of M in oxygen-containing (oxo- or hydroxo-) reactive form at the strictly specified pH value of complexation ( $\text{pH}_{\text{comp}}$ ). In this case the existence of some

of them is limited by fairly narrow intervals of pH [18] that serves as an additional factor determining the specificity of this reaction in the presence of other ions capable of reacting with KAN.

Absolute values of  $\Delta\lambda$  make it possible to refer the reactions under study to high contrast ones, while the values of molar absorption coefficients ( $\epsilon_{\lambda_{\max}}$  from 7500 to 16000) can be referred to quite sensitive. Wide concentration ranges ( $C_{\text{range}}$ ) of compliance with the Beer law (see Table 1) enable us to perform the spectrophotometric determination of the specified metals-toxicants in waters and other entities of natural and industrial origin.

The optimal conditions and multiple ratios of molar concentrations  $M_1 : M_2$ , at which  $M_2$  does not interfere with determination of  $M_1$ , were established as a result of the investigation of the possibility of selective spectrophotometric determination of one of M in dual system  $M_1-M_2$  compiled from the series Mn(VII), Cr(VI), Se(VI), and V(V) at different molar ratios of the target (main)  $M_1$  and accompanying  $M_2$  (Table 2). From this Table it follows that the variation of medium acidity in redox system I from pH 2 to pH 6 makes it possible to determine Mn(VII) in the presence of ten-fold excess of V(V), while in system II—in the presence of 500-fold excess of Se(VI). At the same time the determination of both V(V) and Se(VI) is possible at 50-fold excess of Mn(VII) and practically close parameters of the reaction.

It was established that under optimal conditions (pH 2,  $T_{\text{comp}} = 80^\circ\text{C}$ ) the electronic spectra of system III contain two absorption maximums characteristic for analytical forms of Mn(VII) at  $\lambda_{\max} = 380$  nm and Cr(VI) at  $\lambda_{\max} = 620$  nm (see Table 1). The value  $\Delta\lambda = 240$  nm indicates the possibility of simultaneous determination of Mn(VII) and Cr(VI) ions from one sample, during which the 200-fold excess of Cr(VI) does not hamper the determination of Mn(VII), while the 150-fold excess of Mn(VII) does not hamper the determination of Cr(VI). At  $20^\circ\text{C}$  and pH 2 the determination of Mn(VII) is possible at 100-fold excess of Cr(VI), while at pH 6 the selectivity of KAN with respect to Mn(VII) decreases by one order of magnitude.

**Table 2.** Conditions of spectrophotometric determination of trace amounts of Mn(VII), Cr(VI), Se(VI), and V(V) at different ratios of molar concentrations  $M_1 : M_2$

No.	System	Variable parameters		Ratio of molar concentrations $M_1 : M_2^*$
		pH $\pm 0.02$	$T \pm 1^\circ\text{C}$	
I	V(V)–Mn(VII)–KAN	0	80	V(V) : Mn(VII) = 1 : 50
		2.0	20	Mn(VII) : V(V) = 1 : 5
		6.0	20	Mn(VII) : V(V) = 1 : 10
II	Se(VI)–Mn(VII)–KAN	–0.5	80	Se(VI) : Mn(VII) = 1 : 50
		2.0	20	Mn(VII) : Se(VI) = 1 : 100
		6.0	20	Mn(VII) : Se(VI) = 1 : 500
III	Cr(VI)–Mn(VII)–KAN	2.0	80	Mn(VII) : Cr(VI) = 1 : 200
		2.0	20	Cr(VI) : Mn(VII) = 1 : 150
		6.0	20	Mn(VII) : Cr(VI) = 1 : 100
IV	Cr(VI)–Se(VI)–KAN	2.0	80	Cr(VI) : Se(VI) = 1 : 50
		–0.5	80	Se(VI) : Cr(VI) = 1 : 50
V	Se(VI)–V(V)–KAN	–0.5	80	Se(VI) : V(V) = 1 : 100
		0	80	V(V) : Se(VI) = 1 : 50
VI	V(V)–Cr(VI)–KAN	0	80	V(V) : Cr(VI) = 1 : 500
		2.0	80	Cr(VI) : V(V) = 1 : 10

\* Ratio of molar concentrations of metal ions, at which  $M_2$  does not interference with determination of  $M_1$ .

As regards system IV, the possibility of mutual influence for Cr(VI) and Se(VI) was established at the level of 50-fold excesses and  $\text{pH}_{\text{comp}} 0.5$ . In systems V and VI the optimal conditions of V(V) complexation are pH 0 and temperature  $T_{\text{comp}} = 80^\circ\text{C}$ . Its determination is not hampered by 50-fold excess of Se(VI) and 500-fold excess of Cr(VI). Such noticeable differences in reactive capabilities are related to the peculiarities of physicochemical properties of selenium and chromium in their highest oxidation states. In case of variation of pH value (–0.5 or 2) (typical of reactions Se(VI) and Cr(VI)) and the fixed value of  $T_{\text{comp}}$ , their determination is

not affected by 100-fold and 10-fold excesses of V(V), respectively; this can be explained by noticeable differences in  $\text{pH}_{\text{comp}}$  of KAN with Cr(VI) and Se(VI).

The techniques of spectrophotometric determination of Mn, Cr, Se and V in industrial wastewater were developed on the basis of data obtained. Systems V(V)–Mn(VII), Cr(VI)–Mn(VII) and V(V)–Cr(VI) are found in wastewater at metallurgical, electroplating and chemical production facilities, and also in mining waters, while selenium is most often found in wastewater at facilities of the semiconductor industry and in waters of artesian wells. These techniques were tested at different categories of water, namely, in mining water (Mn, Cr, and V) and in artesian water in the city of Odessa (Mn, Cr, and Se). The results of determination of Mn(VII), Cr(VI), Se(VI) and V(V) with karmoazin are presented in Table 3.

**Table 3.** Results of spectrophotometric determination of Mn(VII), Cr(VI), Se(VI), and V(V) with karmoazin ( $n = 3$ ;  $P = 0.95$ )

Water (determined metals)	Concentration of M, $\text{mg}/\text{dm}^3$	
	introduced	found
Mining (Mn, Cr, and V)	0.30	Mn   $0.64 \pm 0.07$ $0.35 \pm 0.05$
		Cr   $0.49 \pm 0.04$
		V   $0.31 \pm 0.06$
Artesian (Mn, Cr, and Se)	0.25	Mn   $0.34 \pm 0.04$
		Cr   $0.48 \pm 0.09$
	0.40	Se   $0.0012 \pm 0.0002$

The determination of Se involved the need of its preliminary extraction concentrating. It should be noted that usually the determination of Se with KAN in drinking water is not performed. This method is presented here for the purpose of showing that its determination with KAN is not hampered by the majority of accompanying elements, and at the same time Se itself does not interfere with determination of Mn, Cr, and V in real entities.

#### *Construction of the Calibration Graph for Determination of V(V)*

The V(V) solution at concentration  $1 \times 10^{-3} \text{ mol}/\text{dm}^3$  in the amounts of 0.5, 1, 1.5, 2, 2.5, 3, and 3.5  $\text{cm}^3$  was introduced into each of a set of 50  $\text{cm}^3$  beakers; next we set pH 0, then added 15  $\text{cm}^3$  of karmoazin at concentration  $1 \times 10^{-3} \text{ mol}/\text{dm}^3$  to each of the beakers and again adjusted pH to 0 level, and heated the solutions in water bath during 15–20 min. Next these solutions were transferred into a set of 50  $\text{cm}^3$  delivery (graduated) flasks; we added 12.5  $\text{cm}^3$  of ethanol to each flask, added distilled water to the full volume and mixed. The optical density was measured in the range of  $\lambda = 365 \text{ nm}$  in relation to the corresponding concentration of karmoazin. The graph was plotted in coordinates  $A = f(C_M)$ .

#### *Determination of V(V) in Model Solutions of Wastewater at Metallurgical Production Facilities*

The collected water sample was filtered for the removal of mechanical admixtures. Aliquot of 10–25  $\text{cm}^3$  depending of vanadium content was transferred into a beaker. Further performance of analysis was conducted in the same way as during the construction of calibration graph. The V(V) content was determined by using the calibration graph.

*Construction of the Calibration Graph for Determination of Mn(VII)*

The Mn(VII) solution at concentration  $1 \times 10^{-3}$  mol/dm<sup>3</sup> in the amounts of 1, 2, 3, 4, 5, and 6 cm<sup>3</sup> was introduced into each of a set of 50 cm<sup>3</sup> beakers; next we set pH 2, then added 6 cm<sup>3</sup> of karmoazin at concentration  $1 \times 10^{-3}$  mol/dm<sup>3</sup> to each of the beakers and again adjusted pH to pH 2. The solutions were transferred into a set of 50 cm<sup>3</sup> delivery flasks; then water with pH 2 was added to the full volume and mixed. The optical density was measured in the range of  $\lambda = 370$  nm in relation to the corresponding concentration of karmoazin. The graph was plotted in coordinates  $A = f(C_M)$ .

*Determination of Mn(VII) in Model Solutions of Wastewater at Chemical Production Facilities*

The collected water sample was filtered for the removal of mechanical admixtures. For the conversion of ions Mn(II) into Mn(VII) the surplus sodium bismuthate was added to the sample and then the solution was filtered for the removal of mechanical admixtures of unreacted oxidizer. Aliquot of 25–30 cm<sup>3</sup> depending of the content of metal was transferred into a beaker. Further performance of analysis was conducted in the same way as during the construction of calibration graph. The Mn(VII) content was determined by using the calibration graph.

*Construction of the Calibration Graph for Determination of Cr(VI)*

The Cr(VI) solution at concentration  $1 \times 10^{-3}$  mol/dm<sup>3</sup> in the amounts of 1, 2, 3, 4, 5, 6 and 7 cm<sup>3</sup> was introduced into each of a set of 50 cm<sup>3</sup> beakers; next we set pH 2, then added 21 cm<sup>3</sup> of karmoazin at concentration  $1 \times 10^{-3}$  mol/dm<sup>3</sup> to each of beakers and again adjusted pH to pH 2. The solutions were transferred into a set of 50 cm<sup>3</sup> delivery flasks; next the solutions were heated in water bath during 15 min. After cooling distilled water was added to the full volume and mixed. The optical density was measured in the range of  $\lambda = 630$  nm in relation to the corresponding concentration of karmoazin. The graph was plotted in coordinates  $A = f(C_M)$ .

*Determination of Cr(VI) in Model Solutions of Wastewater at Metallurgical Production Facilities*

The collected water sample was filtered for the removal of mechanical admixtures. Aliquot of 5–15 cm<sup>3</sup> depending on the content of metal was transferred into a beaker. Further performance of analysis was conducted in the same way as during the construction of calibration graph. The Cr(VI) content was determined by using the calibration graph.

The determination of total chromium content involved the need of adding the surplus sodium bismuthate to water sample for converting Cr(III) into Cr(VI). The sample was filtered for the removal of mechanical admixtures of unreacted oxidizer.

The proposed techniques are characterized by simple implementation and inexpensive equipment; in addition, they do not require the use of toxic organic solvents.

## CONCLUSIONS

Thus, the key parameters of complexation reactions of ions of mixed valence metals with karmoazin accompanied by their mutual oxidation—reduction include the following ones: ORP of redox pairs of metals and, consequently, their reactive capability, and also the medium acidity and temperature. Therefore the values of these parameters for investigated systems may play a role of predictive ones when it is necessary to obtain the quantitative determination of metals under consideration in case they are jointly present. In real water bodies the specified multivalent metals may be simultaneously present in different oxidation states that involves the need of preliminary conversion of lower oxidation levels into higher ones [4] making it possible to determine the total content of existing oxidation–reduction forms of one and the same metal. Moreover the majority of interfering ions of macro-base intrinsic to multicomponent water bodies do not enter into reaction with karmoazin due to a small ORP value of their redox pairs that mostly determines the selectivity of complexation reactions of karmoazin in relation to Mn(VII), Cr(VI), Se(VI), and V(V). With due regard for the above, karmoazin can be used as a single organic redox reagent for spectrophotometric determination of a number of metals in their highest oxidation states in case of their joint presence; such determination is possible in quite a wide range of concentrations and in different categories of water. In addition, from the ecological

viewpoint, the proposed redox reagent is readily available and low toxic because it belongs to the group of widely used dyes in the food-processing (E 122) [19] and pharmaceutical [20] industries.

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Translated by A. Zheldak