

Express determination of iron microimpurities in technological solutions for growing KH_2PO_4 single crystals by visual test method

*T.I.Ivkova, R.P.Pantaler, A.B.Blank,
E.A.Reshetnyak*, Yu.Eu.Vakhovskaya**

STC "Institute for Single Crystals", National Academy of Sciences of Ukraine,
Institute for Single Crystals,
60 Lenin Ave., 61001 Kharkiv, Ukraine
*V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

Received November 28, 2003

Studied are the conditions for express determination of microamounts of iron with 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) in the form of ionic associate (IA) with NO_3^- ions. A technique is proposed for pumping sorption of the IA from the solution by means of polyurethane foam. The statistically calculated lower limit of the determined Fe (II, III) contents in the "unreliable reaction" region is 0.03 $\mu\text{g}/\text{ml}$, the determination time does not exceed 10 min, the relative standard deviation of the determination of 0.03 to 0.20 $\mu\text{g}/\text{ml}$ of Fe (II, III) is 0.36 and 0.21, respectively ($n = 30$). The developed test is used for express visual determination of iron (II, III) at the level of $5 \cdot 10^{-5} \%$ in the mother liquid for potassium dihydrogen phosphate crystal growth.

Изучены условия экспрессного определения микропримесей железа с 4,7-дифенил-1,10-фенантролином (батифенантролином) в виде ионного ассоциата (ИА) с NO_3^- -ионами. Предложен способ прессингового извлечения ИА из раствора пенополиуретаном. Статистически рассчитанный нижний предел обнаружения Fe (II,III) для области "ненадёжной реакции" составляет 0,03 мкг/мл. Время определения не превышает 10 мин., относительное стандартное отклонение при определении от 0,03 до 0,2 мкг/мл составляет 0,36–0,21 ($n = 30$), соответственно. Предлагаемый тест был применён для определения суммарного содержания Fe (II,III) на уровне $5 \cdot 10^{-5} \%$ в технологических растворах для выращивания монокристаллов KH_2PO_4 .

Optical characteristics of single crystals used in laser radiation controlling devices depend functionally on their microimpurity composition. In particular, content of Fe (II,III) ions plays an essential part in formation of the potassium dihydrogen phosphate crystal morphology [1]. To correct the composition of the mother solutions for KH_2PO_4 crystal growth, a great number of intermediate analyses should be performed outside of laboratory immediately after sampling. The final result must be obtained by one of

standard methods of the analysis under laboratory conditions.

The purpose of the present research is to study the potentialities of solid phase extraction of iron-bathophenanthroline (BP) complex by polyurethane foam (PUF) sorbent for visual test determination of iron (II, III) contained in amounts on the level of $5 \cdot 10^{-5} \%$ in the mother solutions for KH_2PO_4 crystal growth.

Among the existing methods for iron determination, the ones based on the forma-

tion of thiocyanate complexes [2, 3] are to be mentioned first of all. In [4, 5], the optimum conditions and sorption chemism of iron (III)-thiocyanate complexes on PUF sorbents are studied in detail. The method is characterized by high sensitivity, though its selectivity is rather low: the determination process is hampered by the fact that a large number of ions form complexes with iron, which are more stable than those with thiocyanate. The use of more sensitive *o*-phenanthroline reagent in the form of indicator powder [6], on ion-exchange resin [7] or PUF sorbent [8] for express test determination of iron also gives low results in the presence of large amounts of phosphates.

As a reagent, we have chosen BP, a highly selective complexing substance for iron (II). There are but few papers devoted to the use of this reagent for express determination of iron. In particular, described in [9] is a visual method which implies the application of the of BP-sodium disulfonate mixture with indigo carmine in sodium acetate with L-ascorbic acid additive. The polymethyl methacrylate powder with BP immobilized thereon is reported to be used in portable optical fiber probe for Fe(II) determination in water [10]. These two methods are distinguished by high sensitivity. However, the first of them cannot be applied as a test method, since the duration of the analytical procedure is more than 40 minutes. The second method is not applicable in analysis of media with high salt concentrations.

We investigated the possibility to realize visual determination of microgram amounts of iron (II) in the form of its BP complex after sorption on PUF sorbent.

High purity grade KJ, KCl, KBr, KNO₃, NaClO₄, KH₂PO₄, HCl, Fe₂O₃, and acetone, as well as ascorbic acid and chloroform for medical purposes and chemical purity grade *n*-butyl alcohol, KBF₄, and H₃PO₄, were used. The initial 1·10⁻² M iron solution was prepared by dissolution of an iron (III) oxide precise weight in HCl solution (1 + 1).

The solutions with lower iron concentrations were prepared by successive dilution of the initial solution. The iron concentration in the standard solution was determined by complexometry. The solutions with 0.1 M concentrations of KJ, KCl, KBr, KNO₃, KBF₄, NaClO₄ were obtained by dissolution of the corresponding weights in bidistilled water, those with 1·10⁻² M concentration were prepared by dilution of the

initial solutions. The buffer solution with pH = 2.5±0.3 was prepared from 1 M KH₂PO₄ and H₃PO₄ solutions. It was purified from iron by extraction with BP complex using chloroform-butanol mixture (2 + 1).

To obtain 3·10⁻³ M solution of BP in acetone, analytical purity grade recrystallized preparation was used. As the sorbent, PUF of "T25-3,8" trade mark (Ukraine) was utilized. About 10×8×8 mm³ PUF cubes of about 0.03 to 0.05 g mass were cut out of the polymer sheet. Purification of PUF was carried out according to the known technique [11], by keeping it in 0.1 M H₂SO₄ solution during 30 minutes followed by washing first with bidistillate to obtain pH = 6–7 and then with acetone. Then PUF was dried in air and stored in tightly packed glassware. Immobilization of BP on PUF cubes was carried out by saturating the latter with acetone solution of BP 3·10⁻³ M during 5 minutes. Then the cubes were kept in drying chamber at a temperature not higher than 30°C to remove acetone, and then stored in tightly shut dark glassware.

Photometric determination of iron (II) to find its equilibrium concentration before and after sorption was realized in the following way. The solution to be analyzed (1–5 ml) was placed into a 25-ml measuring flask; the mother liquids of KH₂PO₄ were preliminarily diluted with water (1 + 3) or (1 + 2). Then the pH = 2.5±0.3 buffer solution (1–2 ml), 5·10⁻² M ascorbic acid (1 ml), acetone (2 ml), 3·10⁻³ M acetone solution of BP (0.5 ml) and water to obtain the total mixture volume of 25 ml were added into the flask. The light absorption value for the complex [Fe(BP)₃]²⁺ was measured at λ = 530 nm. The extraction degree value (*k*) was determined from the expression $k, \% = (C_0 - C)/C_0 \cdot 100$, where *C*₀ is the iron content in the solution before sorption (introduced), *C*, is that after sorption (found). The iron (II) concentrations in the solutions before and after sorption were established according to the photometric technique developed before, without extraction in water-acetone solutions by means of BP applied in the present research as a standard. The optimum pH value for this method is 2.5±0.3. Further, to determine iron by visual sorption test method with BP immobilized on PUF, the same pH interval was used.

Sorption under static conditions was realized by placing 1 to 5 ml of the KH₂PO₄ solution to be analyzed in a 25 ml flask and adding 1 ml of 0.5 M H₃PO₄, one PUF cube

and water to reach the required total volume of the mixture. The cube was pressed down by a glass stick to remove air bubbles, and the solution was agitated by a magnetic mixer for some time. Then the sorbent was taken out of the flask, pressed between sheets of filter paper and dried in air.

The procedure for measurement of diffuse reflectance spectrum is based on measuring the diffuse reflectance coefficient R at a certain wavelength and calculating the Kubelka-Munk function $F(R)$ using the formula $F = (1 - R)^2/2R = \beta/s = 2.3\epsilon \cdot c/s$, where β is the absorption coefficient; ϵ and c , the molar absorption coefficient and the sorbent concentration, respectively, s , the light scattering coefficient.

In this research, BP was chosen as a complexing substance for test determination of Fe (II, III) in the mother KH_2PO_4 solutions due to high light absorption with a maximum at 530 nm and a molar absorption coefficient of $2.2 \cdot 10^4 \text{ mol} \cdot \text{l}^{-1} \cdot \text{cm}^{-1}$ [12] characteristic of the formed $[\text{Fe}(\text{BP})_3]^{2+}$ complex. Moreover, the complex is known to have a rather high value of $\text{p}K = 21.8$ [13] which essentially exceeds the constants of phosphate iron complexes. This allows to use BP also for iron determination in phosphate media.

Prior to the investigation, we redefined the optimum conditions of the $[\text{Fe}(\text{BP})_3]^{2+}$ complex quantitative formation to determine iron in solutions with high contents of KH_2PO_4 . Increase of the solution ionic strength with KH_2PO_4 concentration within the interval from 0.02 to 0.15 g/ml was found to have no influence on light absorption of the analyzed solutions. As established in our investigations, in the presence of KH_2PO_4 with a concentration reaching 0.1 g/ml, the complex $[\text{Fe}(\text{BP})_3]^{2+}$ is formed during the first 2 or 3 minutes. Then the light absorption of the solutions remains practically unchanged for a long time (up to 30 min). The optical characteristics of the formed iron complex are also constant within the temperature interval from 20 to 60°C.

The influence of a number of factors on iron (II) determination using the developed method was studied. The degree of extraction (k) was chosen as a function of response describing the process of complex formation and the completeness of its sorption.

While developing the test method of iron determination on PUF sorbent, the sorption conditions of the iron-BP complex were preliminarily chosen. Presented in Fig. 1 are

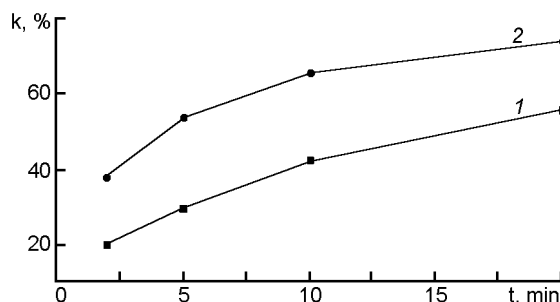


Fig. 1. Time dependence of the extraction degree (k , %) of $[\text{Fe}(\text{BP})_3]^{2+}$ complex in the static (1) and pumping (2) regimes: $m_{\text{PUF}} = 0.03 \text{ g}$, $C(\text{Fe}) = 0.4 \text{ } \mu\text{g/ml}$, $C(\text{KH}_2\text{PO}_4) = 0.1 \text{ M}$.

the extraction degree values for $[\text{Fe}(\text{BP})_3]^{2+}$ complex in static (1) and combined (2) regimes. The latter (further referred to as "pumping regime") is a combination of static and dynamic regimes with elements of forced circulation of the analyzed liquid under pressure through a layer of sorbent. As seen from Fig. 1. the pumping regime is characterized by more complete sorption and shorter time of its attainment. It is convenient to realize the pumping regime in 10 or 20 ml disposable syringes. In this case, after sorption and complete removal of the liquid from the syringe, PUF sorbent becomes almost dry and suitable for subsequent visual color testing.

However, even for the pumping regime, while increasing the concentration of iron ions in the solution up to 0.4 $\mu\text{g/ml}$ and higher, the extraction degree values gradually drop down to about 50 %. To improve the sorption characteristics of the complex, a search for anion partner for the formation of ionic associate was carried out. This was due to the fact that in the considered compounds characterized by a specific influence of the second-sphere particle on the properties of the first-sphere ion, the sorption properties of the system might change. As found while studying sorption of $[\text{Fe}(\text{BP})_3]^{2+}$ complex on PUF sorbent in the presence of some inorganic anions, the sorbent color becomes more intense as the anion radius increases in the $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{NO}_3^- < \text{BF}_4^- < \text{ClO}_4^-$ sequence. Although k values are higher for BF_4^- and ClO_4^- ions, in the presence of nitrate ion, the sorbent color is distributed more uniformly over the surface of PUF sorbent and can be better differentiated. This caused the choice of NO_3^- ion for our research. Shown in Fig. 2 is the dependence of the extraction degree on Fe(II) concentration in the presence/absence of NO_3^- .

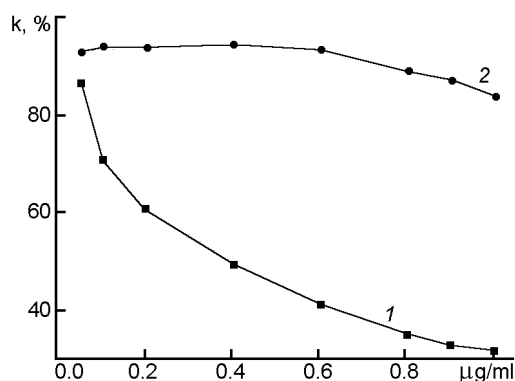


Fig. 2. Dependence of the extraction degree (k , %) of $[\text{Fe}(\text{BP})_3]^{2+}$ (1) and $[\text{Fe}(\text{BP})_3](\text{NO}_3^-)_2$ (2) complexes on iron (II) concentration in the pumping regime: $m_{\text{PUF}} = 0.03$ g, $\tau = 10$ min, $C(\text{KNO}_3) = 2 \cdot 10^{-3}$ M, $C(\text{KH}_2\text{PO}_4) = 0.1$ M.

Thus, the formation of the ionic associate $[\text{Fe}(\text{BP})_3](\text{NO}_3^-)_2$ was found to result in an essential improvement of the sorption properties in the investigated system. Further, all the experiments were conducted in the presence of KNO_3 in the solution ($(2$ to $5) \cdot 10^{-3}$ mol \cdot l $^{-1}$).

The diffuse reflection spectra of the ionic associate $[\text{Fe}(\text{BP})_3](\text{NO}_3^-)_2$ on the PUF sorbent show a sharp maximum at $\lambda = (530 \pm 5)$ nm coincident essentially with the absorption maximum for the complex in the solution. This fact shows that the nature of the coordination environment of iron (II) ions in the complex remains unchanged, and this may testify that the interaction with the polymer matrix of PUF sorbent is absent.

In the course of this research, the range of linear dependence between the Kubelka-Munk function $F(R)$ and the Fe(II) concentration in the solutions was established. As follows from Fig. 3, the linear dependence is observed up to 0.8 $\mu\text{g}/\text{ml}$ of iron (II) in the solution. For the model solutions with higher iron concentrations, the $F(R)$ function values do not change and form a plateau on the plot, which testifies to maximum saturation of the sorbent.

As to the time dependence of the of $[\text{Fe}(\text{BP})_3](\text{NO}_3^-)_2$ sorption completeness on PUF sorbent, it is seen from Fig. 4 that the complete extraction of IA from the solution where the initial content of iron (II) is up to 0.8 $\mu\text{g}/\text{ml}$, is observed since 6 to 7 minutes after the beginning of the procedure.

To estimate the detection limit for iron in the proposed test method, we used the

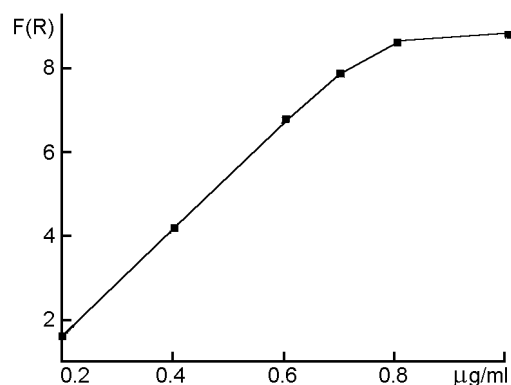


Fig. 3. Dependence of the diffuse reflection $F(R)$ of $[\text{Fe}(\text{BP})_3](\text{NO}_3^-)_2$ complex on the iron (II) concentration: $m_{\text{PUF}} = 0.03$ g, $\tau = 10$ min, $C(\text{KNO}_3) = 2 \cdot 10^{-3}$ M, $C(\text{KH}_2\text{PO}_4) = 0.1$ M, pH = 2.8, $\lambda = 525$ nm.

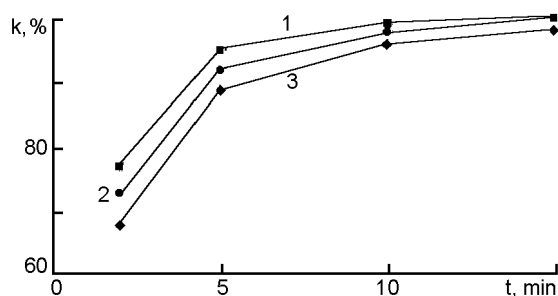


Fig. 4. Time dependence of the extraction degree (k , %) of $[\text{Fe}(\text{BP})_3](\text{NO}_3^-)_2$ complex on the concentration of iron (II) in the pumping regime: $m_{\text{PUF}} = 0.03$ g, $C_{\text{Fe(II)}} (\mu\text{g}/\text{ml})$: 0.2 (1), 0.6 (2), 0.8 (3), $C(\text{KNO}_3) = 2 \cdot 10^{-3}$ M, $C(\text{KH}_2\text{PO}_4) = 0.1$ M, pH = 2.8.

approach based on study of the so-called "unreliable reaction" region (in this region, low concentrations give approximately equal number of positive and negative detection results [14]). As found experimentally, for the considered method such a region corresponds to the interval of iron(II) concentrations from 0.004 up to 0.020 $\mu\text{g}/\text{ml}$.

It must be preliminarily established by independent observers using a color scale, which of the four types of distribution — normal, lognormal, exponential or Waybull distribution — allows to quantitatively estimate iron (II) content most satisfactorily. Presented in Table 1 are experimental rates of iron (II) detection in the mentioned concentration interval and some calculated auxiliary functions. Parameters of the linearized dependences of the experimental rates of C_{Fe} for the said distributions are contained in Table 2. For all the compared distributions, experimental points fall on

Table 1. Experimental rates of iron (II) detection limit and some calculated auxiliary functions for determination of distribution type

c_i	N_i	n_i	$\hat{P}(c_i)$	$-\ln c_i$	$\ln z_i$	$\ln \ln z_i$	$\Psi[\hat{P}(c_i)]$
0.004	168	37	0.2203	5.521	0.2488	-1.3511	-0.7722
0.008	"	67	0.3988	4.828	0.5088	-0.6756	-0.2559
0.012	"	95	0.5655	4.423	0.8335	-0.1821	0.1636
0.02	"	132	0.7857	3.912	1.5404	0.4320	0.7926
0.028	"	161	0.9583	3.576	3.1773	1.1560	1.7279
0.04	156	154	0.9872	3.219	4.3567	1.4717	2.2323

* c_i is the Fe concentration in the i -th experimental series; N_i , the number of observations; n_i , the number of detections; $P(c_i) = n_i/N_i$, the experimental frequency of detections; $\Psi[\hat{P}(c_i)]$, the function reciprocal to the Gauss function; $z_i = [1 - \hat{P}(c_i)]^{-1}$.

Table 2. Types of distribution for Fe(II)-PUF test-method

Distribution	x	y	s_y^2	r_{xy}
Normal	C_i	$\Psi[\hat{P}(c_i)]$	0.2077	0.9872
Lognormal	$\ln c_i$	$\Psi[\hat{P}(c)]$	0.2863	0.9755
Exponential	C_i	$\ln z_i$	0.2787	0.9884
Waybull	$\ln c_i$	$\ln \ln z_i$	0.1303	0.9943

the calculated straight lines of $y = a + bx$ type. Comparison of the estimated linear correlation coefficients r_{xy} as well as the dispersions s_y^2 for characterization of the scatter of the experimental points y_i with respect to the corresponding straight lines does not give reasons for choosing one preferable distribution type. Therefore, the detection limit was calculated assuming the normal distribution. To determine C_{min} , the formula $C_{min} = C_{0.5} + 2.5q$ was used (where $C_{0.5}$ is the average revealed concentration, i.e. the concentration detected with 0.5 probability and equal to 0.011 $\mu\text{g/ml}$; q , the probable deviation which characterizes the width of the "unreliably" revealed iron concentration region and equal to 0.008 $\mu\text{g/ml}$; 2.5 is the coefficient which provides 0.95 probability for detection of the concentration equal to C_{min}). Thus, the calculated value of detection limit for the described test method is $C_{min} = 0.03 \mu\text{g/ml}$ Fe (II, III).

The method was tested while analyzing mother solutions of potassium dihydrogen phosphate used for crystal growth. Test determinations of iron were carried out in 10 or 20 ml disposable syringes according to the following procedure. Using a syringe (without needle) containing one PUF cube with immobilized BP and several crystals of ascorbic acid and plugged by its plunger, collected were: 4–5 ml of the analyzed KH_2PO_4 solution preliminarily diluted with

water, 2 ml of KNO_3 $1 \cdot 10^{-2}$ M dissolved in 0.5 M solution of H_3PO_4 and water to obtain 10 ml volume of the mixture. Then the syringe with plugged cannula was being shaken for a certain time. After sorption, the liquid was squeezed out of the syringe under pressure through a sorbent layer. The iron concentration was determined visually, by comparing the sorbent color intensity with that preliminarily obtained for standard iron solutions using a computer-simulated color scale.

The results of the performed investigation were used as a base for visual test determination of the total iron (II, III) content in the mother solutions of potassium dihydrogen phosphate used for crystal growth. The metrological characteristics of the developed test method and its validity verification results in comparison with those of the photometric method of iron determination based on t -criterion are contained in Table 3. As seen from the presented results, the method described in the present paper has no systematic error, the relative standard deviation of the determination of 0.03 to 0.20 $\mu\text{g/ml}$ of Fe (II, III) are 0.36 and 0.21 ($n = 30$) and lies within the limits permissible for semi-quantitative test determination of such a type.

Table 3. Comparison of the KH_2PO_4 solution analysis results obtained by photometry and express methods

Sample No.	Found iron				$Z = C_T/C_{Ph}$
	Test method		Photometry method		
	$C \cdot 10^4$ %	N	$C \cdot 10^4$ %	N	
1	2.3±0.2	30	2.03±0.05	6	1.1
2	4.6±0.4	"-	4.05±0.07	"-	1.1
3	3.3±0.3	"-	2.87±0.05	"-	1.15
4	2.1±0.2	"-	2.53±0.05	"-	0.8
5	0.60±0.08	"-	0.69±0.04	"-	0.9
6	6.0±0.6	"-	5.10±0.06	"-	1.2
7	1.8±0.2	"-	2.30±0.05	"-	0.8
8	1.4±0.2	"-	1.62±0.04	"-	0.9
9	1.7±0.2	"-	1.98±0.05	"-	0.9
10	0.8±0.2	"-	0.77±0.04	"-	1.0

References

1. B.L.Timan, O.M.Smirnova, Yu.N.Velikhov et al., *Zh. Phys. Khim.*, **43**, 2092 (1989).
2. H.J.M.Bowen, *J. Chem. Soc.(A)*, **7-8**, 1082 (1970).
3. M.N.Abbas, A.Vertes, T.Braun, *Radiochem. Radianal. Lett.*, **54**, 17 (1982).
4. B.Nabivanec, V.Sukhan, E.Lusenko, V.Gorlach, in: *Abstr. Int. Congr. on Analyt. Chem. Moscow (1997)*, v.2, p.k-17.
5. S.G.Dmitrienko, O.A.Kosyreva, V.K.Runov, Yu.A.Zolotov, *Mendeleev Commun.*, No.1, 75 (1991).
6. V.G.Amelin, *Zh. Analyt. Khim.*, **55**, 917 (2000).
7. A.F.Alyukaeva, V.M.Ivanov, A.G.Tsytsarin, *Zh. Analyt. Khim.*, **57**, 1197 (2002).
8. S.G.Dmitrienko, L.N.Pyatkova, V.K.Runov, *Zh. Analyt. Khim.*, **51**, 600 (1996).
9. T.Kaneda, S.Takano, *Chem. Abstr.*, No.1289906c, **106** (1987).
10. Liu Xue-mei, Xing Wan Li, Ou Yuo-rong, Liangjun, *Anal. Sci.*, **16**, 473 (2000).
11. T.Braun, J.D.Navratil, A.B.Farag, *Polyurethane Foam Sorbents in Separation Science*, Boca Raton, CRC Press (1985).
12. A.Umland, A.Janssen, D.Thierig, G.Wunsch, *Theorie und Praktische Anwendung von Komplexbildnern*. Akadem. Verlagsgesel, Frankfurt am Main, (1971).
13. L.G.Sillen, A.E.Martell, *Stability Constants of Metal-Ion Complexes. Spec. Publ., No.17*, The Chem. Soc., Burlington House, W1V OBN London, (1964), p.727.
14. R.P.Pantaler, A.K.Timchenko, L.I.Avrachenko, A.B.Blank, *Zh. Analyt. Khim.*, **52**, 384 (1997).

Швидке визначення мікродомішок заліза візуальним тест-методом у технологічних розчинах для вирощування монокристалів KH_2PO_4

Т.І.Івкова, Р.П.Панталер, А.Б.Бланк, О.А.Решетняк, Ю.Є.Ваховська

Вивчено умови експресного визначення мікродомішок заліза з 4,7-дифеніл 1,10-фенантроліном (батифенантроліном) у вигляді іонного асоціату (ІА) з NO_3^- -іонами. Запропоновано пресінгговий спосіб вилучення ІА з розчину пінополіуретановим сорбентом. Статистично розрахована нижня межа визначення Fe (II,III) у області "ненадійної реакції" дорівнює 0.03 мкг/мл, відносно стандартне відхилення при визначенні від 0.03 до 0.2 мкг/мл дорівнює 0.36–0.21 ($n = 10$), відповідно, час визначення не перевищує 10 хвилин. Запропонований тест було застосовано для визначення сумарного вмісту Fe (II,III) на рівні $5 \cdot 10^{-5}$ % у технологічних розчинах для ви вирощування монокристалів KH_2PO_4 .