

# DEVELOPMENT OF METHODS FOR THE DETERMINATION OF BENZIMIDAZOLONE SUBSTANCES IN THE COMPOSITION OF FERTILIZERS

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## Abstract

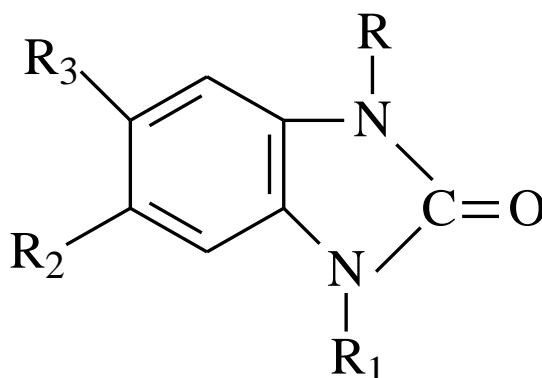
The article presents the results of the development of methods for the spectrophotometric and gas chromatographic determination of the physiologically active substances introduced into the fertilizers - benzimidazolones.

**Keywords:** physiologically active substances, UV spectra, carbamide, maximum, absorption curves, bathochromic shift, ammonium phosphate, mixing, humidity, composition, temperature, solubility, concentration, chromatographic peak, correction factor, katharometer.

## Introduction

Of the numerous structural analogs of biotin, benzimidazolones stand out for their high physiological activity. Benzimidazolone and its derivatives are of great interest both from the point of view of practical application and in theoretical terms. Individual derivatives of benzimidazolone have fungicidal [1-3], herbicidal [91], and growth properties [4-6].

Fungicides are low toxic and are substances that can penetrate the plant and move along its conducting system. The antivitamin and fungitoxic activity of a number of benzimidazolone derivatives with the general formula:



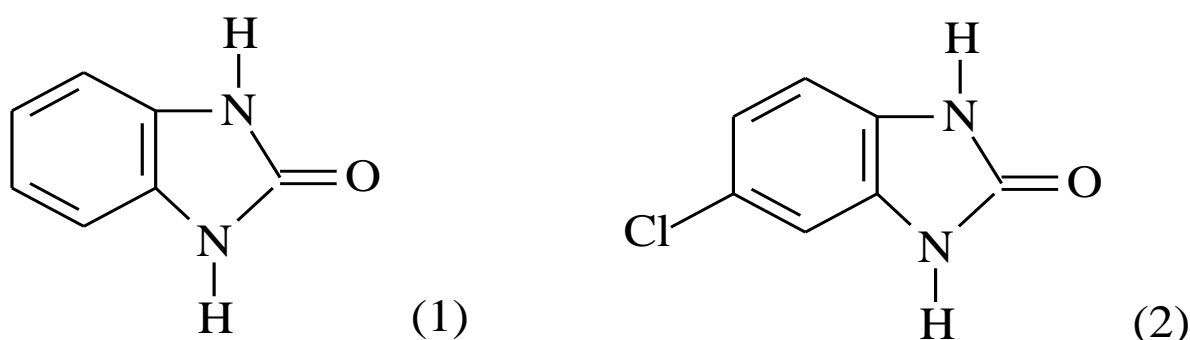
To develop technical specifications and put products into production, reliable methods for monitoring and determining the content of the studied PAS in the composition of the finished product are necessary.

We have studied the possibility and developed procedures for the determination of FAS in carbamide and ammophos by the spectrophotometric method of additives [7]. To develop technical specifications and put products into production, reliable methods for monitoring and determining the content of the studied PAS in the composition of the finished product are necessary. We have studied the possibility and developed procedures for the determination of FAS in carbamide and ammophos by the spectrophotometric method of additives.

The authors of [8, 9] made a comparative study of some physicochemical properties of benzimidazolone derivatives, herbicidal activity and, on this basis, revealed the relationship between activity and structure, and made the same conclusion as in [9] that the correlation between structure and activity in the series of benzimidazolones, it should be associated with the properties of atoms of the hetero ring or at two points - at carbonyl and nitrogen atoms.

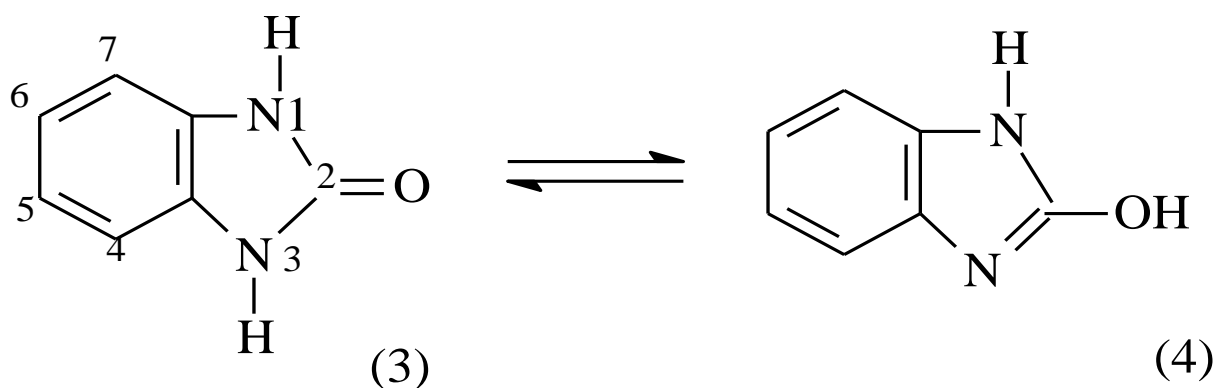
The study of the herbicidal activity of 6-acylbenzimidazolin-2-ones [10] showed that isomers with a normal acyl chain are more active than isomers with a branched part of the acyl.

The structural formulas of benzimidazolin-2-one (1) and 5-chlorobenzimidazolin-2-one (2) are as follows:



Molecular weight (1) is 134, and (2) - 168.5, odorless substance. After recrystallization from alcohol with activated carbon, light brown brilliant crystals are obtained. Poorly soluble in benzene, chloroform, hot water, soluble in alcohol, acetone, and acids.

Benzimidazolone can exist, in two forms: orthophenyleneurea (3) and 2-hydroxybenzimidazole (4):



## Methods

The essence of the visual-polythermal method. To study the solubility of phases in water-salt systems, a visual-polythermal method of analysis was used, developed by A.G. Bergman [11-13]. The essence of the visual-polythermal method is to determine the crystallization temperature by visual observation of the temperature of the appearance of the first crystals, which are released during slow cooling and vigorous stirring of the solution, and the temperature of the disappearance of the last crystals upon heating, after which a composition-temperature diagram is plotted crystallization.

The main advantage of the visual-polythermal method is simplicity, speed, wide temperature range of research, versatility of the method, which makes it possible to investigate aqueous, anhydrous, saline, oxide, organic metal, etc., the possibility of visual fixation of the separation phenomenon in the system and evaluating the nature of the crystallizing phase, sufficient accuracy. This method makes it easier to detect unstable and metastable equilibria, which are excluded in the isothermal method. To study technological processes in industry, it is necessary to know the solubility of system components in a wide and concentration range.

Along with the listed positive aspects, this method has its drawbacks. The most significant of them is the impossibility of studying this phase, the difficulty when working with opaque solutions, the possibility of obtaining inaccurate data when studying systems prone to overcooling and in which equilibrium is established for a long time, the subjectivity of obtaining data by the researcher, insufficient knowledge of the methodology of this method. Despite these shortcomings, the visual-polythermal method has been widely used in applied and scientific research. The solubility diagram of the system was studied using internal polythermal cuts. Based on the data obtained for the sections and for binary systems, a complete polytherm of solubility of ternary systems was built in the form of a right-angled triangle using the Rosebom method. Solution concentrations were expressed in mass percent. In order to refine the nodal points and the steepness of the crystallization surface, projections of the polytherm onto the lateral sides of the system were constructed [14]. All projections of the polytherm on the sides are given in Appendix 1, Fig. 1.

## Method of chemical analysis

When performing research, recrystallized salts of the "analytical grade" grade were used. and "h.h." and laboratory-synthesized BION, 5-HBION, IVIN, TPN [15-17].

Analyzes were carried out according to known methods for the content of phosphorus [18], nitrogen according to the Kjeldahl method [19-21], water according to the Fischer method [22].

The content of biuret in the melt of carbamide with FAS was analyzed according to the known method [23].

Method of physical and chemical analysis. The data of physicochemical studies of C<sub>7</sub>H<sub>9</sub>NO, C<sub>7</sub>H<sub>11</sub>NO, C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>OCl are not available in the literature. The identification of the latter was carried out using modern methods of physical and chemical analysis. Research is necessary in order to further evaluate the possibility of using these characteristics when creating complex fertilizers based on urea and ammophos.

IR spectra were recorded on a spectrophotometer VR - 20 in the frequency range 400-4000 cm<sup>-1</sup>. Samples were prepared in vaseline oil and also in the form of tablets with KBr. Mass spectra were recorded on an MX-1303 spectrometer; UV spectra were recorded on a Hitachi-EPS-3T spectrometer (solvent, ethanol) and on an SF-4A spectrometer (solvent, methanol).

Thermogravimetric analysis was carried out on a MOM-Budapest (Hungary) [24, 25] derivatograph at a heating rate of 12 K/min at a maximum temperature of 600°C. We used platinum-platinum-rhodium thermocouples isolated from substances. The analysis was carried out in platinum crucibles with a lid. The sensitivity of the galvanometer was DTA - 1/10, DTG -1/15, sample - 0.15 g, standard - calcined aluminum oxide.

X-ray patterns of the studied compounds were taken on a DRON-2.0 diffractometer with a Cu anticathode.

or the purpose of quantitative determination of IVIN, BIONa, 5-ChBION in the composition of urea and ammophos, methods have been developed for monitoring PAS in the composition of the latter by the spectrophotometric method of additives [26].

The essence of the method lies in the fact that the optical densities of the standard solution of FAS (A<sub>st</sub>) and the studied solution of the composition (A<sub>x</sub>) are determined. Taking into account the dilutions of the studied solutions and weighing of the studied samples of the compositions according to the well-known formula:

$$C_x = (C_{ct} * A_x) / A_{ct}$$

We find the percentage of FAS in the compositions, where:  $C_x$  - the desired concentration of PAS, mg / ml,  $A_x$  - optical density of the investigated solution of the composition,  $C_{ct}$  - concentration of standard solution of FAS, mg/ml,  $A_{ct}$  - optical density of the standard solution of PAS.

Mathematical analysis of the research results was carried out according to [27]. A technique has been developed for determining TPN in the composition of TPN-containing carbamide and ammophos, the method is based on gas chromatographic separation of mixture components in a column filled with a sorbent, followed by their registration with a flame ionization detector (FID) or a thermal conductivity detector (katharometer).

Quantitative calculation of the mass fractions of the components is carried out by the method of internal standardization. Benzonitrile (BN) is used as an internal standard.

The density was determined by the cyclometric method [28, 29]. The thoroughly washed and dried pycnometer was weighed on an analytical balance and filled with the test solution or melt using a funnel. Then the pycnometer was placed in a thermostat and kept in it for 15-20 minutes. After this time, the pycnometer was removed from the thermostat and weighed. A 10 ml pycnometer was used.

The viscosities of solutions and melts were studied by the capillary method using a viscometer with an internal capillary diameter of 0.99 mm and 1.12 mm [30].

The main commercial and physical-mechanical properties of complex fertilizers were determined: hygroscopicity, moisture capacity, granule strength, caking, initial moisture capacity according to known methods [31].

The hygroscopicity of fertilizers was determined by the eicoicator method at 25°C. The hygroscopic point was calculated according to the equations:

$$Q = \frac{a * 180 * 100}{B S}$$

where:  $Q$  - is the amount of moisture absorbed by a unit of surface per unit of time,

$a$  - moisture gain,  $B$  - absorption time, in min,  $S$  - is the area of the upper base of the bottle, cm<sup>2</sup>.

$$h = \frac{Q_2 h_1 - Q_1 h_2}{Q_2 - Q_1}$$

where:  $h$  - is the hygroscopic point of the product,  $h_1$  and  $h_2$  - relative air humidity (in %) in each desiccator,  $Q_1$  and  $Q_2$  - moisture gain corresponding to relative air humidity in desiccators in g per 100 cm<sup>2</sup> for 3 hours.

The sorption moisture capacity of fertilizers was determined by us at the average and maximum relative humidity of the air in Central Asia, i.e. at 60 and 80% by daily recording of moisture gain. The caking was determined using a device for pressing samples.

## Results and discussion

The UV spectra of IVIN and urea were studied (Fig. 6.15). It can be seen from the figure that at  $\lambda = 260$  nm, the effect of urea on the absorption band of IVIN is practically absent, and therefore this band was chosen as a characteristic one for the quantitative determination of IBIN in IVIN containing urea.

Under laboratory conditions, figurative fertilizers were obtained by evaporation at 100°C of carbamide solutions containing various quantity of IVIN. The study of polythermal systems and spectrophotometric analysis showed that IVIN does not undergo physical and chemical changes.

The content of IVIP in the samples was on the same level with similar "dry compositions". When fusion of carbamide and IVIN for 10-15 minutes at a temperature 135°C and re-weighing followed by cooling in the analysis of it was found that IVIN did not undergo changes in the selected range of parameter variation, and, therefore, retains all the properties of a physiologically active compound (Fig. 1-2, Table 1).

The content of IVIN in IVIN-containing carbamide is determined with an accuracy of 0.003%.

Fig. 1. UV spectra: 1-Urea, 2-  $C_7H_9NO$

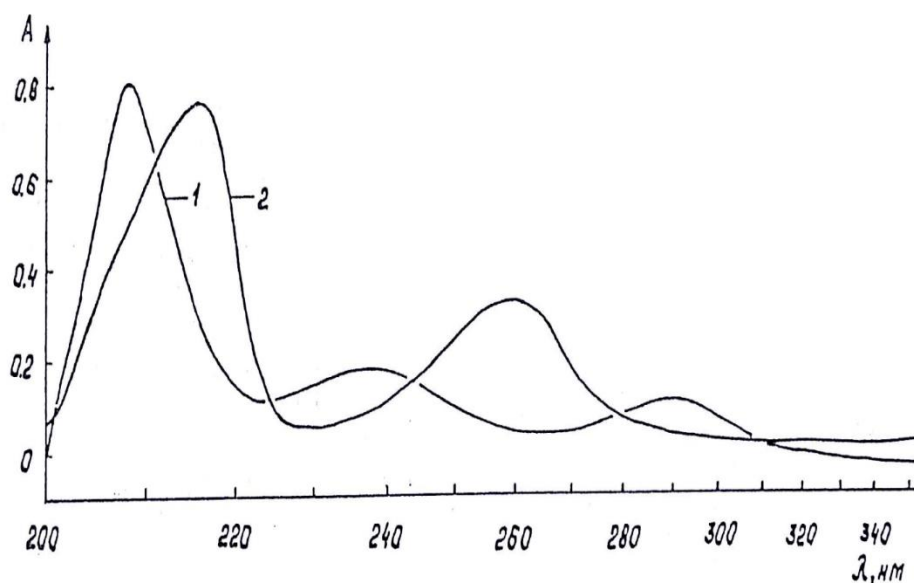


Fig. 2. UV spectra: 1-Ammophos, 2-  $C_7H_9NO$

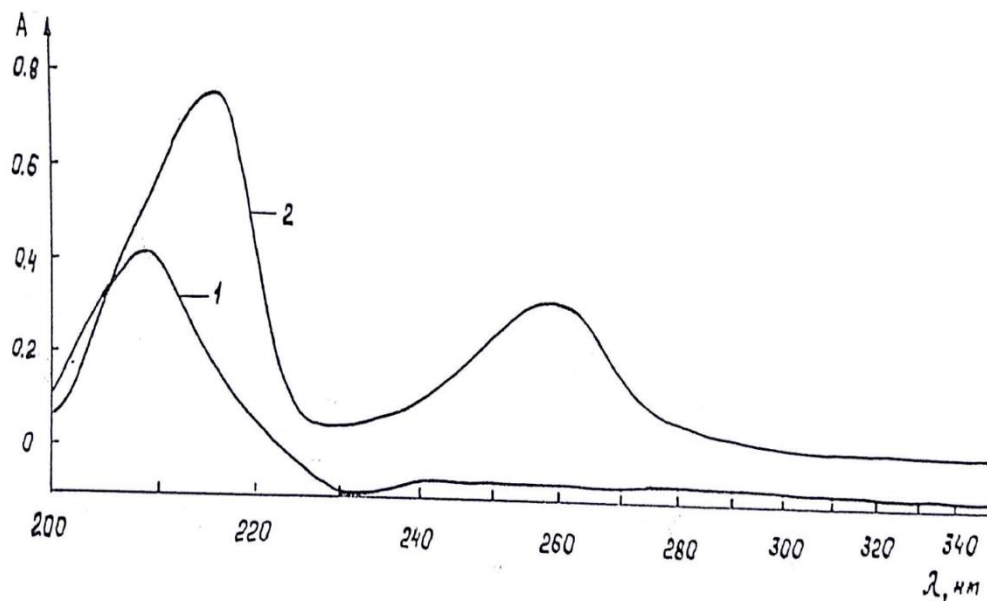


Table 1 Statistical processing of the results of the analysis of IVIN and IVIN-containing urea

№	Taken,%	Found,%	$\Delta X$	$\Delta X_i - \Delta X^+$	$(\Delta X_i - \Delta X^+)^2$	S	$S_x$	$\xi, \%$
1	0.050	0.049	0.001	-0.0054	$2.916 \cdot 10^{-5}$	$4.64 \cdot 10^{-3}$	$1.4 \cdot 10^{-5}$	0.003
2	0.070	0.071	0.001	-0.0054	$2.916 \cdot 10^{-5}$			
3	0.100	0.105	0.005	-0.0014	$0.20 \cdot 10^{-5}$			
4	0.300	0.298	0.002	-0.0044	$1.94 \cdot 10^{-5}$			
5	0.500	0.503	0.003	-0.0034	$1.16 \cdot 10^{-5}$			
6	0.700	0.702	0.002	-0.0044	$1.94 \cdot 10^{-5}$			
7	1.0	0.989	0.011	0.0046	$2.12 \cdot 10^{-5}$			
8	2.0	2.013	0.013	0.0066	$4.36 \cdot 10^{-5}$			
9	3.0	2.988	0.012	0.0056	$3.14 \cdot 10^{-5}$			
10	4.0	3.989	0.011	0.0046	$2.12 \cdot 10^{-5}$			
11	5.0	5.009	0.009	0.0026	$0.68 \cdot 10^{-5}$			

Due to the fact that BION and 5-HBION are insoluble in aqueous solutions of carbamide, therefore they are introduced only into the hot melt of carbamide, which has a temperature of 135°C, we have developed methods for monitoring PAS in urea.

We studied the UV spectra of urea, BION (1), and 5-ChBION (2). Spectra (1) and (2) are characterized by the corresponding three maxima. An analysis of the absorption curves clearly records the bathochromic shift of all three bands (1) compared to (1), which is explained by the presence of the substituent cl and position "5" of compound (2). Content (1) has the following absorption bands:  $\lambda=206\text{nm}$  ( $\log \xi=3.57$ ),  $\lambda=225\text{nm}$  ( $\log \xi=2.08$ ) and  $\lambda=280\text{nm}$  ( $\log \xi=1.89$ ), while (2):  $\lambda=208\text{ nm}$  ( $\log \xi=2.43$ ),  $\lambda=227\text{nm}$  ( $\log \xi=1.83$ ) and  $\lambda=288\text{nm}$  ( $\log \xi=1.68$ ). The most optimal for spectrophotometric determination of (1) and (2) in the composition of carbamide is for (1)  $\lambda=280\text{ nm}$  (Fig. 3, Table 2) and for (2)  $\lambda=288\text{ nm}$  (Fig. 4, Table 3), where the effect of urea uptake is minimal.

Thus, the content (1) and (2) in the composition "urea-1" and "carbamide-2" is determined with an accuracy of 0.0061 and 0.026%, respectively.

To develop methods for monitoring IVIN, BION, 5-HBION in the composition of PAS-containing ammophos, UV spectra of PAS and ammophos were also taken (Fig. 5-6). The characteristic absorption bands for the quantitative determination of IVIN were  $\lambda=260\text{ nm}$ , for BION -  $\lambda=280\text{ nm}$ , for 5-HBION -  $\lambda=227\text{ nm}$ .

The developed methods for the determination of the above PAS are suitable in the case of analyzed compositions containing IVIN, BION, 5 HBION, of various concentrations.

Techniques for the gas chromatographic determination of the ESRD drug (tetranil) in compositions with urea and ammophos have been developed. The method is based on gas chromatographic separation of mixture components in a column filled with a sorbent followed by their registration by a flame ionization detector (FID) or a thermal conductivity detector (katharometer).

Fig. 3. UV-spectra: 1-Urea; 2-C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O

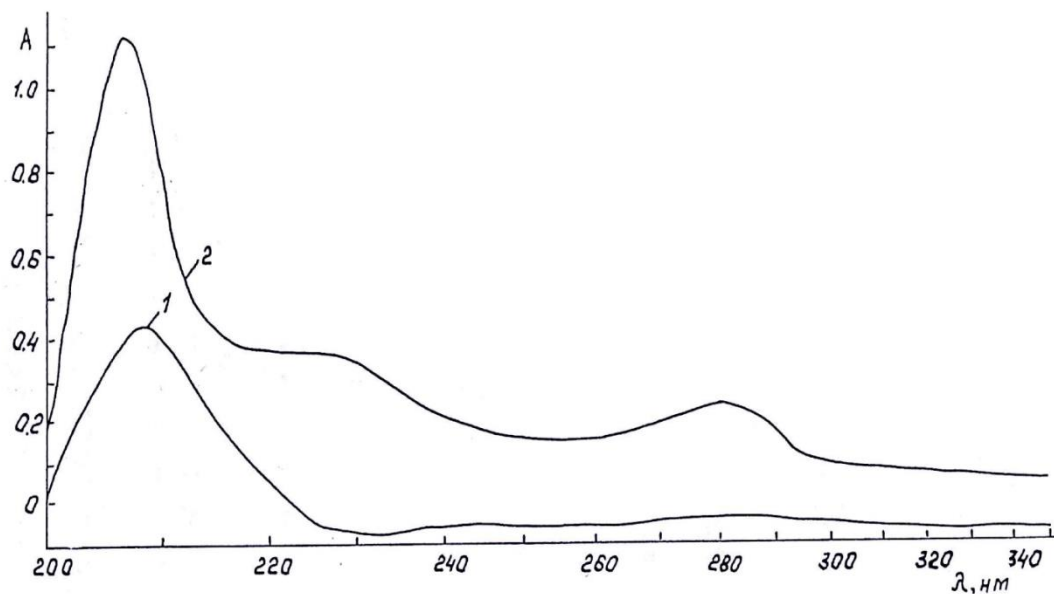


Fig. 4. UV-spectra: 1-Urea; 2-C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>OCl

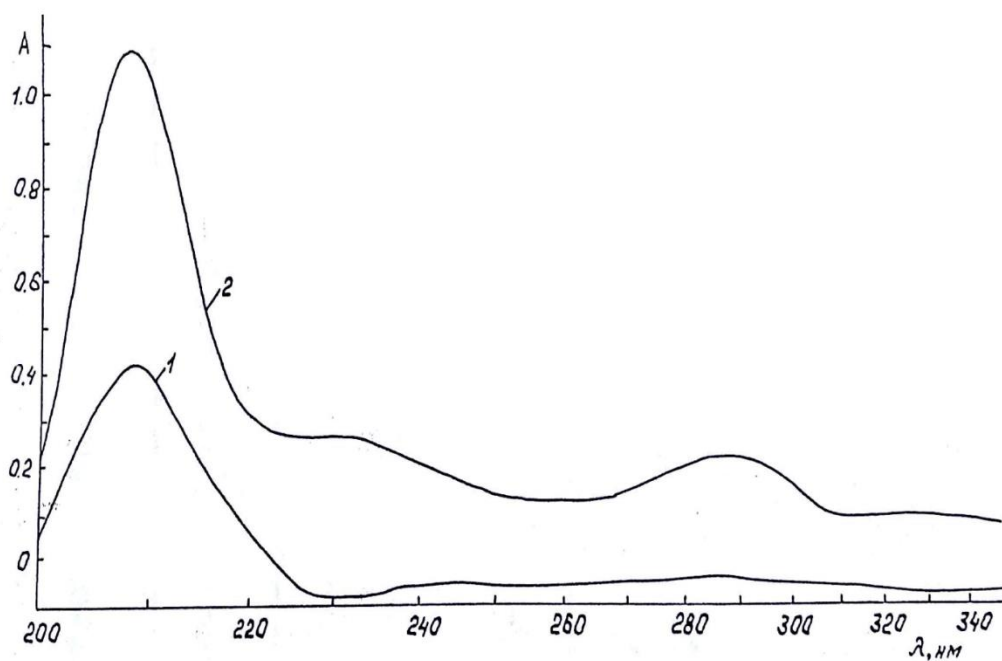


Table 2 Statistical processing of the results of the analysis of BION and BION-containing urea

№	Taken, %	Found, %	$\Delta X$	$\Delta X_i - \Delta X^+$	$(\Delta X_i - \Delta X^+)^2$	S	S <sub>x</sub>	$\xi, \%$
1	0.010	0.013	0.003	-0.005	0.000025	0.0065	0.0025	0.0061
2	0.030	0.028	0.002	-0.006	0.000036			
3	0.050	0.048	0.002	-0.006	0.000036			
4	0.10	0.083	0.017	0.009	0.000081			

5	0.30	0.314	0.014	0.006	0.000036			
6	1.0	1.076	0.0014	0.006	0.000036			
7	2.0	2.010	0.010	0.002	0.000004			

Table 3 Statistical processing of the results of the analysis of 5-ChBION and 5-ChBION-containing urea

№	Taken,%	Found,%	$\Delta X$	$\Delta X_i - \Delta X^+$	$(\Delta X_i - \Delta X^+)^2$	S	$S_x$	$\xi, \%$
1	0.010	0.013	0.003	-0.0055	0.003025	0.072	0.026	0.026
2	0.030	0.032	0.002	-0.0060	0.003600			
3	0.050	0.056	0.006	-0.0025	0.000625			
4	0.10	0.099	0.001	0.0075	0.005625			
5	0.30	0.314	0.014	0.0055	0.003025			
6	0.50	0.515	0.015	0.0065	0.004225			
7	1.0	1.018	0.018	0.0950	0.009025			
8	2.0	1.983	0.017	0.0085	0.007225			

Fig. 5. UV-spectra: 1-Ammophos, 2-C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O

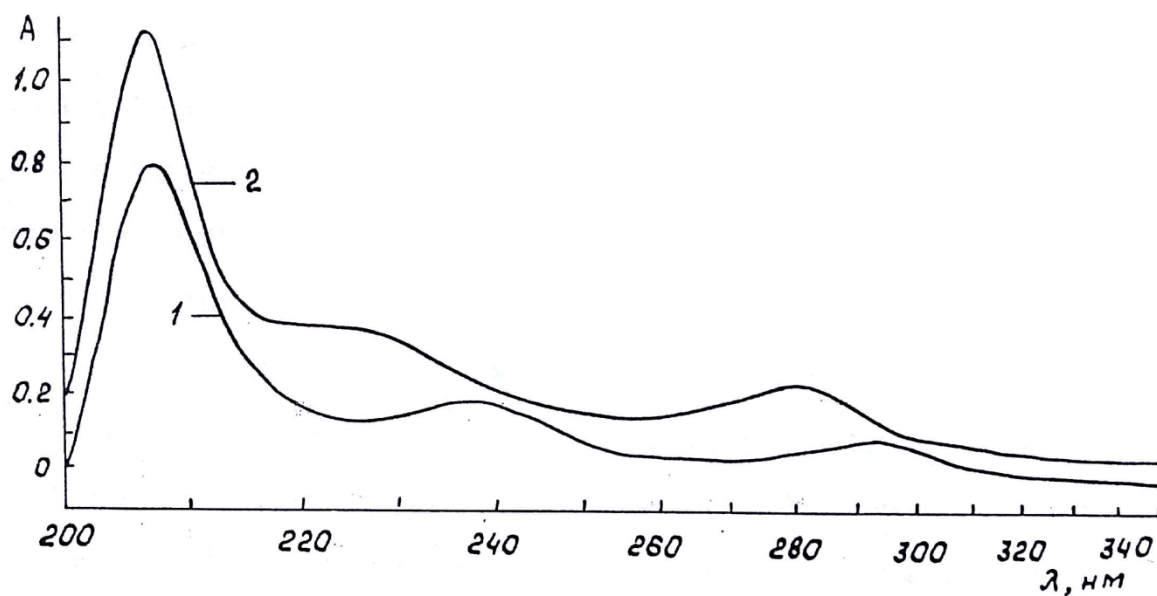
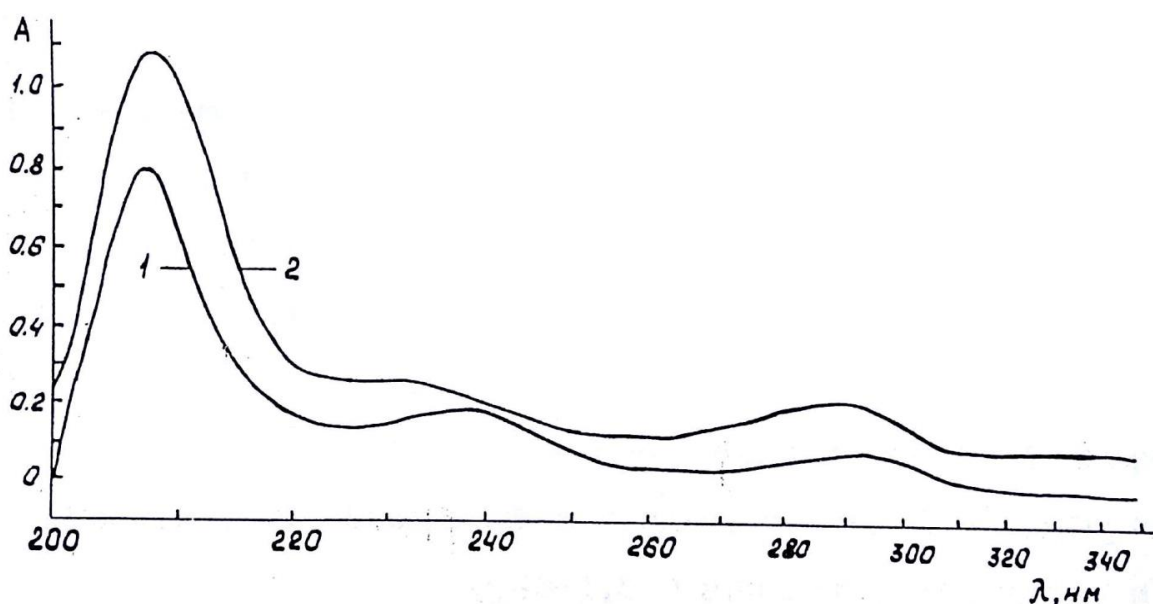


Fig. 6. UV-spectra: 1- Ammophos, 2-  $C_7H_5N_2OCl$



Determination of the calibration (perfect) coefficient for WBC (tetranyl) relative to benzonitrile (BN).

To determine the correction factor, artificial mixtures are prepared, consisting of pure components (WBC and BN) in various ratios to each other. Weighing is carried out with an accuracy of up to 0.0002 g. Mixtures are prepared in flasks with ground stoppers with a capacity of 5 cm<sup>3</sup> and diluted with a solvent (acetone, DMF) for better mixing. Store in the refrigerator for no more than 5 days. Chromatograph each artificial mixture at least 5 times. The correction factor is calculated by the formula (1)

$$K_{TPN} = (R_{TPN} \cdot BN) / (R_{BN} \cdot TVN) \quad (1)$$

Where:  $R_{TPN}$ ,  $R_{BN}$  - hitches of TVN and BN (in g),  $TPN$ ,  $BN$  - areas of chromatographic peaks, respectively,  $TPN$  and  $BN$ , in mm<sup>2</sup>.

Calculate the average value of the correction factor for WBC in each artificial mixture. Determination of the content of TPN in the mixed composition (in carbamide and ammophos), %. Weigh in a conical flask with a ground stopper with a capacity of 5 cm<sup>3</sup> 0.15-1.5 g of the analyzed mixture with an accuracy of 0.0002 g. Add a sample of the internal standard - (0.01 - 0.1 g) of benzonitrile. The mixture is dissolved in the minimum amount of solvent (DMF) and injected into the chromatograph several times.

The determination is carried out on at least two samples for each sample. In case of discrepancy in the result, another sample is taken.

The calculation of the content of TPN in the analyzed mixture is carried out according to the formula (2)

$$S_{TPN}\% = (K_{TPN} \cdot S_{TPN} \cdot P_{BN} \cdot 100) / (S_{BN} \cdot m)$$

where:  $K_{TPN}$  - correction factor for WBC for benzonitrile (BN),  $S_{TPN}$ ,  $S_{BN}$  - areas of chromatographic peaks of TPN and BN (mm<sup>2</sup>),  $P_{BN}$  - sample of benzonitrile (g),  $m$  - weight of sample of the analyzed mixture (g).

To develop the technique, we obtained compositions of urea and ammophos with different contents of WBC from 0-13%. TPN was introduced into the hot melt of urea, having a temperature of 135°C. At certain intervals (0, 15, 30, 60 minutes), samples were taken and analyzed for the content of ESRD. To obtain TPN-containing ammophos, TPN was introduced into ammophos pulp neutralized with ammonia, since its decomposition is possible when mixing TPN with phosphoric acid.

## Conclusions

Thus, the studies carried out show that the organization of large-scale production of urea and ammophos containing IVIN, BION, 5-HBION, TPN does not present any particular difficulties. It should be emphasized that the latter are available physiologically active substances. Methods have been developed for the spectrophotometric determination of BIONa, 5-ChBION, IVIN and the gas chromatographic determination of TPN in the composition of the obtained fertilizers.

## References

1. Фунгициды /отв. ред. Н.Н.Мельников. –Ташкент.Фан, 1980. -156 с.
2. Халиков С.С. Синтез потенциальных пестицидов в ряду С – и N-алкил(амил) – бензимидазолин-2-она и его иролзподных. Автореф. дис. .. канд.хим. наук. -Ташкент, 1984, - 23 с.
3. Эркаев А.У., Турсунова И.Н., Мардонов У.М. Применение расчетно-графических и спектрофотометрических методов для исследования системы “NO<sub>2</sub>-H<sub>2</sub>O-X”// Химия и химич. технол. науч-техн. жур.- 2009. - №2.- С. 6-8.
4. Мардонов, И.Н. Турсунова, Р.М. Шукуруллаева, Т.И. Нурмуродов, Н.О. Юнязева, Ш. Ходжаева. Исследование процессов растворения карбоната и фосфата кальция под действием диоксида азота.// Сборник научных статей. межд. науч. конф. «Инновация». Ташкент. - 2004. – С. 56-59.
5. Нурмуродов Т.И., Турсунова И.Н., Мардонов У.М., Шукуруллаева Р.М., Эркаев А.У., Раимжонов Б.Р. Использование диоксида азота в переработке фосфоритов Центрального Кызылкума. // Сборник трудов международной науч.-техн. конф. «Ресурсовоспроизводящие, малоотходные и природоохранные технологии освоения недр». - Москва-Бишкек.- 2004.- С.158-160.
6. Турсунова И.Н., Шукурбекова З.Ф., Журабекова Г.К., Мардонов У.М. Изучение растворения нитрозных газов системе “NO<sub>2</sub>–H<sub>2</sub>O”// Труды межд. конф. молодых ученых “Перспективы развития фундаментальных наук”. - Томск. - 20-23 мая, 2008. - С.208-210.
7. Крешков А.И. Основы аналитической химии. –М:Химия, 1975, -Т. 2. -С 306.
8. Химия и пестицидная активность некоторых замещенных бензимидазолин-2-онов/Акбарова М., Аюпова А.Т., Халиков С.С, Молчанов Л.В., Кадыров Ч.Ш.- Фергана: Ферганский политехнические институт, 1985. - 31 с.
9. Кадыров Ч.Ш. Химия и пестицидная активность бензимидазолов//Регуляторы роста растений и гербициды. –Ташкент.Фан. 1978. –С.65-123.
10. Андрей Георгиевич Бергман. Некролог /Ленешков И.Н, Проценко Н.И., Ильясов И.Н., и др. // Журн. неорган. химии. - 1974. -Т. 19. -№6. -С.1684-1687.
11. VI Всесоюзный Менделеевский съезд по теоретической и прикладной химии (25 октября – 1 ноября 1932 г.) //Тез. докл. - Харьков, 1932. -Т.2. -Вып.1. -С.631-637.
12. Трунин А.С, Петрова Д.Г. Визуально-политермический метод. -Куйбышев: Куйбышевский политехнический институт, 1977. -94 с.-Рук. Деп. В ВИНТИ 6 февраля, 1978. №584-78.
13. Кельман Ф.Н., Бруцкас Е.Б., Ошеревич Р.Х. Методы анализа при контроле производства серной кислоты и фосфорных удобрений.-М.:Госхимиздат, 1963. - 351 с.
14. Clark R.L., Resselano A.A// J Am Chem Soc.-1958. -V. 80. -p. 1657.
15. Симонов А.М., Подарский Л.С. //Журн. орг. химия, -IX3. -Т. 3о. -8, 380.
16. Ельцов А.В., Кузнецов В.С., Колесова М.Б. //Журн. орг. химии. -1965. - Т.1.-№6. -С. 1117.
17. Dovoll J//J Chem.Soc.-1960.-С.308.
18. Dovoll J., Loney D.H.// J Chem.Soc.-1960.-С.314
19. Руководство по анализу и производству фосфора, фосфорной кислоты и удобрений /Под ред. И.Б.Мойжеса. – Л.:ЛенМИИГИПРОХИМ. Химия, 1973,-216 с.
20. Мидерль Д., Нидель В. Микрометоды количественного органического анализа. –М.:Госхимиздат, 1949. -С.73-94.
21. ГОСТ 24614-81. Кулонометрический метод определения воды. М.:Изд-во стандартов, 1981.

22. ГОСТ 2081-75. Карбамид. Изд. официальное. М. :Изд-во стандартов, 1975. и 1981.
23. Практическое руководство по термографии /Л.Г.Берг, Н.И.Бурмистрова, М.И. Озерова, Г.Г.Пуринов. –Казань: Казан. ун-т, 1976. -222 с.
24. Берг Л.Г. Введение в термографию.- М.:Наука, 1969. - 395 с.
25. Булатов М.И., Калинин И.П. Практическое руководство по фотометрическим методам анализа. -Л.:Химия, 1986. -С. 178.
26. Аносов В.Я., Озерова М.И., Фиалков Ю.А. Основы физико-химического анализа. -М.-Л.:АН СССР, 1947. -876 с.
27. Физические метода органической химии /Под ред. Л.Байсберга.-М.:ИЛ,1950.-Т.1.-582 с.
28. Кульман А.Г. Физическая и коллоидная химия. 3-е изд.–М.:Пищепромиздат, 1963. -504с.
29. Позин М.Е., Копылев Б.А., Тумаркина Е.С., БельченкоГ.В. Руководство к практическим занятиям по технологии неорганических веществ. /2-е изд. перер. и доп. -Л.:Госхимиздат, 1968. -С.93 (376 с).
30. Пестов Н.Е. Физико-химические свойства зернистых и порошкообразных и химических продуктов. –М.-Л.:АН СССР. 1947. - 238 с.
31. Кучерявый В.И., Лебедев В.В. Синтез и применение карбамида.-Л. .Химия, 1970. -448 с.