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Study and development of a means of colorimetric control of the properties of materials and products

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Abstract

The solution to the scientific and practical problem of developing and studying the operation of an electronic digital colorimeter is considered. The study was not only to determine the percentage composition of the base colour in the controlled object for further unambiguous identification of it with another control object, which is studied using an electronic digital colorimeter, but also to check its metrological reliability. The functional scheme of the developed digital colorimetric sensor for measuring the colour properties of materials and products is presented, the principle of operation of which is also provided. Experimental data were obtained for three measurement channels of the digital colorimetric sensor, namely: the channel of red, green, and blue photodiodes. A statistical analysis of the series of observation results was carried out, which allowed establishing the levels of unbiased estimates of dispersions for three measurement channels. The change in the percentage of the base colour of the sample across the measurement channels is associated with a change in the characteristics of the surface being controlled (the presence of damage, contamination, etc.). Graphic images of the determination of the level of blue colour across control areas in three samples are obtained. Calculations of the uncertainty budget for three measurement channels of an electronic digital colorimeter are presented.

The results obtained allow further improvement of methods and means of control of the metrological reliability of means of colorimetric control by using statistical methods of analysis of the measurement results obtained using them. The use of a fuzzy logic apparatus for identifying objects of colorimetric control among themselves is promising.

Keywords: colorimetry; digital sensor; statistical analysis; variance analysis; measurement uncertainty; error.

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Introduction

Colorimetry, as a branch of optics, is aimed at the quantitative study of colour perception and hence it is an indispensable tool for the detection of chemical compounds, organic pollutants, heavy metal ions and biomolecules for biological study, medical tests on blood composition and diagnostics of any skin disease. Colorimetry, physics, chemistry, and biology are inextricably linked, and hence it provides an understanding of such phenomena as structural colour, pigment composition, and others.

One of the most common measuring instruments of colour properties is an electronic digital colorimeter (EDC). It offers several advantages, namely: express colour control, ease of use, sufficiently high measurement accuracy and economic feasibility. The capabilities of the EDC significantly exceed the capabilities of other similar instruments.

The issues of colorimetric control are associated with the need to constantly increase the sensitivity, reproducibility, and reliability of the results obtained. The interest of the world scientific community in solving the problems is confirmed by numerous publications [1–8] in leading world scientific editions.

Thus, further improvement of the capabilities of the EDC and study of the features of its use are relevant and promising tasks for both developers of such devices and scientists.

Analysis of recent studies and publications

Colorimetric sensors (CSs) used in electronic colorimeters have hold appeal for scientists in terms

of various applications due to the possibility of rapid analysis, ease of use, cost-effectiveness, and even the possibility to observe the results of the control with the naked eye. The collection of scientific papers [1] presents the results of studies on CSs for the detection of small molecules, including cations, anions, neutral particles, and important cellular components associated with living human systems, in solutions and biological samples, as well as for therapeutic and diagnostic purposes. The paper [1] also discusses the principles, mechanisms, and methods of manufacturing CSs, their corresponding applications in various industries, the principles and mechanisms of colorimetric sensing, nanomaterials for colorimetric biosensors for biomedical applications, paper CSs, CSs for cations, anions, and biomolecules. In [2], information is presented on modern innovative methodologies for the development and production of food CSs, such as electrospun nanofibers, electrochemical sheet, inkjet printing, sol-gel technologies, and paper-based CSs. In addition, recent advances in the development of CSs, smartphone-based sensor platforms, and mini-programs for assessing food safety and quality were documented. In [3], it is stated that recently, the introduction of advanced nanomaterials has given a new impetus to the development of CSs. Moreover, it describes the necessary actions that need to be taken to increase the sensitivity of CSs and considers the design of CSs based on several typical nanomaterials, including graphene and its derivatives. Future trends and challenges in the development and operation of CSs are discussed. In [4], it was found that due to the similarity of the molecular structure of biothiols, the development of simple, fast, efficient and sensitive CSs has great prospects for clinical cancer diagnostics. CSs for quality control of poultry and red meat are considered in [5]. In [6], a colorimetric method for the analysis of polyphenols in black tea was proposed. It was proven that the method is effective for the analysis of both fresh and fermented samples of black tea leaves. The aim of [7] is to analyse colorimetric changes in light transmitted through special filters manufactured by different manufacturers. The study [8] determined that during colorimetric assessment of enzymes, test samples play an important role in ensuring high accuracy and increasing the reliability of results. By comparing the control results with the test samples, researchers can identify and correct any sources of errors that could affect the experimental results.

Considering the interest of the world scientific community in colorimetry, the task of ensuring high accuracy of comparative analysis of colour properties of materials and products arises when conducting both criminal examination and establishing a medical diagnosis for sick patients. The task can be solved through the implementation of statistical analysis methods. The feasibility of such a statement is based on the results presented in some papers [9, 10].

Study of metrological reliability of the EDC

To determine the percentage composition of the base colour in a controlled object for the purpose of further unambiguous identification of it with another control object (for example, in forensics when establishing the identity of the colour of a car suspected of committing a crime), it is advisable to use EDC, which is a convenient measuring instrument.

One of the parts of such an EDC is a digital sensor (Fig. 1), which works both on the reflection of light and on the lumen of the controlled medium. The functional diagram of the sensor consists of LEDs

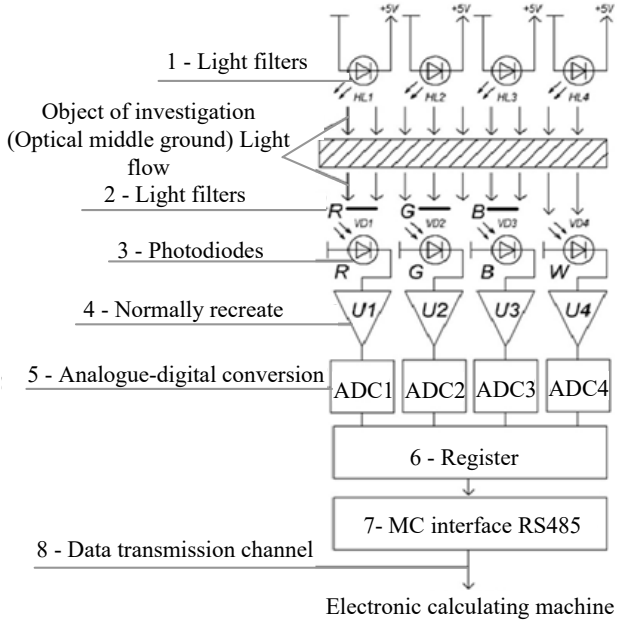

Fig. 1. Functional diagram of a digital sensor

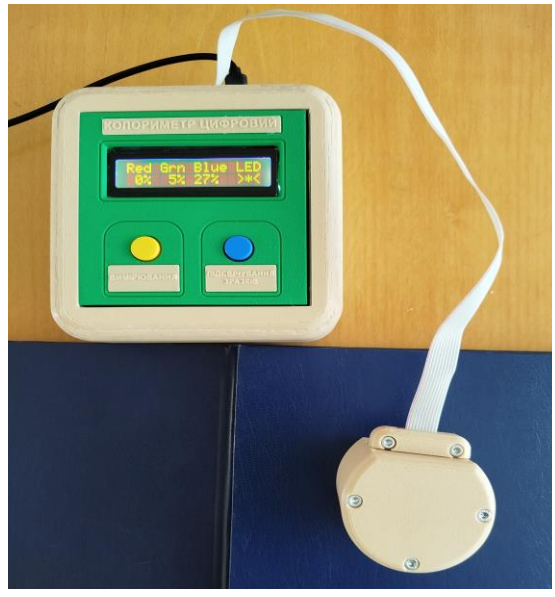

Fig. 2. Electronic digital colorimeter (EDC)

HL1 – HL4 — Fig. 1 (1), three light filters: Red (R), Green (G), Blue (B) — Fig. 1 (2); photodiodes VD1 – VD4 — Fig. 1 (3), normalizing amplifiers — Fig. 1 (4), ADC — Fig. 1 (5), status register — Fig. 1 (6), interface chip — Fig. 1 (7), and data transmission channel to a personal computer — Fig. 1 (8). The sensor uses white LEDs HL1 – HL4 with a temperature of 5600 K [11].

On its display, the EDC indicates the percentage of one of the three colours (red, green, blue) in the sample being examined. The design of an EDC is presented in Fig. 2.

During experimental studies, data were obtained on the level of blue content in three samples, presented in Fig. 3.

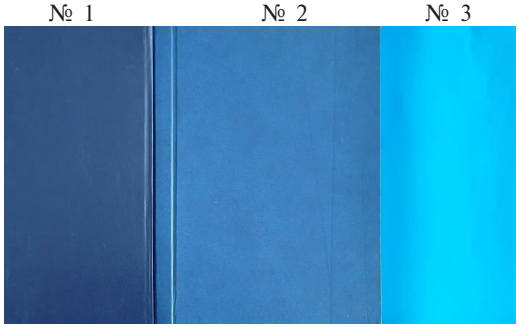

Fig. 3. Samples for colorimetric control

Under experimental conditions, the sensor was moved across the monitored surface at thirty points with a step of 1 cm. Since the main colour monitored is blue, the other two channels (red and green LEDs) were not considered in the calculations.

For further studies, the obtained dependences of the output signal on the channels of red, green and blue photodiodes were used, and they were designated as L_i, $i=\overline{1,n}$, where n is the number of observations in the series. Under the experimental conditions, the results of observations are considered independent and equally accurate. In general, they may contain systematic and random components of measurement error. The confidence probability is set at the level of $P = 0.99$ (significance level $\alpha = 0.01$).

To ensure high reliability of the colorimetric control of the presented objects, it is necessary to control the operation of the sensor. The importance of the problem is due to the fact that the confidence intervals are quite wide for the root-mean-square errors. It is advisable to solve the problem using the variant of the analysis of variance, which consists in comparing the variances and selecting the larger variance from many according to the Cochrane criterion [12]. This criterion requires the same number of experimental results in each series.

To solve the problem, the results of the experiments given in Table 1 ($n = 30$). were used. The values of the variances were calculated $D_1 ... D_3$ and the largest of the obtained variances was compared with the sum of all variances according to the formula

$$G = \frac{D_{max}}{D_1 + D_2 + D_3}. \quad (1)$$

The case when the value (1) turns out to be greater than the critical value obtained from the Cochrane criterion tables, in accordance with the established significance level, and hence the difference in the maximum dispersion value from the others is significant, the colorimetric sensor is recognized as unreliable from metrological point of view and requires replacement. A graphical representation of the processes of determining the level of blue colour by control areas in samples № 1, № 2, № 3 is presented in Fig. 4, Fig. 5, Fig. 6, respectively.

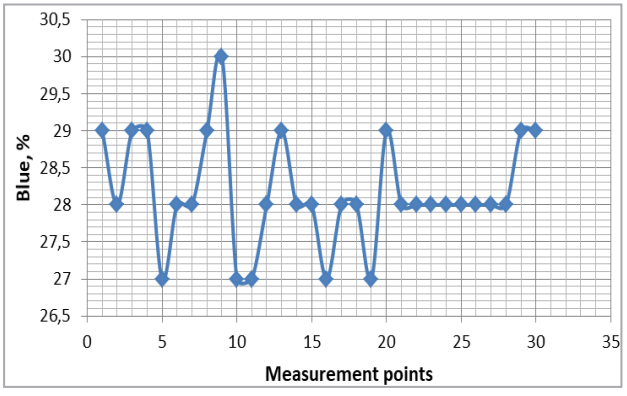

Fig. 4. The process of determining the level of blue colour across control areas in sample № 1

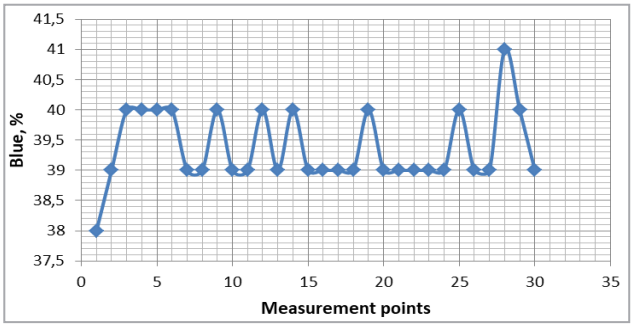

Fig. 5. The process of determining the level of blue colour across control areas in sample № 2

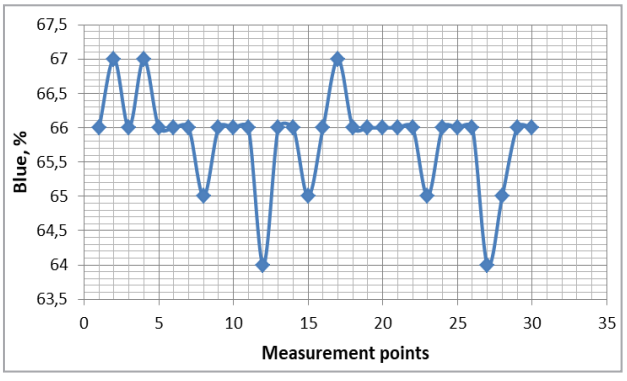

Fig. 6. The process of determining the level of blue colour across control areas in sample № 3

The unbiased point estimate of the variance of the results of multiple measurements of the blue colour level across areas in samples № 1, № 2, № 3 is determined by the formula

Table 1

Output data of two-dimensional

№ of measurement	Sample №1			Sample №2			Sample №3		
	Red,%	Green,%	Blue,%	Red,%	Green,%	Blue,%	Red,%	Green,%	Blue,%
1	0	5	29	0	7	38	0	44	66
2	0	4	28	0	7	39	0	43	67
3	0	4	29	0	13	40	0	43	66
4	0	4	29	0	14	40	0	44	67
5	0	4	27	0	19	40	0	43	66
6	0	4	28	0	13	40	0	42	66
7	0	4	28	0	12	39	0	44	66
8	0	4	29	0	13	39	0	43	65
9	0	4	30	0	13	40	0	43	66
10	0	4	27	0	12	39	0	43	66
11	0	4	27	0	13	39	0	43	66
12	0	4	28	0	13	40	0	46	64
13	0	4	29	0	13	39	0	43	66
14	0	4	28	0	14	40	0	43	66
15	3	0	28	0	12	39	0	42	65
16	0	5	27	0	19	39	0	44	66
17	2	0	28	0	13	39	0	43	67
18	0	4	28	0	19	39	0	43	66
19	2	0	27	0	13	40	0	44	66
20	0	8	29	0	13	39	0	42	66
21	0	4	28	0	12	39	0	43	66
22	0	4	28	0	12	39	0	44	66
23	0	5	28	0	13	39	0	43	65
24	2	0	28	0	13	39	0	42	66
25	0	4	28	0	13	40	0	43	66
26	0	4	28	0	13	39	0	43	66
27	0	4	28	0	13	39	0	47	64
28	0	4	28	0	14	41	0	42	65
29	0	4	29	0	13	40	0	42	66
30	0	4	29	0	13	39	0	43	66

$$D_L = \frac{1}{n-1}\sum_{i=1}^{n}\left(L_i - \bar{L}\right)^2. \qquad (2)$$

The calculated dispersions across areas for samples № 1, № 2, № 3 according to formula (2) were performed using Microsoft Excel:

1. Sample № 1: $D_1 = 0.56\%^2$;
2. Sample № 2: $D_2 = 0.38\%^2$;
3. Sample № 3: $D_3 = 0.49\%^2$.

According to formula (1), the value of the sum of all variances is equal to

$$G = \frac{0.56}{0.56 + 0.38 + 0.49} = 0.392.$$

The critical value of the deviation G at a confidence probability of $P = 0.99$ and significance level $\alpha = 0.01$ is determined according to the Cochrane distribution table [12] $G_{kr} = 0.5696$

$$G_{kr} = 0.5696 > G = 0.392.$$

The calculated critical value G is less than the critical value G_{kr} at $\alpha = 0.01$, hence the difference of the maximum dispersion is $D_2 = 0.56$ from the others, and, thus, the colorimetric sensor is considered metrologically reliable.

The standard measurement uncertainty of the results was calculated.

The standard type A uncertainty was calculated as a statistical estimate of the standard deviation of the arithmetic mean [13] by the formula

$$u_A\left(\bar{L}_i\right) = \sqrt{\frac{\sum_{q=1}^{n_i}\left(L_{iq} - \bar{L}_i\right)^2}{n_i\left(n_i - 1\right)}}, \qquad (3)$$

where n_i is the number of observations made during measurement L_i.

The standard type A uncertainty of measurements of the blue colour level across control areas in sample № 1 is calculated by the formula (3)

$$u_A\left(\bar{L}_1\right) = 0.136\%.$$

Similarly, calculations were performed for control areas in sample № 2 using formula (3):

$$u_A\left(\bar{L}_2\right) = 0.112\%,$$

and also for control areas in sample № 3:

$$u_A\left(\bar{L}_3\right) = 0.127\%.$$

The calculation of the standard type B uncertainty was performed based on the assumption of normality of the distribution law according to the formula

$$u_B(x) = \frac{b-a}{2} = \frac{\Theta}{2}, \quad (4)$$

where a and b are the left and right limits of the distribution of the unexcluded systematic error (USE), respectively. For the developed EDC, the limits $\pm\Theta$ of the USE interval are $\pm 1.0\%$.

The standard type B uncertainty of measurements of the blue colour level across control areas in sample № 1 according to formula (4) has the value

$$u_B\left(L_1\right) = 0.5\%.$$

Similarly, calculations were performed for control areas in sample № 2 using formula (4):

$$u_B\left(L_2\right) = 0.5\%,$$

and also for control areas in sample № 3:

$$u_B\left(L_3\right) = 0.5\%.$$

The combined standard uncertainty of the initial quantity L has the form [13]

$$u_c(y) = \sqrt{\sum_{i=1}^{m} u_i^2(y)}. \quad (5)$$

The combined standard uncertainty was calculated for each of samples № 1, № 2, № 3, respectively:

$$u_c(L_1) = \sqrt{\left(u_A\left(\bar{L}_1\right)\right)^2 + \left(u_B\left(L_1\right)\right)^2} = 0.518\ \%.$$

$$u_c(L_2) = \sqrt{\left(u_A\left(\bar{L}_2\right)\right)^2 + \left(u_B\left(L_2\right)\right)^2} = 0.512\ \%.$$

$$u_c(L_3) = \sqrt{\left(u_A\left(\bar{L}_3\right)\right)^2 + \left(u_B\left(L_3\right)\right)^2} = 0.516\ \%.$$

The expanded uncertainty was calculated for each of samples № 1, № 2, № 3 using formula (6) [13]

$$U(L) = k \cdot u_c(L), \quad (6)$$

where k is the coverage ratio; $u_c(L)$ is the total standard uncertainty.

The coverage coefficient k was found according to the Student distribution for probability $P = 0.95$ and the effective number of degrees of freedom ν_{eff} [13] by the formula

$$k = t_{0.95}(\nu_{eff}), \quad (7)$$

where ν_{eff} is the effective number of degrees of freedom, with $\nu_{eff} \to \infty$, $k = 2$ (with a normal distribution and $P = 0.95$).

The effective number of degrees of freedom is determined by the formula [13]

$$\nu_{eff} = \frac{u^4(L)}{\sum_{i=1}^{n} \frac{u_i^4(L)}{\nu_i}}, \quad (8)$$

where ν_i is the number of degrees of freedom of the i-th input variable.

Given that during the study on the operation of the EDC a series of direct multiple measurements have $n = 30$, formula (8) can be written in the form [13]

$$\nu_{eff} = (n-1)\frac{u_c^4(L)}{u_A^4(L)}. \quad (9)$$

The expanded measurement uncertainty of the initial value for each of samples № 1, № 2, № 3 was calculated using formula (6), respectively:

$$U(L_1) = 1.036\%;\ \ U(L_1) = 1.024\%;\ \ U(L_1) = 1.032\%.$$

Conclusions

The analysis showed the need to continue the work on improving colorimetric control tools to increase their accuracy and reliability.

For the first time, a digital device to measure the uniformity of optical media coverage has been developed, which has contributed to solving the scientific and practical problem of measuring the uniformity of optical media coverage and constructing a scheme of zones with uniform permeability, as well as simultaneous measurement of a large area of material.

Thanks to the use of dispersion analysis of the measurement results of the conducted metrological control of the EDC, namely the digital sensor, which is part of the electronic colorimeter, the metrological reliability of the EDC was established, which makes it possible to assert that high measurement accuracy is ensured.

Дослідження та розробка засобу колориметричного контролю властивостей матеріалів і виробів

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Анотація

Розглянуто розв'язання науково-практичної задачі розробки та дослідження роботи електронного цифрового колориметра. Дослідження полягало у визначенні відсоткового складу базового кольору в контрольованому об'єкті для подальшої однозначної ідентифікації його з іншим об'єктом контролю, що досліджується за допомогою електронного цифрового колориметра, а також у перевірці його метрологічної надійності. Представлено функціональну схему розробленого цифрового колориметричного сенсора для вимірювання кольорових властивостей матеріалів і виробів, наведено принцип його роботи. Отримано експериментальні дані по трьох каналах вимірювання цифрового колориметричного сенсора, а саме: канал червоного, зеленого та синього фотодіодів. Проведено статистичний аналіз серій результатів спостережень, який дозволив встановити рівні незміщених оцінок дисперсій по трьох каналах вимірювання. Зміна відсотків базового кольору зразка по каналах вимірювання пов'язана зі зміною характеристик поверхні, що контролюється (наявність пошкоджень, забруднень тощо). Отримано графічні зображення визначення рівня синього кольору по ділянках контролю у трьох зразках. Наведено розрахунки бюджету невизначеності по трьох каналах вимірювання електронного цифрового колориметра.

Отримані результати дозволяють проводити подальше вдосконалення методів і засобів контролю метрологічної надійності колориметричних засобів контролю, шляхом використання статистичних методів проведення аналізу результатів вимірювань, що отримані з їх допомогою. Перспективним є використання апарату нечіткої логіки для ідентифікації об'єктів колориметричного контролю між собою.

Ключові слова: колориметрія; цифровий сенсор; статистичний аналіз; дисперсійний аналіз; невизначеність вимірювань; похибка.

References

1. Patil V., Chandole T., Borase T. Substrates for Colorimetric Sensors Array. *Smart Nanosensors. Smart Nanomaterials Technology*. Singapore, Springer, 2025. doi: https://doi.org/10.1007/978-981-96-3878-9_6
2. Haroon Elrasheid Tahir, Xiaowei Huang, Zou Xiaobo, Zhihua Li. Chapter Three – Recent advances in colorimetric sensors: Design and fabrication. *Colorimetric Sensors*, 2024, pp. 37–64. doi: https://doi.org/10.1016/B978-0-443-13218-6.00012-4
3. Yu Wu, Jing Feng, Guang Hu, En Zhang et al. Colorimetric Sensors for Chemical and Biological Sensing Applications. *Sensors*, 2023, vol. 23(5), 2749. doi: https://doi.org/10.3390/s23052749
4. Yin Li, Yumeng Liu, Yueqin Zhang, Mengmeng Dong et al. A simple Ag–MoS_2 hybrid nanozyme-based sensor array for colorimetric identification of biothiols and cancer cells. *RSC Advances*, 2024, vol. 14, issue 43, pp. 31560–31569. doi: https://doi.org/10.1039/d4ra05409a
5. Xiaowei Huang, Haroon Elrasheid Tahir, Zhihua Li et al. Chapter Eight. Colorimetric sensors for poultry and red meat quality control. *Colorimetric Sensors,* 2024, pp. 161–185. doi: https://doi.org/10.1016/B978-0-443-13218-6.00013-6
6. Kokoro Matsushita, Chihiro Honda, Yoriyuki Nakamura, Shigenori Kumazawa. Comparison of colorimetric methods for the analysis of total polyphenols in black tea extracts. *Food Science and Technology Research,* 2025, vol. 31, issue 2, pp. 163-168. doi: https://doi.org/10.3136/fstr.FSTR-D-24-00220
7. Sanchez-Cano A., Orduna-Hospital E., Aporta J. Colorimetric and Photobiological Properties of Light Transmitted Through Low-Vision Filters: Simulated Potential Impact on ipRGCs Responses Considering Crystalline Lens Aging. *Life*, 2025, vol 15(2), 261. doi: https://doi.org/10.3390/life15020261
8. Kavindra Borgaonkar, Ranjit Patil. Clinical importance of control in colorimetric estimation of enzymes. *Journal of Research in Medical and Dental Science,* 2024, vol. 11, issue 3, pp. 09–12.

9. Horoshajlo Yu., Sezonova I., Chumakov V., Efimenko S., Levitskaya G. The Possibility of Using the Concept of Colorimetric Functions in Applied Research. Proceedings of *IEEE 8th International Conference on Advanced Optoelectronics and Lasers* (*CAOL*), 2019, pp. 225–227. doi: https://doi.org/10.1109/CAOL46282.2019.9019456
10. Yefymenko S., Hryhorenko I., Khoroshilo Iu., Hryhorenko S., Petrovska I. Evaluation of Informativeness of Indicators in Colorimetric Control Using Discriminative Analysis Models. *XXXII International Scientific Symposium Metrology and Metrology Assurance (MMA)*, Sozopol, Bulgaria, 2022. doi: https://doi.org/10.1109/MMA55579.2022.9992712
11. Pat. u2019 10509 Ukraine, IPC G01J 3/46, G01R 21/133, G02B 5/20, F21V 9/00. Digital device for measuring the uniformity of the coating of optical media. Khoroshailo Yu., Semenov S., Lymarenko V., Podhayko O., Yefymenko S.; applicant and patent owner Kharkiv National University of Radioelectronics. – No. 142432; filed 10/21/2019; publ. 06/10/2020, Bull. No. 11, 2020 (in Ukrainian).
12. Johnson N.L. Statistics and Experimental Design in Engineering and the Physical Sciences. Second edition. John Wiley & Sons Publ., 1977. 1082 p.
13. Zakharov I., Neyezhmakov P., Botsiura O. Expanded uncertainty evaluation taking into account the correlation between estimates of input quantities. *Ukrainian Metrological Journal*, 2021, no. 1, pp. 4–8. doi: https://doi.org/10.24027/2306-7039.1.2021.228134