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INTEGRAL MEASUREMENTS OF THE COLOR OF NANODIMENSIONAL RADIATORS

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The use of an integral colorimeter of heightened sensitivity constructed with the use of a physiological colorimetric system is considered. The color characteristics of the radiation of low-dimension sources with absolute error in the determination of the chromaticity coordinates 0.002 units may be measured by the new colorimeter.
Keywords: *remote measurements, small size of measured quantity, integral colorimeter, correction filter, chromaticity coordinates.*

Nanotechnology is an area of science and technology concerned with the study of the properties of small particles. The measurement of the radiation in integral form emitted by a small object does not present any special difficulties. Special equipment and methods that assure the uniformity of the measurements are needed to determine the spectral power density. Reliability and certainty of the equipment and measurements are achieved through optimization of the metrological assurance of such measurements.

Let us consider an example that reveals the essence of the problem. The most common source of radiation today (radiating diode) has a luminous intensity of 5 cd and at a distance of 1 m creates an illuminance of 5 lx for any color of radiation. Such a magnitude does not present any problems when the radiation is estimated by a standard measuring instrument, since it is the lower limit of the measured magnitude, even in the case of an area of radiation of 10^{-6} mm^2. A measured flux of radiation is determined by the aperture angle of the detector, which is not equal to the aperture angle of the radiation source. The total flux from this source in a spectral interval near the wavelength of 550 nm and with a solid angle $\omega \approx 0.79$ sr is $\Phi_v \approx 3.95$ lm or $\Phi_e \approx 5.78 \cdot 10^{-3}$ W.

For modern measuring instruments with diameter of the entrance pupil $D = 10$ mm and at a distance of 1 m to the radiation source, the solid angle $\omega \approx 7.85 \cdot 10^{-5}$ sr, consequently, the flux of radiation incident on the entrance pupil $\Phi_e \approx 5.78 \cdot 10^{-7}$ W. The incident flux may be increased by decreasing the distance from the measuring instrument to the source down to a magnitude equal to the diameter of the entrance pupil of the detector which, by the law of inverse square of distances, is equal to 100 mm (i.e., a distance $r = 100$ mm). Thus, the measured flux may be increased 100-fold and or $\Phi_e \approx 5.78 \cdot 10^{-5}$ W. Recalling the spectral sensitivity $S(\lambda)$ of the radiation detector ($S(550) = 0.1$ A/W), we find that the strength of the current arising in the detector circuit $i \approx 6 \cdot 10^{-6}$ A. This value of the strength of current may be measured by modern measuring instruments with the lowest measurement limit of 10^{-6} A with specified conventional error.

The chromaticity of nanodimensional radiation sources must be measured with absolute error 0.002 units. This cannot be done by means of modern series-produced spectrocolorimeters, since the color of the radiation reflected and transmitted by a source is determined by the small size of the radiating or reflecting element. Such equipment includes displays based on a liquid crystal, gas-discharge, or light-diode indicators; color comparison scales used in printing; light-diode

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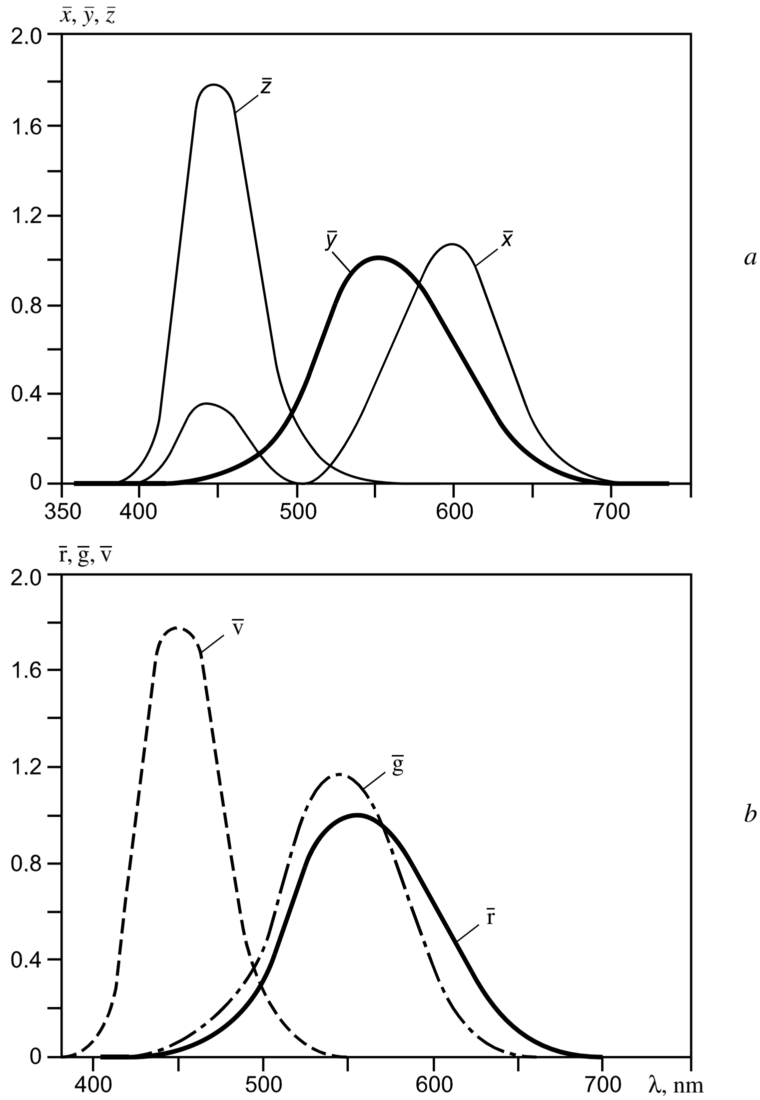
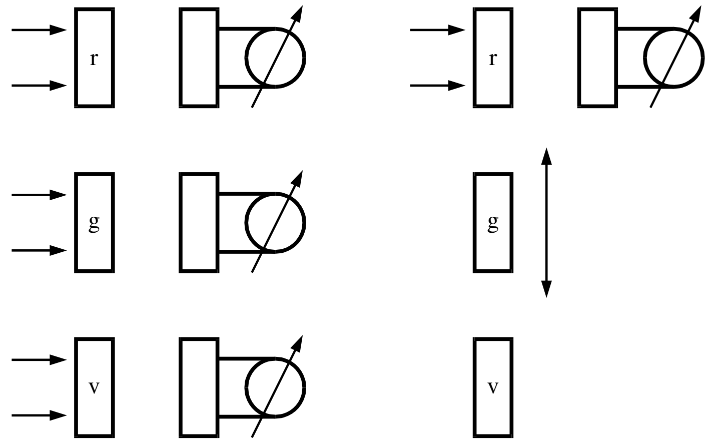


Fig. 1. Addition functions of colorimetric systems: *a*) standard (*XYZ*); *b*) physiological colorimeter system.

screens, etc. The dimension of the observed objects ranges from several millimeters (light-emitting diode cluster) to hundreds of nanometers (sub-pixels).

The method used to measure color with the use of a spectrocolorimeter may not be employed for such radiating surfaces. It is only possible to measure the total radiation in a given spectral range by means of a photodetecting device based on a photomultiplier. With the use of the most precise color meter, the radiation must be decomposed by wavelength with spectral interval of 10 nm. This reduces the spectral density of the radiation flux in a limited spectral interval incident on the photodetector by a factor of 30 (disregarding attenuation of the optical circuit of the colorimeter and the spectral composition of the radiation). Such a method of color measurement should never be used in the case of small dimensions of the radiating surface. It is only possible to measure the total radiation in a given spectral range and, moreover, a photodetecting device based on a photomultiplier with least value of the measured flux 10^{-13} W must be used. Series-produced photometers of heightened sensitivity and the YaRM-3 brightness meter, which reliably measure the brightness of an element with diameter of 100 and 30 μm, may serve as an analog of such a device.



a *b*

Fig. 2. Flow charts of three-color colorimeters with one (*a*) and three (*b*) radiation detectors.

The process of determining the chromaticity coordinates in modern series-produced colorimeters is generally performed in the plane of the chromaticity diagram on the basis of the standard colorimetric system (*XYZ* system) adopted by the International Commission on Illumination in 1931 [1]. This coordinate system has a number of advantages, for example, the addition functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ do not have any negative values (Fig. 1*a*), the brightness coefficients of the basic colors L_X and L_Z are equal to zero, while the coefficient L_Y determines the brightness of the measured object; the chromaticity of a mixture of radiators *X*, *Y*, and *Z* (in equal proportions) coincides with the chromaticity of the radiation of white color *E* (the radiating power is the same for all wavelengths in the visible range).

A drawback of the *XYZ* system is the existence of an additional maximum on the curve $\bar{x}(\lambda)$, which makes it necessary to use a fourth radiation detector and to correct it. The elimination of this drawback led to the construction of the physiological colorimetric system (PCS), the basic colors of which (r, g, v – red, green, violet) were selected according to the relative sensitivity of each of three receptors of the human eye to the required color. Each color in the PCS system as well as in the *XYZ* system may be expressed as follows:

$$\begin{cases} \mathrm{r}' = y' = V(\lambda); \\ \mathrm{v}' = z'; \\ x' = 2.9526\mathrm{r}' - 2.1720\mathrm{g}' + 0.2195\mathrm{v}'; \\ \mathrm{g}' = -0.4604x' + 1.3593y' + 0.1011z'. \end{cases} \tag{1}$$

In the PCS system, the ratio of the brightness coefficients is as follows: $L_\mathrm{r}{:}L_\mathrm{g}{:}L_\mathrm{v}$ = 1:0:0, hence the addition function $\bar{\mathrm{r}}(\lambda)$ (Fig. 1*b*) coincides with the relative spectral light efficiency $V(\lambda)$ and determines the brightness of a color.

The principal advantages of the PCS system are the simplicity of the process of correcting the radiation detector, the correspondence of the addition functions of the relative spectral sensitivity of the three receptors of the human eye, and simple conversion to the standard *XYZ* system.

There are two essentially different methods of determining the color coordinates and chromaticity: a spectrophotometric method and a photoelectric colorimetric method (method of integral three-color detector). In the first case, the spectral distribution of the power density of the measured radiation is determined, while the chromaticity coordinates are calculated. The color coordinates may be determined by the spectrophotometric method with relative error 0.2%, since standardized data of the addition functions of monochromatic radiation are used. The method is employed where heightened requirements are imposed on the precision of colorimetric measurements, for example, when calibrating standard specimens of sources and colored transparent or reflecting materials.

The second method of determining the chromaticity coordinates is based on the use of photoelectric colorimeters. Such colorimeters utilize three radiation detectors (Fig. 2*a*) with relative spectral sensitivity similar to the curves of the addition functions $\bar{r}(\lambda)$, $\bar{g}(\lambda)$, $\bar{v}(\lambda)$ (Fig. 1*b*) or related to the latter by linear relationships. This analogy is achieved through the use of glass or liquid correcting light filters. A single radiation detector in front of which three combinations of light filters are successively placed may be used (Fig. 2*b*).

The first method of measuring the color of radiation does not require calibration by means of standard specimens or standard radiation. Uniformity of measurements of the chromaticity is achieved by calibration of the spectral equipment with respect to a photometric scale and wavelengths with the use of required tabulated values of the addition functions of a selected colorimetric coordinate system. The second method assures uniformity of measurements of the chromaticity of radiation with mandatory calibration of a three-color colorimeter relative to the standard radiation of the *XYZ* system or relative to the transit (reflection) of this radiation through (from) colored glass (standard paint) with known spectral transmission (reflection) coefficient. In this case, the chromaticity coordinates of standard radiation are known [2].

The chromaticity coordinates of radiation are determined from the values of the corresponding photoelectric currents i_r, i_g, and i_v in the circuit of the photodetector device (PD) of a three-color colorimeter. Under these conditions, the currents i_r, i_g, and i_v of detectors with correcting light filters are related to the color coordinates (r′, g′, v′) by the following relationships:

$$r' = \alpha_r \int \varphi_A(\lambda) S_{FEU}(\lambda) \tau_r(\lambda) d\lambda = \alpha_r i_r;$$

$$g' = \alpha_g \int \varphi_A(\lambda) S_{FEU}(\lambda) \tau_g(\lambda) d\lambda = \alpha_g i_g;$$

$$v' = \alpha_v \int \varphi_A(\lambda) S_{FEU}(\lambda) \tau_v(\lambda) d\lambda = \alpha_v i_v,$$

where α_r, α_g, and α_v are scale factors; $\tau_r(\lambda)$, $\tau_g(\lambda)$, and $\tau_v(\lambda)$, the spectral transmission coefficients of the corresponding correcting light filters; and $\varphi_A(\lambda)$, the spectral density of a flux of standard radiation.

When measuring white equal-energy radiation, the signals in the detector circuit are equal and the factors α_r, α_g, and α_v must confirm this. The creation of white light *E* is a difficult additional problem that leads to an increase in the error in measurements of color. For this reason, calibration is performed with respect to the radiation of a source *A* the reproduction of which by means of a tungsten incandescent lamp with color temperature 2856 K led to a comparison with the state standard based on a black body.

The chromaticity of standard radiation of type *A*, the relative spectral power distribution of which is standardized by the International Commission on Illumination in the PCS system, is calculated by means of tables of addition functions compiled from Fig. 1*b*, and determined by the coordinates r(λ) = 0.4455, g(λ) = 0.3962, and v(λ) = 0.1583. Thus, adopting the signal i_r for component r as the unit (r:g:v = 1.000:0.8893:0.3553), we obtain the following expressions for use in determining α_r, α_g, and α_v in calibration relative to standard radiation of the International Commission on Illumination of type A:

$$\alpha_r = 1 i_r / i_r; \quad \alpha_g = 0.8893 i_r / i_g; \quad \alpha_v = 0.3553 i_r / i_v.$$

The color coordinates and chromaticity of the physiological colorimeter system are calculated from measured currents in the circuit of the photodetector device and are also recalculated from formulas (1) in the analogous coefficients of the *XYZ* system. The last transition is necessary, since the *XYZ* colorimetric system is a generally accepted system for determining color. It is only by means of this system that the results of color measurements by means of instruments from different countries and different domestic firms can be compared.

FEU-84 photoelectric multipliers (produced in St. Petersburg) were selected as the radiation detector in a mock-up of an integral colorimeter. FEU data exhibit a linear dependence between the photoelectric current of the anode and the incident flux of radiation within four orders. The optical circuit of an integral colorimeter serves as a circuit for measuring brightness with sight: level of brightness measurement 10^5–10^{-4} cd/m^2 ($1.5 \cdot 10^{-7}$ W/sr·m^2); dimension of measured object

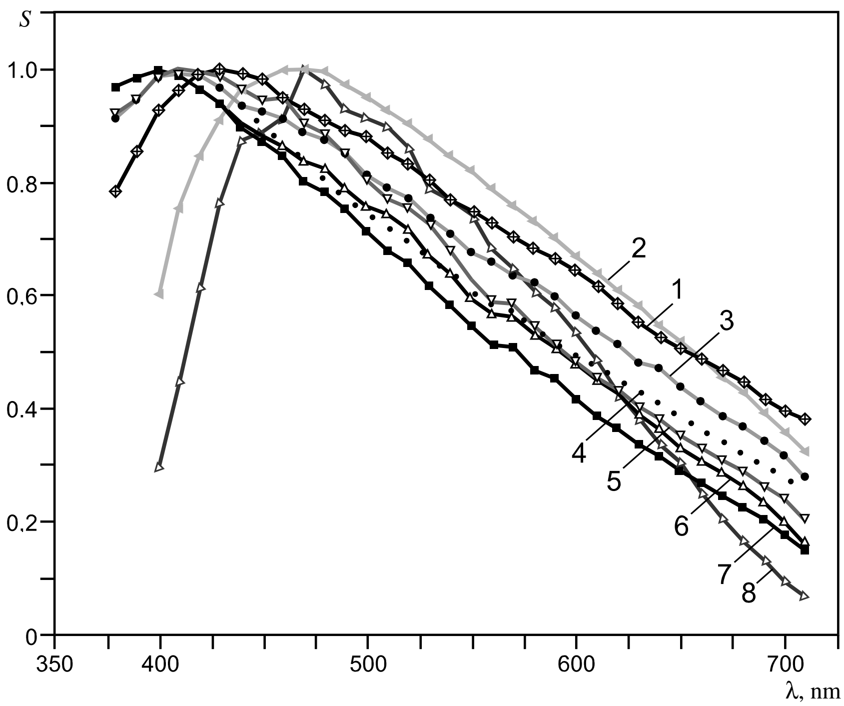


Fig. 3. Random sample of relative spectral sensitivities of different photoelectric cathodes of the FEU-84 photoelectric multiplier: *1*) fem9713; *2*) fem5975; *3*) fem4273; *4*) mean value; *5*) fem9214; *6*) fpc852088; *7*) fem3911; *8*) fpc841008.

TABLE 1. Error in Measurement of Chromaticity and Color with the Use of a Mock-Up of the Physiological Colorimetric System

Color of radiation	Maximal deviation of measured chromaticity from reference chromaticity		
	$\pm\Delta_r$	$\pm\Delta_g$	$\pm\Delta_v$
Neutral	0.001	0.002	0.001
Red	0.009	0.008	0.002
Orange	0.004	0.003	0.001
Green	0.002	0.001	0.002
Blue	0.007	0.002	0.005
Purple	0.002	0.003	0.001

0.050–5.000 mm; distance from measured object to entrance pupil of mock-up around 70 mm. With least area of the measured radiation element $8\cdot10^{-7}$ m^2 and $\omega = 0.4$ sr, the lower threshold of a measured flux is $5\cdot10^{-12}$ W.

The relative spectral sensitivity of a photoelectric multiplier was corrected relative to the bias curves of the new colorimetric system by means of methods presented in [3]. Photoelectric multipliers [4] whose maximal sensitivities are in the range 420–480 nm (Fig. 3) were first selected. Photoelectric multipliers for which the correction error for a specified composition of the correcting light filter does not exceed 0.01 were taken from this sample. The correcting filters were fabricated individually for each photoelectric multiplier from SS4, S3S21(23), 3S8, Zh3S18, ZhS3(11), and OS5 glass in different combinations and different thicknesses (total thickness not greater than 8 mm).

TABLE 2. Comparison of Measurements of the Chromaticity of Reference Specimens (PCS – physiological colorimetric system)

Chromaticity coordinate	Coloring	Compared devices				
		Carry	N-Vision	TKA VD	Minolta	Prototype of integral PCS
		Maximal deviation of coordinate of colored radiation from reference				
x	Red	0.003	0.010	0.013	0.042	0.003
	Blue	0.002	0.013	0.012	0.035	0.005
	Green	0.003	0.008	0.011	0.039	0.002
y	Red	0.002	0.010	0.010	0.031	0.005
	Blue	0.004	0.005	0.012	0.022	0.006
	Green	0.003	0.007	0.009	0.025	0.005
z	Red	0.002	0.009	0.014	0.027	0.001
	Blue	0.003	0.017	0. 009	0.023	0.002
	Green	0.003	0.013	0.010	0.025	0.002
Mean value		0.0028	0.0102	0.0111	0.0298	0.0034

Verification of the quality of the measurements by means of an integral remote colorimeter and estimation of the errors in the measurements of the color and chromaticity of unknown radiation were performed using standard specimens of color in accordance with the requirements of modern metrology [5, 6]. The three-color coefficients of standard radiation were determined by measuring the spectral transmission coefficient of 34 different types of colored glass, or "color specimens," for the distribution of the spectral power density of standard radiation *A* or *D* of the *XYZ* system and from known mixing functions of the colorimetric system. The results of a calculation of the maximal absolute error in measurements of the chromaticity coordinates of individual radiators are shown in Table 1. It should be noted that the errors of the color measurements by this colorimeter do not depend on the selected representation of a particular colorimetric system. We should keep in mind the equality between the absolute measurement error of the chromaticity of radiation and the relative error in the color of the radiation: $\Delta_{\mathrm{rgv}} = \Delta_{XYZ}$.

The error in measurements of the color of radiation should not be estimated from the absolute deviations of the measured values from reference values. The color of radiation depends to a significant degree on the quantity of color, i.e., its brightness. Therefore, the relative error in the measurement of the color coordinates δ_{rgv} is determined by the relative errors in the measurements of the chromaticity ($\delta_{\mathrm{a}} = \Delta_{\mathrm{a}}/\mathrm{T}$, where Δ_{a} is the absolute error in the measurement of the chromaticity coordinate and T the true value of the chromaticity coordinate) and brightness δ_{b}.

The result of a measurement determined from five series of measurements each containing five observations of 34 color samples was calculated in order to analyze the error of the color measurements. Statistical processing of the results of measurements by a mean-square estimate of the arithmetic mean of the absolute error of the chromaticity coordinate $S_{\bar{\Delta}} = 0.002$ for each coordinate is therefore entirely applicable. The value of the total relative error δ_{Σ} of the device:

$$\delta_{\Sigma} = 1.1\left(\sum \delta_i^2 + \frac{1}{3}\sum Q_j^2\right)^{0.5},$$

where $\sum \delta_i^2$ is the sum of the random errors in measurements of the chromaticity and the spectral quantities; $\sum Q_j^2$, sum of the nonexcluded part of the systematic measurement error basically caused by the error in the transmission of the units from the state standard to the measuring instrument; the coefficient 1.1 corresponds to a 0.95 confidence level of the measurements.

As a result of estimating the error in color measurements caused by the use of a mock-up of the physiological colorimetric system (a mock-up is a new measuring device or prototype of a measuring device), the basic relative error in measurements of color was 8% with absolute error in the measurement of the chromaticity coordinates not greater than ±0.003 units.

The comparison of the measurement results of the same quantities by different methods and different devices confirms the reliability and certainty of the measurements by any of the devices. A comparison of measurements of the chromaticity of radiation of different spectral composition was performed by measurements of the above reference set of colors by means of five different instruments for color measurements. The least difference in the determination of the chromaticity among all the different meters was found for the Carry spectrophotometer and the prototype of the measuring instrument and does not exceed 0.005 units (Table 2). The Carry and TKA VD devices are spectrocolorimeters, the first of which has a resolved spectral interval of 0.01 nm and error of the photometric scale of 0.001%. An integral colorimeter from the firm of Minolta contains four radiation detectors with relative spectral sensitivities corrected with respect to the four addition functions of the *XYZ* colorimetric system, while a color analyzer of architectural glass from the firm of N-Vision is close in terms of measurement method to the prototype of the physiological colorimetric system, but lacks a function for measurement of brightness.

Conclusion. Only the prototype of the integral colorimeter of the physiological colorimetric system, which is one of the devices involved in the comparisons of the colorimetric meters, may be used for remote measurements of low-dimension objects. The prototype of a three-color colorimeter exhibits an error in the measurement of the chromaticity that is at the level of the spectrophotometric measurement method, which is the most accurate of all existing colorimeters.

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