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A Colorimeter for Pyrotechnic Smokes*

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A tristimulus photoelectric colorimeter has been designed to measure the chromaticities of pyrotechnic smokes having highly saturated colors. To minimize edge effects and rear-wall reflection, the smoke chamber was designed as a 36-inch cube. Three filters were designed to approximate the daylight CIE standard observer functions for the source-filter-phototube combinations of the instrument. As the CIE $\bar{y}$- and $\bar{z}$-functions are unimodal, little difficulty was encountered in designing filters to approximate these functions. The CIE $\bar{x}$-function, which is bimodal, required a divided filter to approximate its two lobes. The filter constructed was composed of two sectors, one approximating the "blue lobe", the other approximating the "red lobe" of the $\bar{x}$-function. Satisfactory results have been obtained with this colorimeter, using Munsell papers as standards.

1. Introduction

In 1931 the International Commission on Illumination [1] [1] (CIE) adopted a system for reducing spectrophotometric data to color coordinates in three-space. The reduction of such data for a single specimen entails a considerable amount of computation. To avoid this computation, Twyman and Perry [2] suggested in 1930 that three filters duplicating the then proposed standard-observer functions could be used in a photoelectric instrument. Several such instruments, now called photoelectric colorimeters [3], have been designed since then. The photosensitive elements in colorimeters have been barrier photocells [4, 5], vacuum phototubes [6], and multiplier phototubes [7, 8].

This paper describes a colorimeter, using multiplier phototubes, designed at the request of representatives of the Army Chemical Center to be used for evaluating the colors of pyrotechnic smokes. This instrument was needed to determine progress in the development of saturated smoke colors and to check on reproduction of specified smoke colors.

2. Filter Design

The colorimetric spectral functions approximated in this colorimeter by combined source-filter-phototube response are those established by the CIE. The theory of the design of filters is based on two propositions (1) that the three CIE observer functions represent the colorimetric system of the average normal observer, and (2) that each of these functions can be approximated by the proper selection of optical filters in combination with a light source and a phototube. As the instrument is intended to evaluate the color of nonfluorescent smokes as if they were viewed in daylight (6,500° K), even though in the colorimeter they are illuminated by incandescent-lamp light (2,780° K), the proper correction was incorporated in the filter design. Had the colorimeter been intended to evaluate the color of fluorescent, as well as nonfluorescent, smokes as viewed under daylight, the approximation of the CIE function would be accomplished by phototube and filter combination alone, but the illuminator would then be required to yield artificial daylight.

The CIE spectral-response functions, $\bar{x}$, $\bar{y}$, and $\bar{z}$, under daylight spectral conditions, E_v, are respectively, $\bar{x}E_v$, $\bar{y}E_v$, and $\bar{z}E_v$. If the illuminator yields spectral distribution, E_i, the spectral responses, S_x, S_y, and S_z, of the phototubes for each of these functions must be altered by filters having spectral transmittances T_x, T_y, and T_z, respectively, in order to refer to viewing by daylight. This condition may be stated mathematically:

$$\left.\begin{aligned} E_iT_xS_xK_x&=\bar{x}E_v\\ E_iT_yS_yK_y&=\bar{y}E_v\\ E_iT_zS_zK_z&=\bar{z}E_v \end{aligned}\right\},\qquad(1)$$

where K_x, K_y, and K_z are proportionality constants, independent of wavelength for their respective functions. The desired relative spectral transmittances then are determined by solving eq (1) for K_xT_x, K_yT_y, and K_zT_z.

The filter design is accomplished by determining the proper combination of colored glasses. Where the transmittance, T_0, of a glass of stock thickness d_0, is to be changed to a transmittance, T_1, the following equation must be solved for the new thickness, d_1:

$$T_1=(T_0)^{d_1/d_0}(k^2)^{1-(d_1/d_0)},\qquad(2)$$

where k is unity minus the Fresnel reflectance of the glass. The approximate value of k for glass is 0.96. To minimize the work entailed in this computation a thickness-transmittance nomograph was used [9].

Figure 1 shows the spectral-response curves of several multiplier phototubes (RCA 5819) as calibrated by the NBS Radiometry Laboratory. The first phototube purchased had the response shown by curve A. Because of the relatively high response of this phototube in the region about 580 mμ the spectral transmittances of required filters for CIE functions must have absorption bands in this region.

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[1] Figures in brackets indicate the literature references at the end of this paper.

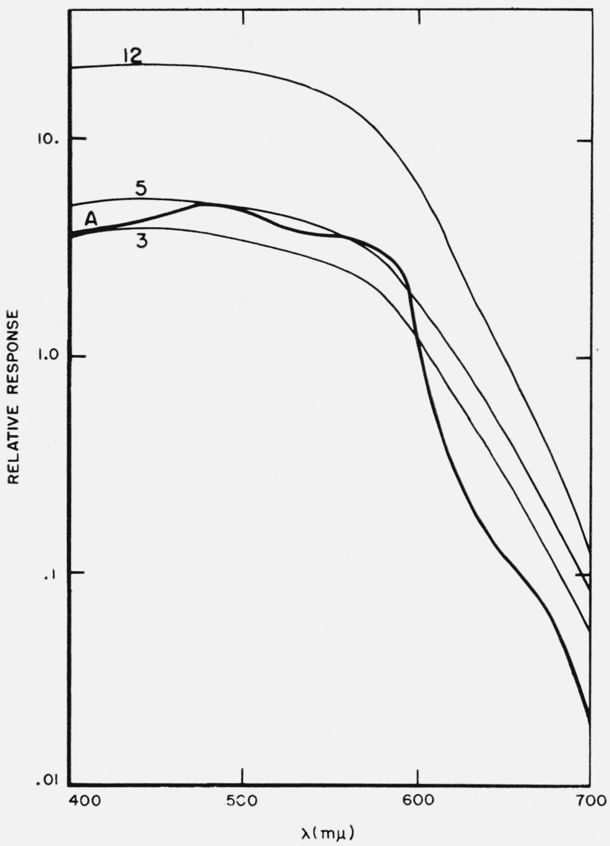

FIGURE 1. *Spectral-response curves of several multiplier phototubes*

To duplicate these complex transmittance curves the technique of divided-disk filters was devised. Fortunately, the phototubes purchased later had normal responses, as shown by curves 3, 5, and 12, of figure 1, thereby simplifying the filter-design problem. The phototubes having these curves are the ones used in the colorimeter for functions y, x, and z, respectively.

As no combination of glasses has ever achieved duplication of the bimodal $\bar{x}$-function in a single filter, the divided-disk technique devised for the complex transmittances required for phototube A was applied to the design of the bimodal $\bar{x}$-function. This division requires that one part of the single filter approximate the "blue lobe" and the other part approximate the "red lobe" of the $\bar{x}$-function. The transmittance of the ideal filter, T_x, for the $\bar{x}$-function may be divided into its two lobes, T_{xb} and T_{xr}, thus $T_x = T_{xb} + T_{xr}$. In terms of relative transmittance, this becomes

$$K_xT_x = K_x(T_{xb} + T_{xr}). \tag{3}$$

The actual approximation consists of a disk, area A, with one fraction, a/A, of the total area having spectral transmittance T'_{xb}, and the remaining fraction $1-(a/A)$, having spectral transmittance T'_{xr}. Then the transmittance, T'_x, of the actual filter is

$$T'_x = \frac{a}{A}T'_{xb} + \frac{A-a}{A}T'_{xr}. \tag{4}$$

The conditions that the spectral lobes of the approximate filter be properly proportional to those of the ideal filter are: The summation under each lobe of the approximation must equal the corresponding summation under the ideal filter, thus

$$\begin{aligned}\sum K_{xb}T'_{xb} &= \sum K_xT_{xb}\\ \sum K_{xr}T'_{xr} &= \sum K_xT_{xr}.\end{aligned} \tag{5}$$

The ratio of the summation under the two lobes in the approximate filter must equal the ratio of the summation under the two lobes of the ideal filter, thus

$$\frac{\sum \frac{a}{A}T'_{xb}}{\sum \frac{A-a}{A}T'_{xr}} = \frac{\sum T_{xb}}{\sum T_{xr}}. \tag{6}$$

But substituting the values of T'_{xb} and T'_{xr} from eq (5) into eq (6) gives

$$\frac{a}{A} = \frac{K_{xb}}{K_{xr}+K_{xb}}. \tag{7}$$

The area of the disk of radius r may be divided into either segments or sectors. Consider the segment division. The total area, A, is πr^2, and the area of the segment, a, is $(r^2/2)(\theta - \sin\theta)$, where θ, in radians, is the central angle subtended by the segment, as shown in figure 2,a. Then

$$\frac{a}{A} = \frac{1}{2\pi}(\theta - \sin\theta). \tag{8}$$

After the value of θ is computed, the segment is determined by computing, $x = r\cos(\theta/2)$.

Although relatively easy to construct, a filter with this type of division of the disk has two major difficulties. The disk, once constructed, is useful only with a circular opening of radius r. As the segment is displaced from the center of the disk, one must assume that the spectral response of the photosensitive surface of the phototube is completely uniform.

Consider now the sector division of a disk filter. The area of the sector (see fig. 2,b) is equal to $r^2\theta/2$, where θ, the sector angle, is in radians. Then $a/A = \theta/2\pi$. If the sector angle, expressed in degrees, is ρ, then

$$\frac{a}{A} = \frac{\rho}{360°}. \tag{9}$$

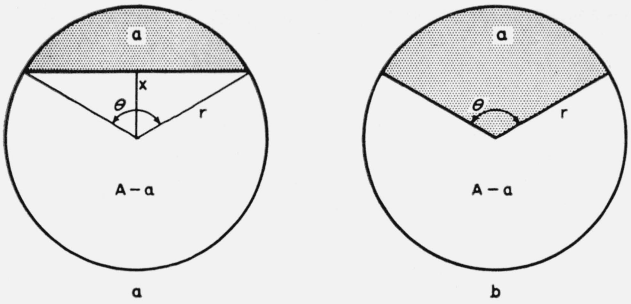

FIGURE 2. *Divided disks for $\bar{x}$-function filter*

a, Segment division; b, sector division.

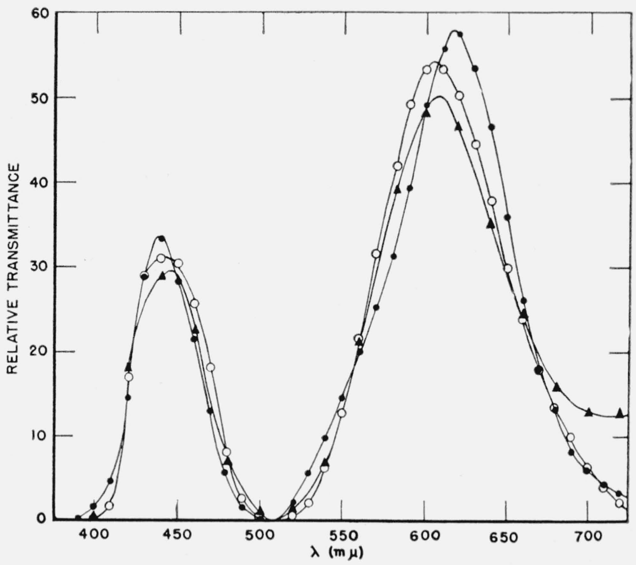

FIGURE 3. *Spectral transmittance of the desired (●), expected (▲), and actual (○) filters for CIE $\bar{x}$-function.*

This type of division, although more difficult to construct, does overcome the major difficulties of the segment division. The spectral character of the transmitted light is independent of the radius of the disk. One must assume only that the spectral response of the photosensitive surface of the phototube is radially symmetrical. This is a reasonable assumption for the head-on-type phototube used, as the photosensitive surface is evaporated onto the center of the cathode, thereby yielding a close approach to radially symmetrical sensitivity. This radial symmetry can readily be tested, furthermore, by rotating the sectored filter in its own plane and observing if the output of the phototube changes. For either type of division the center of the disk must be carefully positioned over the center of the photosensitive surface.

Because of the advantages outlined above, the sector division of the filter was used. On the basis of the application of eq (2) to the published spectral transmittance of stock glass, the combinations yielding the best expected approximation to the two lobes of the $\bar{x}$-function were chosen. The design data are shown in table 1. The sector angle was determined by substituting eq (7) into eq (9), giving

$$\rho = 360° K_{xb}/(K_{xr}+K_{xb}). \tag{10}$$

for the $\bar{x}$-function filter designed for this colorimeter, $K_{xb}=0.915$, $K_{xr}=5.483$, and $\rho=51.5°$. The expected relative transmittance, $K''_x T''_x$, for this filter is shown in figure 3 compared with the desired relative transmittance, $K_x T_x$, and the achieved relative transmittance, $K'_x T'_x$, of the actual filter. The actual filter proved to be a better approximation to the desired filter than had been expected from the design data.

TABLE 1. *x-function filter design data*

λ	$K_x T_x$	$K_x T_{xb}$ (blue lobe)	$K_x T_{xr}$ (red lobe)	T''_{xb} 5433[a] (7.5 mm) 3389[a] (1 mm)	T''_{xr} 9788[a] (3 mm) 3304[a] (6 mm)	$T''_{xb} K_{xb}$ $K_{xb}=0.915$	$T''_{xr} K_{xr}$ $K_{xr}=5.483$	$K''_x T''_x$
				%	%			
380	0.1	0.1	--------	0	----------	0	----------	0
400	1.6	1.6	--------	0	----------	0	----------	0
20	14.7	14.7	--------	19.8	----------	18.1	----------	18.1
40	33.4	33.4	--------	31.8	----------	29.1	----------	29.1
60	21.5	21.5	--------	24.6	----------	22.5	----------	22.5
80	5.8	5.8	--------	7.5	0	6.9	0	6.9
500	0.2	0.1	0.1	0.7	0.09	0.6	0.5	1.1
20	2.2	--------	2.2	0	.29	0	1.6	1.6
40	9.9	--------	9.9	----------	1.23	----------	6.7	6.7
60	20.1	--------	20.1	----------	3.86	----------	21.2	21.2
80	31.5	--------	31.5	----------	7.17	----------	39.3	39.3
600	49.2	--------	49.2	----------	8.85	----------	48.5	48.5
20	57.5	--------	57.5	----------	8.49	----------	46.6	46.6
40	46.6	--------	46.6	----------	6.43	----------	35.3	35.3
60	26.1	--------	26.1	----------	4.43	----------	24.3	24.3
80	13.0	--------	13.0	----------	2.92	----------	16.0	16.0
700	6.1	--------	6.1	----------	2.36	----------	12.9	12.9
20	3.5	--------	3.5	----------	2.36	----------	12.9	12.9
	343.0	77.2	265.8	84.4	48.48	77.2	265.8	343.0

[a] Corning glass code numbers.

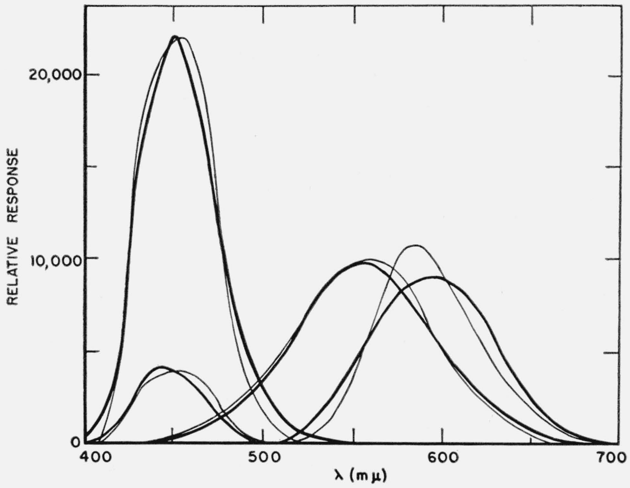

FIGURE 4. *CIE tristimulus functions (heavy lines) and the approximate functions of the colorimeter.*

As the CIE $\bar{y}$- and $\bar{z}$-functions are unimodel little difficulty was encountered in designing filters to approximate these functions. For the source-filter-phototube combinations of this colorimeter, the approximations (light lines) to the CIE tristimulus functions (heavy lines) are shown in figure 4.

3. Description of Apparatus

3.1. Chamber

Most of the colorimeters heretofore designed have been used for measurement of colors of opaque or transparent media. For these media, where edge effect is negligible, the size of the illuminated and viewed area of the medium was determined by the sensitivity of the instrument. The instrument here described is being used to measure the color of translucent media, pyrotechnic smokes. As the smokes are translucent, that is, light scattering as well as transmitting, and reflecting, a rather large chamber having a uniformly illuminated window is required to minimize edge effects.

Figure 5 shows a general view of the apparatus. The chamber is a 1-yd cube made of Dural. One side of the cube has a ¼-in. plate-glass window 32 in. sq. To determine if the window was sufficiently large, circular openings of increasing size were placed over the window. The aperture effect decreased to zero when the opening was still well within the window size. To determine if reflection from the chamber walls would affect the results obtained when the chamber is filled with smoke, measurements were made on a smoke by using alternately a black and a white rear wall. As the wall reflection and window size had little effect upon the measurements, the conclusion was reached that the chamber had been made sufficiently large.

A blower is installed either to stir the smoke in order to obtain uniform distribution in the chamber or to exhaust the smoke after colorimetric measurements are made. A door serves as access to the chamber for purposes of placing a smoke grenade in the chamber and firing it. To facilitate entering the chamber in order to clean the window, an additional door was constructed on the side of the chamber (not shown in fig. 5).

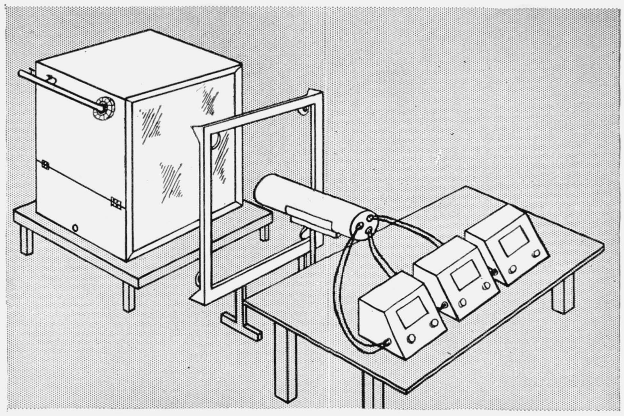

FIGURE 5. *General view of apparatus, showing smoke chamber, illuminators, optical-assembly tube, and photometers.*

3.2. Optical Arrangement

The smoke is illuminated by four 150-w incandescent floodlamps, mounted on a frame. The uniformity of illumination on the window was checked by means of a foot-candle meter.

The smoke is viewed perpendicularly through a lens that focuses upon a central region of the window. The lens is mounted at one end of a brass tube equipped with baffles to minimize stray light. The tristimulus filters are mounted in front of the phototubes. To achieve compactness of the viewing assembly, head-on-type phototubes were used.

3.3. Photometers

To measure accurately the chromaticity coordinates of saturated colors, a colorimeter is required to evaluate low reflectance in one spectral region and high reflectance in another spectral region with equal precision. As the colors of the pyrotechnic smokes are highly saturated and further development will improve their saturation, this colorimeter requires highly sensitive photometers and phototubes. To satisfy these requirements and for expediency, commercially available multiplier photometers and phototubes were used. The Photovolt Multiplier Photometer, model 520–M, known to be reasonably sensitive and stable, was chosen for use in the colorimeter. One minor adaptation of the photometers, required to permit the use of 5819 phototubes, instead of 1P21 phototubes for which the photometer was designed, was the replacement of the 10-prong socket with 9 dynode resistors by a 14-prong socket with 10 dynode resistors. To obtain direct readings of tristimulus values, X, Y, and Z, on the corresponding photometers, modification of the microammeter circuit of each photometer was anticipated, but only the Z-scale photometer required an increase in meter sensitivity.

4. Results With Colorimeter

As the source-filter-phototube combination does not completely duplicate the CIE functions, best results are obtained by calibrating the colorimeter with standards having spectral selectivities similar to those of the smokes. But as no spectral data are available for any smokes, standards of Munsell charts having colors similar to those of the smokes investigated were chosen and gave satisfactory results. Table 2 shows the Munsell notations for three different smokes reduced from data obtained with the colorimeter at the time of firing (t_0) and within 10 min (t_{10}) of that time, compared with notations obtained simultaneously by visual estimates through a daylight filter. The instrumental colorimetric data were converted to Munsell book notation, so that comparisons could be made with the visual estimates obtained by comparison with the color scales in a Munsell book of color. The colorimeter yields hues and values in substantial agreement with visual estimates, but yields generally higher chromas than visually obtained estimates. The uncertainty in a visual estimate of hue and value is approximately one half-step. As the Munsell book does not contain chips with chromas as high as those of these smokes, the uncertainty in visual estimates of chroma is of the order of two steps. One possible reason for the discrepancy between the instrumentally and visually obtained chromas is that the approximation to the $\bar{z}$-function is deficient in the region between 500 and 550 mμ, thereby yielding relatively low Z-values for yellow and red smokes.

TABLE 2.

Smoke color	Munsell notations		Time
	Instrumental	Visual	
Red	3R3.5/15	5R4/10	t_0
	3.5R 3/13	4$R$4/10	t_{10}
Do	4.5R3.5/14	5$R$4/12	t_0
	5R 2/10	5$R$2/7	t_{10}
Yellow	5Y6.5/10	5$Y$6/8	t_0
	5Y 4/6	4.5$Y$5/6	t_{10}

Table 3 shows Munsell notations of three different smoke colors taken on smokes fired under outdoor daylight (clear, sunny day) compared with notations obtained by reduction of instrumental data for duplicate smokes. The satisfactory correspondence between the sets of data indicates that the smokes were not strongly fluorescent and that the CIE functions had been adequately approximated.

TABLE 3.

Smoke color	Munsell notations	
	Instrumental	Visual
Red	5$R$3/14	5$R$5/14
Yellow	7$Y$8/12	7.5$Y$7/10
Green	4$G$2/3	3$G$3/3

5. References

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WASHINGTON, November 9, 1953.