

FT

NRL Report 5933

UNCLASSIFIED

FLUORESCENT COLOR SPECIFICATION BY MEANS OF THE BECKMAN MODEL DK-2 SPECTROPHOTOMETER

G. E. Rohl and J. E. Cowling

Organic and Biological Chemistry Branch
Chemistry Division

and

C. H. Presbrey, Jr.

Electrochemistry Branch
Chemistry Division

June 11, 1963



U. S. NAVAL RESEARCH LABORATORY
Washington, D.C.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
SPECTROPHOTOMETRY AS A MEANS OF FLUORESCENT COLOR MEASUREMENT	1
INSTRUMENTATION	3
Instrumentation Studies	3
Instrument Development	4
Standard Light Source	6
Standard White Reference Surfaces	7
Photomultiplier Detectors	9
Recorder Chart and Chromaticity Diagram	11
EVALUATION OF THE INSTRUMENT ASSEMBLY	12
Methods for Determining Tristimulus Values	12
Preparation of Fluorescent Test Panels	13
DISCUSSION OF RESULTS	17
CONCLUSIONS	18
REFERENCES	19
APPENDIX A - Composition of Davis-Gibson Solution Filters for Source C	20
APPENDIX B - Design Details of the Photomultiplier Detector Assembly	21
APPENDIX C - Enlargement of a Portion of the Chromaticity Diagram	25
APPENDIX D - Special Recorder Paper Designed for the DK-2 Spectrophotometer Used in this Study	27
APPENDIX E - Tristimulus Value Calculation Sheet for Use with the New Selected-Ordinate Chart Paper for I.C.I. Illuminant C	29

ABSTRACT

There is a general trend toward the specification of color by methods which are entirely independent of human acuity in color perception. Such methods are based upon a determination of the electromagnetic spectrum of the color in question, from which tristimulus values and chromaticity coordinates are calculated for that color.

The principles of tristimulus colorimetry originally were derived for the specification of nonfluorescent colors, but recently these principles have been extended to the specification of fluorescent colors as well. This has generated problems in reflectance spectrophotometry which heretofore were nonexistent.

Some of the major problems involved in determining the tristimulus values of fluorescent paints are: determining the spectral radiance of a fluorescent specimen that is both emitting and reflecting light, irradiating the specimen with sufficient source energy so that the sample emits and reflects an ample intensity of light for spectroanalysis, taking into account the fact that the angle of illuminating and viewing the specimen influences the results obtained, establishing and maintaining a standard reference surface, and choosing a suitable source of illumination.

The adaptation of the Beckman DK-2 spectrophotometer to the measurement of fluorescent paint colors involved mainly the development of an instrument assembly capable of determining, with high resolution, the spectral radiance of fluorescent colors. This included a comparison of photomultiplier detectors for sensitivity, the development of improved chart paper for plotting and recording the spectral character of colors, and the production of an enlarged, multicolor chromaticity diagram to ease eye strain and insure greater user accuracy.

PROBLEM STATUS

This is a final report. Work on this problem has been completed; the problem will be considered closed 30 days after the issuance of this report.

AUTHORIZATION

NRL Problem C03-12
WepTask No. RRMA-52-022/652-1/R007-08-001

Manuscript submitted February 21, 1963.

FLUORESCENT COLOR SPECIFICATION BY MEANS OF THE BECKMAN MODEL DK-2 SPECTROPHOTOMETER

INTRODUCTION

In 1954 the U.S. Naval Research Laboratory (NRL), acting upon request of the Bureau of Aeronautics, commenced developmental research on high-visibility paints of the fluorescent type. The initial purpose of this research was to develop a fluorescent-type paint with superior attention-attracting properties and with a minimum serviceable life (i.e., without excessive fading) of six months when applied to aircraft operating in Florida latitudes. Fluorescent paints having a useful life much in excess of the initial objectives were developed (1,2), and these, in time, became the basis of several military specifications (3-5).

The adequate measurement and specification of fluorescent colors proved to be one of the most difficult and time-consuming tasks associated with the above undertaking. The measurement of fluorescent colors was an area where standards did not exist and where there was even an absence of general agreement on methods of instrumentation and approach to the problem. It was apparent, however, that if the Navy was to procure and make use of these new materials in large quantity, at least a limited standardization of a reliable method of fluorescent color measurement had to be established. The difficulties NRL encountered in these color measurements prompted the Bureau of Naval Weapons to authorize an extension of the Laboratory's research efforts into the area of color measurement, with the general view of effecting maximum simplicity of instrumentation and technique consistent with accuracy.

Rather shortly after undertaking this added research task, it became obvious to the authors that if they were to avoid making a career of fluorescent color measurement studies, some arbitrary decisions concerning instrumentation and method would have to be made. The first, and most important, of these decisions was to point this research directly at the color measurement problem as it concerned specifically the fluorescent paints conforming to military specifications for aircraft usage (3, 4). This decision, therefore, excluded consideration of the wider-in-scope problem of developing a general method for determining the colors of all fluorescent materials, many of which are largely, or even solely, activated by ultraviolet radiation. The latter normally important consideration could be disregarded in this instance because all fluorescent high-visibility aircraft paints meeting current military specifications utilize a clear, light-stabilizing topcoat that absorbs ultraviolet energy. This, then, eliminated the need of choosing a source of illumination that includes ultraviolet energy and led to the choice of I.C.I. Illuminant C (Source C) as the illuminant for these studies. It should be pointed out, however, that almost any standardizable light source could be used, as long as all persons seeking agreement in their results used sources having similar spectral characteristics.

SPECTROPHOTOMETRY AS A MEANS OF FLUORESCENT COLOR MEASUREMENT

Spectrophotometric methods of color specification are recognized as being superior to all others, with the possible exception of visual color matching by the most experienced individuals having perfect color perception. Color spectrophotometry affords the distinct advantage of being completely objective in nature and is independent of the peculiarities of the human eye. Furthermore, this instrumental method affords information on the

spectral distribution and intensity of light reflected by complex mixtures of pigments and dyes in producing the psychophysical response of color sensation. Such information is useful to color formulators.

The principles of tristimulus photometry long have been established and are perhaps best presented in Hardy's "Handbook of Colorimetry" (6). The handbook clearly defines the importance of the spectral distribution of light under which a color is viewed in determining the psychological response of the observer. It further defines Illuminant C (also called Source C) as being the best available laboratory approximation of daylight.

Only recently has spectrophotometry been applied to the tristimulus specification of colors that are fluorescent. The reason for this is largely attributable to the principles embodied in the design of spectrophotometers. Most spectrophotometers used in color measurements function on the principle of illuminating the specimen surface with successive narrow bandwidths of light (called monochromatic light) concurrently sensing the intensity of the reflected light by a suitable detector such as a photocell. The intensity of each narrow bandwidth of light reflected by the specimen is compared with the intensity of the same bandwidth of light reflected by a suitable reference surface, frequently freshly smoked magnesium oxide. Modern spectrophotometers, with recording attachments, continuously plot the ratio of light intensities spectrally reflected by the specimen as compared to the spectral reflectance of the reference surface. The significance of the resulting curve is directly dependent on the nature of the reference surface, and while a number of so-called working standards are in use, it is commonly accepted that a freshly smoked surface of magnesium oxide affords the most uniform reflection of the visible light spectrum.

The results of a spectrophotometric color analysis may be expressed in tristimulus values, which are fundamentally related to the concept that any color can be matched, additively, by a proper mixture of three primary color standards. These are specifically defined hues of red, green, and blue.

To determine the tristimulus values of a fluorescent paint, the paint must be treated as a source of radiant energy. This requires that the fluorescent surface be energized by the full light spectrum to which it will characteristically be exposed, causing it to emit a composite flux of reflected and fluoresced light. Then the light emanating from this surface is spectrally analyzed by a spectrophotometer or other appropriate optical device.

The authors believe that the earliest published work on the spectrophotometric specification of fluorescent colors was by L. J. Boardman, et al. (7), of the U. S. Naval Research Laboratory in 1947. About two years later, A. J. Derr of the Naval Air Material Center carried out measurements on the specification of the color of fluorescent fabrics (8). In order to obtain an achromatic illumination of the fluorescent fabrics, Derr designed and constructed a cylindrical mirror reflectance attachment for a Model DU Beckman spectrophotometer, which he used in conjunction with Source C illumination. However, Derr did not express his color measurements in terms of tristimulus values. Rather, he specified the relative intensity of his fluorescent colors when compared to a reference surface of magnesium oxide at a series of specified wavelengths.

Richard A. Ward extended the principles involved to the specification of daylight fluorescent paints (9). The methods described by Ward simplified the reflectance device used by Derr with the Model DU Beckman spectrophotometer and retained Illuminant C as the source of artificial daylight. Ward's apparatus was capable of yielding reproducible results between laboratories. Its main shortcoming stemmed from the time-consuming laborious procedure required.

The possibility exists for converting any spectrophotometer to a spectroradiometer by illuminating any desired surface with any desired source of light, then dispersing and

measuring the combined reflected and emitted light (emitted only if the surface is luminescent). Data obtained in this manner can be used in determining the tristimulus values of any visible light (color), whether it be from a fluorescent, phosphorescent, or entirely nonfluorescent source. However, some spectrophotometers are very much more difficult than others to adapt to this method, and in many instances the adaptation will preclude use of the instrument in more customary work. The Beckman Model DK-2 (also DK-1) instrument, however, is readily converted to a spectroradiometer without impairing its usefulness for other spectrophotometric work. The DK-2 is a ratio-recording spectrophotometer built around a monochromator and optical system similar to that of the Model DU. As with most automatic recording instruments, it is not as precise as the manually operated Model DU, but it is speedy and dependable.

The Beckman Company advertises the fact that their DK instruments can be used to evaluate fluorescent colors through a process involving reversal of the normal light path (10). However, the authors have found that when the DK instruments, as supplied by the Beckman Company, are used in the manner suggested to measure fluorescence, they do not afford the high resolution required to precisely specify color in terms of tristimulus values. The problem stems from the relatively low levels of energy available to a detector from light sources of any reasonable intensity when the optics of the instrument are reversed in the manner suggested. Although the collective fluorescent and reflected energy from a luminous surface may appear quite bright to the eye, the spectrophotometer must disperse and analyze this energy in very small increments (bandwidths), which is essential to obtain the high order of spectral resolution necessary for the determination of tristimulus values of high accuracy.

In using the reversed light path (as recommended by the Beckman Company), the integrating sphere of the reflectance attachment is illuminated with the chosen light source. The sphere then, in turn, becomes a hemispherical source of diffuse illumination for the specimen to be analyzed. With this method it is not possible to concentrate a large amount of source energy on the specimen. In fact, a relatively low level of illumination, just adequate to provide a signal to the detector, is desirable for, among other things, it has been found that when very large amounts of source energy are concentrated on fluorescent samples, there is a significant increase in their temperatures. This increase in temperature results in less fluorescence than when cooler surfaces are maintained. Stray light also becomes a factor when the source intensity is too great. Obviously there must be some compromise between light intensity, instrument resolution, and detector sensitivity.

The installation of a more sensitive detector than the 1P28 photomultiplier, normally furnished with the DK machines, appeared to be one essential step in solving the problem.

INSTRUMENTATION

Instrumentation Studies

The adaptation of the DK-2 spectrophotometer to the measurement of color of fluorescent paints involved mainly the following five studies:

1. The development of an instrument assembly capable of determining, with high resolution, the spectral radiance of fluorescent, colored surfaces.
2. Improvization of a suitable source of illumination. At the outset it was decided that this source should have the spectral characteristics of the best available, standardized, approximation of average daylight.
3. A study of standard reference surfaces against which to compare the colored specimens.

4. A comparison of photomultiplier detectors, specifically the following:

a. RCA 1P28 furnished as standard equipment with the DK instruments. This is a nine-stage, side-on photomultiplier with an S-5 response (11).

b. RCA 1P21, a nine-stage, side-on photomultiplier having an S-4 response (11).

c. RCA 7265, a 14-stage, end-on photomultiplier having an S-20 response (12).

Other photomultipliers that might have been considered were passed over either because their characteristics were similar to one of the above types, or because their sensitivity was grossly inadequate for the intended use.

5. Development of an improved chart paper for plotting and recording the spectral character of colors, and the production of an enlarged, multicolor chromaticity diagram to ease eye strain and insure greater user accuracy.

Instrument Development

The Beckman DK-2 recording spectrophotometer, with a reflectance attachment incorporating an integrating sphere, has a normal light path such as that shown in Figs. 1 and 2. Light is passed through a prism and slit mechanism, then focused alternately on reference and sample surfaces located at openings in an integrating sphere. The reflected light is sensed by a photomultiplier located at the top of the sphere.

By interchanging the light source and the detector, a method of reversing the light path is established, as illustrated in Figs. 3 and 4.

It is beyond the scope of this article to describe in detail the method of operation and the electromechanical features of the Beckman DK instruments. These details are familiar to spectroscopists. It is sufficient to point out only that this particular equipment is very versatile and dependable in operation and is fully amenable to the modifications and procedures subsequently to be described.

The apparatus which NRL assembled is comprised of four essential subassemblies, the light source (Source C), the Beckman Model DK-2 spectrophotometer with integrating sphere reflectance attachment, the detector assembly consisting of an RCA 7265 photomultiplier, and the auxiliary power supply (Fluke Model 405). A more complete discussion of this equipment and accompanying studies leading to its development follows.

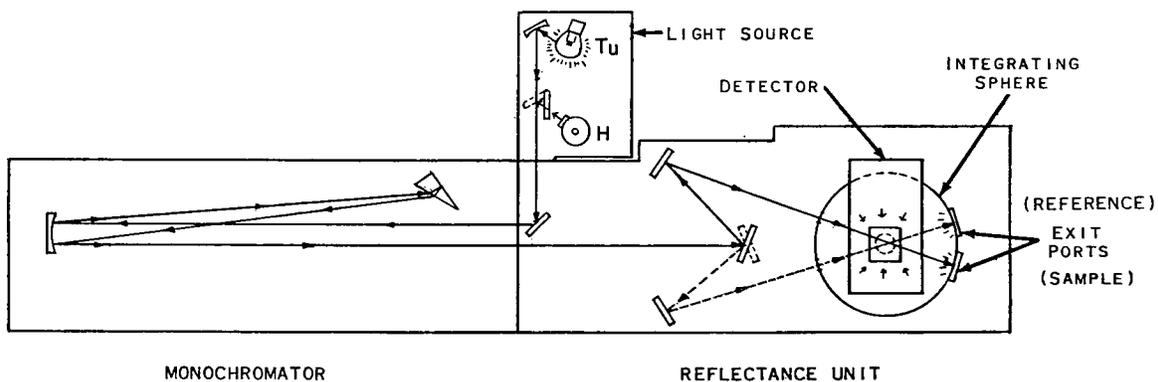


Fig. 1 - Monochromatic illumination light path

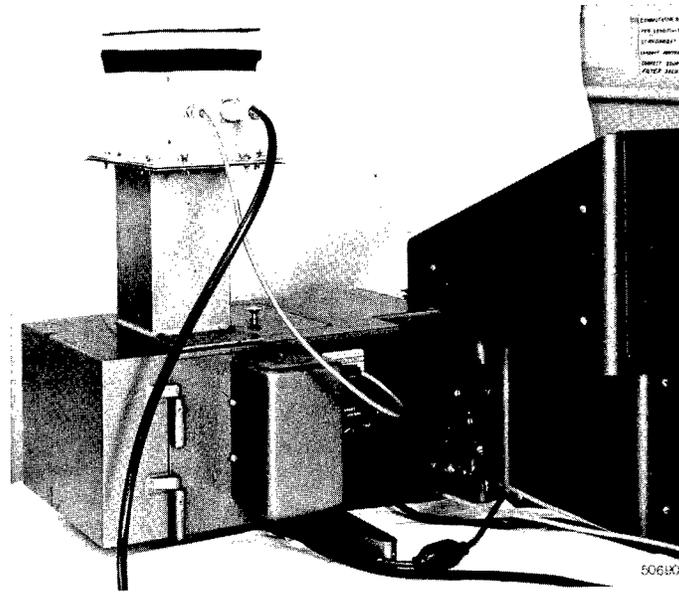


Fig. 2 - Beckman DK-2 reflectance attachment with high-sensitivity photodetector assembly positioned above and viewing interior of the integrating sphere

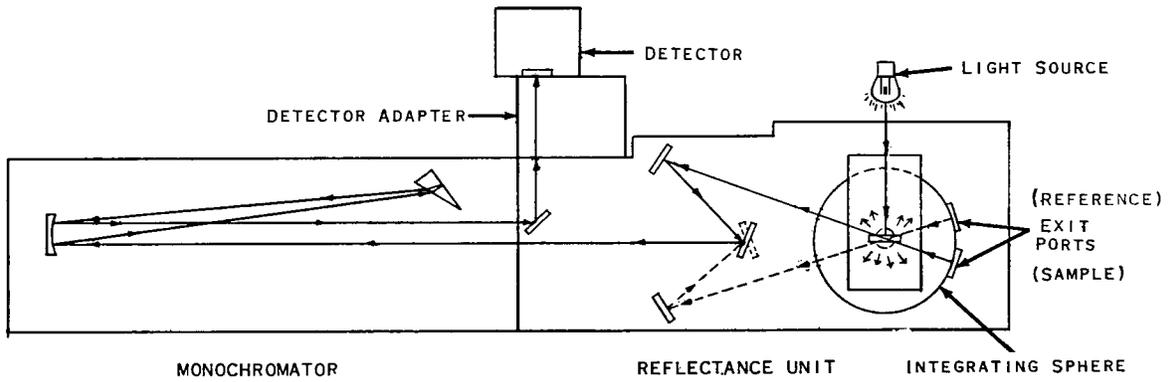


Fig. 3 - Monochromatic detection light path (reverse light path of Fig. 1)

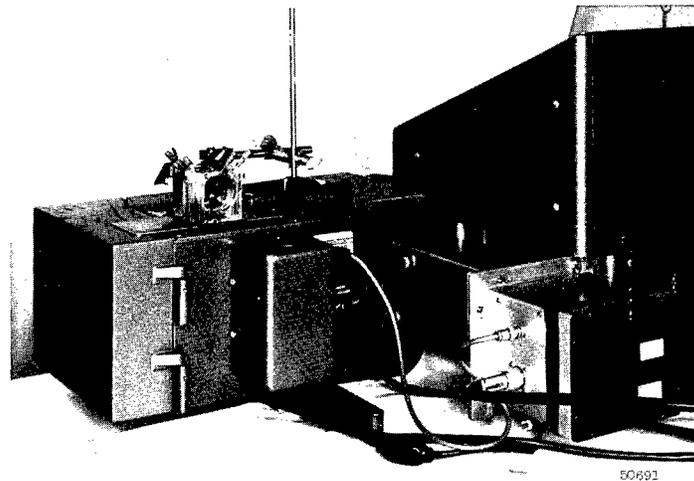


Fig. 4 - Beckman DK-2 reflectance attachment with high-sensitivity photodetector assembly properly positioned for use of the reversed light path. On top of the reflectance attachment are located the Source C filters and a front-surface mirror by which light is directed into the integrating sphere. (Compare with Fig. 2.)

Standard Light Source

As mentioned in the opening paragraphs of this report, Source C was an arbitrary but logical choice of illuminant for these color measurement studies. It is the best available source of artificial daylight, and its characteristics have been standardized and widely accepted for optical usage.

The apparatus assembled to provide a source of artificial daylight is similar to that designed by Ward (9). Its principal components are a 750-watt, Model GK Delinescope (i.e., a projector) made by the American Optical Company, a standard lamp operated at a precise color temperature, and Davis-Gibson Source C filters (13). Source C consists of filtered radiation from a gas-filled tungsten filament lamp operated at a color temperature of 2854°K. Without filters this radiation is defined as Source A.

The composition of the Davis-Gibson solution filters is given in Appendix A. The solutions must be contained in one-centimeter-thick (inside measurement) cells made of nonselective optical glass. Because of the intense light source required, a heat-absorbing filter of distilled water, contained in a cell of nonselective optical glass, is placed between the Davis-Gibson filters and the tungsten lamp. Additional cooling is achieved by directing a fan or blower on the filters while the equipment is in operation. The cells must be sealed to prevent evaporation. Periodic checks of their transmission characteristics is essential because of deterioration induced by heat and light. The spectral transmission of the Davis-Gibson solutions is easily monitored by making a permanent record of the transmissivity curve of the new, pure solutions for comparison with similar curves as the solutions age. A change of two percent in the relative spectrum of these filters justifies their renewal. To retard deterioration of the filter solutions when not in use, it is recommended that they be stored away from light.

To maintain a nonvarying, standard light source, it is necessary to use a constant-voltage transformer in the lamp power supply. Tungsten filament bulbs, calibrated for proper operating voltage and current to give the correct color temperature, are obtainable

from the National Bureau of Standards, Washington, D.C., and from individual lamp companies. A variable transformer for regulating the operating voltage and an accurate voltmeter are necessary accessories. A precision voltmeter is very important as it has been observed that an error of two or three volts in setting the correct operating voltage results in a very significant error in calculating the excitation purity of a fluorescent color. The Laboratory used a Weston Model 341 Electrodynamometer voltmeter (with resistance box) having a maximum error of $1/4$ of 1% of full-scale (120V) deflection. The accuracy of this meter is periodically checked against standard instruments. It is suggested that a voltmeter having an error of no greater than $\pm 1/2$ volt should be used.

The lenses used in the projector must be of nonselective optical glass which is obtainable on special order. The projector is supplied with a heat-absorbing glass filter to prevent overheating of the condenser lenses. Ward recommends removal of this filter to improve the quality of source energy (9). This Laboratory observed only a slight difference in tristimulus values determined with and without the heat-absorbing glass. The trichromatic coefficients of Source C are $x = .310$ and $y = .316$, while of the heat-absorbing filter they are $x = .300$ and $y = .316$. The heat-absorbing filter removes about 26% of the total Source C energy entering it but induces less than a $\pm 1\%$ change in the relative energy spectrum below 570 millimicrons (0.57μ). Above $570\text{ m}\mu$, however, its absorption is sufficient to have a slight effect on the X and Y tristimulus values.* It appears that in order to evaluate material which is marginal in meeting color specifications, it would be necessary to remove the heat-absorbing glass from the optical system. With the filter omitted, the condensing lenses become very hot. This overheating caused the fracture of the first set of lenses procured for these experiments. All subsequent work by NRL on this problem was done with the heat-absorbing filter in place.

Standard White Reference Surfaces

The accuracy of tristimulus values determined from reflectance spectrophotometry is directly dependent upon a knowledge of the color characteristics of a reference surface - usually white - against which the color sample is compared.

A number of different white reference surfaces are in use with optical instruments, but the best known are magnesium oxide, magnesium carbonate, and Vitrolite.† It is generally accepted that the best of these is a freshly smoked surface of magnesium oxide of sufficient thickness to be opaque. Such a surface has a relatively uniform response to the visible spectrum, reflecting between 97 and 98% of all incident energy between 0.4μ and 0.7μ . However, magnesium oxide has several disadvantages. It is a very fragile surface and is susceptible to gradual yellowing and hydrolysis by atmospheric moisture. In addition, there is considerable difficulty in making exact duplicates in different laboratories and from run to run in the same laboratory. When used, it should be prepared in accordance with NBS Letter Circular LC-547 (14) or in accordance with instructions contained in the Beckman Reflectance Attachment Manual.

The freshly scraped surface of a magnesium carbonate block sometimes is used as a substitute for magnesium oxide. Its major advantage is its ease of preparation, involving nothing more difficult than scraping the surface of the block with a sharp razor blade before each day's use. This provides a fresh surface of relatively uniform optical quality on a day-to-day basis. However, the use of magnesium carbonate blocks incurs several disadvantages, namely, (a) not so high and not so uniform a reflectance as that afforded by a properly prepared magnesium oxide surface, and (b) nonreproducible optical properties from block to block of magnesium carbonate. The latter difficulty seems largely

*See Ref. (6) for a detailed explanation of the calculation and use of X, Y, and Z tristimulus values as the basis for the trichromatic coefficients x and y .

†Registered trade name of the Libby-Owens-Ford Company.

attributable to block density, and perhaps particle (crystal) size, and is very difficult to overcome. It is felt that this problem with magnesium carbonate renders it unsuitable as an optical standard for the tristimulus specification of fluorescent paints by widely separated laboratories.

Vitrolite is a relatively satisfactory reference surface for optical measurements in the visible spectral region because of the permanence of its optical qualities. Its disadvantages lie in its considerably lower reflectance as compared to magnesium oxide (87 to 91% for Vitrolite versus 97 to 98% for freshly prepared MgO) and in its slightly less than linear response over the visible region compared to a properly prepared magnesium oxide surface. The lower reflectance of Vitrolite causes some sacrifice in resolution, but its variance from uniform linear reflectivity is so slight as to be an insignificant factor in determining the tristimulus values of red-orange fluorescent paints. Working standards of calibrated Vitrolite are obtainable from the National Bureau of Standards (15), together with correction factors necessary for their use in color measurement photometry.

In addition to these very practical considerations, a characteristic inherent in the design of the Beckman DK-2 spectrophotometer permits its operation in such a manner that the lower overall reflectance of Vitrolite as compared to magnesium oxide can be compensated automatically in the machine as it plots the spectrum of the color being analyzed. This feature obviates the necessity of calculating the required corrections which otherwise would be necessary to obtain accurate tristimulus values. This is easily accomplished by setting the reflectance of the reference standard, i.e., the reflectance of Vitrolite at its proper value as compared to magnesium oxide. NRL's Vitrolite samples have 89% of the reflectance of a freshly prepared MgO surface. If then the reference reflectance is set at 89%, the spectrum of the color being analyzed will be automatically compensated by the machine in such a manner as to reference it to the magnesium oxide. It has been found that when this method of using Vitrolite as a reference is employed, the spectra obtained for red-orange fluorescent paints is virtually identical with similar spectra for the same colors analyzed directly against a freshly smoked surface of magnesium oxide. In no instance have the spectral traces against a Vitrolite standard differed by more than 1% in any part of the spectrum as compared to the spectral radiance of the same fluorescent specimen when run directly against magnesium oxide.

If it is desired that the spectral radiance of the color under analysis be plotted as a function of the intensity of the source itself, this too can be accomplished by taking into account the reflectance of a freshly smoked surface of magnesium oxide - which is about 0.97 if it has been prepared properly. Multiplying 0.97 by the reflectance of Vitrolite (0.89) gives 0.86. Then, using the Vitrolite reference and adjusting the recorder to 0.86 (or 86 on standard chart paper), the spectral radiance of the color under analysis will be plotted as though one were using a perfect reference surface, i.e., one with a reflectance of 100%.

It is very important that the integrating sphere be coated with a magnesium oxide surface of excellent quality. The interior of the sphere provides diffuse illumination of both the reference surface and sample. As the MgO coating ages its efficiency as a reflector decreases, probably due to some take-up of water and other contaminants from the atmosphere. This, then, reduces the light intensity within the instrument, resulting in loss of resolution and in error in the determination of tristimulus values. Of additional significance is the fact that the spectral response of MgO changes nonuniformly for different regions of the spectrum. Specifically, it decreases more rapidly in the blue region than in longer wavelength portions of the spectrum. Thus, when using the reverse light path, this will alter the characteristics of source illumination (Source C). This, then, would lead to an error in the calculation of tristimulus values. Fortunately, the spectral characteristics of a freshly smoked magnesium oxide surface change rather slowly, introducing but slight error if the sphere is resmoked at reasonably frequent intervals. It is recommended that the integrating sphere be recoated with magnesium oxide at least

once every three months, using either the method developed by the National Bureau of Standards (14) or that described in the Beckman Reflectance Attachment Manual.

This deterioration problem with magnesium oxide points up the need for a more stable, high-reflectance surface for the interior of optical spheres. It was beyond the scope of this particular study to make a comprehensive investigation of other substances that might be satisfactory coatings for the interior surfaces of integrating spheres. However, very early in the Laboratory's research there was a limited amount of work with a slurry of barium sulfate (barytes) in an ethyl cellulose matrix as the interior coating of an integrating sphere. This coating provides a diffusely reflecting surface. The results were promising and appear to be worthy of further investigation.

It also has occurred to the authors that a highly polished, specularly reflective, nonselective optical surface might prove fully satisfactory for the interior coating of a sphere used only for color measurements on fluorescent paints by the methods described in this report. This idea was not investigated, however, in the course of these particular studies.

Photomultiplier Detectors

The Beckman DK machines are supplied with two detectors, one of which is a specially selected 1P28 photomultiplier, and the other a lead-sulfide photodetector. The latter is intended for use in the infrared region, while the former is intended for use in the visible and ultraviolet regions of the spectrum. There is a region of overlap from about 0.6 to 0.7 μ where either can be used in ordinary absorption spectroscopy. However, the sensitivity of both of these detectors is wholly inadequate for sufficient resolution when making color measurements on fluorescent surfaces. The reasons for this stem from the reversal of the normal optical path which is necessary to obtain achromatic illumination of the fluorescent specimen, as described in an earlier section of this report.

It was known that the red sensitivity of 1P21 photomultipliers was generally a little better than that of the 1P28's. Consequently, several dozen 1P21 photomultipliers at the Laboratory were screened for good red-sensitivity and low noise in operation. It is to be noted that these characteristics vary by at least two orders of magnitude among a batch of several dozen 1P21's. The basic difficulty in using 1P21's, as with 1P28's, is their rapid decrease in response to the red region of the spectrum. The majority of energy reflected and fluoresced by red-orange fluorescent paints is in the region above 0.6 microns where the sensitivity of the 1P21 is very low, though not so low as that of the 1P28. In the first tests with the best of the 1P21's available, there was insufficient energy available to the detector to yield data having any meaning whatsoever. However, following the adaptation of an RCA 7265, 14-stage photomultiplier to the Beckman DK-2 spectrophotometer (more fully described below), the integrating sphere was resmoked, thereby substantially improving its efficiency. This resulted in a considerable improvement in the operation of the instrument and prompted a retest of the 1P21. On this occasion, satisfactory results were obtained, though based on somewhat less than the desired order of resolution in the red region of the spectrum.

The 1P21 photomultiplier is interchangeable with the 1P28 furnished with the DK-2 spectrophotometer and requires no change in power supply or other modification of the instrument. However, the very small percentage of 1P21's having enough sensitivity for this work would appear to preclude the general acceptance of this type of detector. Further, even the most sensitive 1P21's are satisfactory only when used in conjunction with a freshly smoked sphere and while employing near-maximum adjustable sensitivity of the instrument, thereby incurring excessive background noise.

From these experiments it was apparent that a detector having much greater sensitivity than the average 1P21 and 1P28 was essential to the dependable operation of DK-2 spectrophotometers used in determining the tristimulus values of red-orange fluorescent paints. Unfortunately, all detectors which afford this additional sensitivity make use of a greater number of stages than the 9-stage 1P21 and 1P28's, and they operate at higher voltage. Thus, an auxiliary power supply is required, and no alternative solution to this problem has been found.

The Laboratory selected an RCA 7265 photomultiplier of 14-stages, head-on type and S-20 response, as being most suitable. This photomultiplier can be used with readily available, standard, commercial power supplies and does not involve modifications to the basic DK-2 spectrophotometer. The S-20 response is considerably more favorable at the red end of the spectrum than the S-4 and S-5 response curves characteristic of the 1P21 and 1P28 photomultipliers. A comparison of typical characteristics of the 1P21 and 7265 RCA photomultipliers is illustrated in Figs. 5 and 6.

A detailed description of the RCA 7265 detector assembly, with auxiliary equipment, appears in Appendix B. This equipment proved to be outstandingly suitable for the intended purpose, as will be shown in subsequent portions of this report.

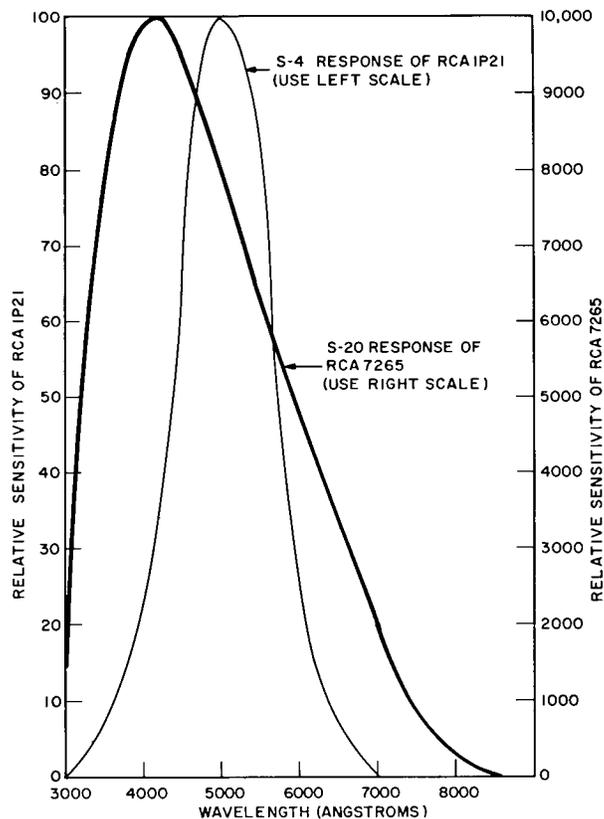


Fig. 5 - Spectral response (relative sensitivity) of RCA photomultiplier tubes 1P21 and 7265 at maximum operating voltage. Notice the great difference (100x) between the two scales.

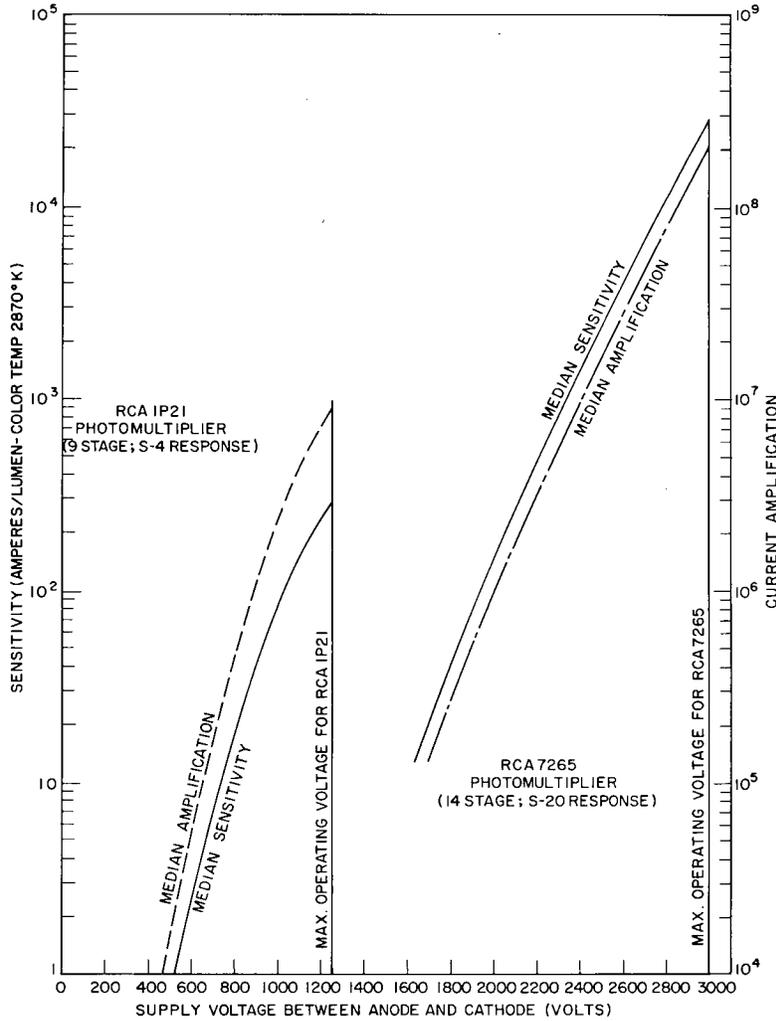


Fig. 6 - Median sensitivity and median current amplification for the RCA 1P21 and 7265 photomultiplier tubes as a function of supply voltage between anode and cathode

Recorder Chart and Chromaticity Diagram

Operator fatigue was found to be a source of error when color measurements on a large number of surfaces required the more-or-less continuous operation of the equipment. Errors were more prevalent when using the manually operated spectrophotometer (the Beckman DU) than when using the Model DK-2. With the DK-2, operator errors could be traced largely to the misreading of recorder charts and the chromaticity diagram; with the manually operated equipment (the Model DU), misreading and maladjustment of dials was a prime source of errors in addition to those resulting from error in reading the chromaticity diagram.

The chromaticity coordinates of red and orange daylight fluorescent paints conforming to military specifications fall within a relatively small area of the chromaticity diagram. Therefore, this sector of the diagram was redrawn in three colors and to a much enlarged scale, significantly reducing the errors attributable to misreading. An example of this improved diagram is included as Appendix C.

It also was apparent that a special recorder paper for the DK-2, designed solely for the purpose of determining chromaticity coordinates by the selected ordinate method, would be helpful. An example of such a chart is shown in Appendix D. This chart paper shows all of the selected ordinates that must be read where crossed by the spectral radiance curve plotted by the machine. Also, it should be noted that the vertical scale of the chart paper has been plotted to a range of 150. This is necessary to allow for the measurement of fluorescent colors having a peak spectral radiance of well over 100% by comparison with standard white reference surfaces. Such conditions are readily handled with the Beckman DK-2 by merely setting the 100% line to the ordinate 100 of the chart paper. Frequently, a new fluorescent surface will display a spectral radiance in excess of 150%. In these cases, the 100% line of the Beckman DK-2 is set to 50 on the chart paper, thereby automatically doubling the ordinate values of the chart. Such a procedure will permit the handling of fluorescent colors with a spectral radiance as high as 300% using the chart illustrated by Appendix D.

A tristimulus value calculation sheet for use in conjunction with this new selected-ordinate chart paper is illustrated in Appendix E.

EVALUATION OF THE INSTRUMENT ASSEMBLY

Methods for Determining Tristimulus Values

The method of determining the spectral radiance (i.e., the sum of fluorescent and reflected light at each wavelength) of a fluorescent specimen is unique by comparison with the treatment of nonfluorescent surfaces. In the spectroanalysis of a fluorescent color, the basic problem is one of illuminating the specimen with a sufficiently intense source of polychromatic light so as to cause the emission and reflection of an ample intensity of energy by the specimen. This then permits instrument detection in the very narrow bandwidths which are essential for high accuracy. Ward accomplished this by the direct, normal illumination of his fluorescent and reference surfaces with Source C light. The surfaces were mounted in such a manner that the light reflected and/or fluoresced from them was viewed at an angle of 45 degrees by a Beckman Model DU spectrophotometer. The apparatus which has been assembled at NRL differs from that designed by Ward in only one essential, namely, in the method of illuminating and viewing the colored and reference surfaces. The NRL equipment is arranged for hemispheric, diffuse illumination of the specimens, with the subsequent viewing of the reflected and fluoresced energy taking place at an angle of 90 degrees (normal) to the surfaces.

When employing the apparatus assembly designed by Ward to determine the tristimulus values of fluorescent paints, it was observed that the value obtained for the excitation purity of a new paint almost always was very high - sometimes exceeding 99%. Such unusually high values seem illogical, although it never has been shown that they are incorrect. It was felt, however, that the validity of any method of determining the tristimulus values of fluorescent colors would be established if correct tristimulus values of non-fluorescent colors could be obtained from the same instrument setup used with the fluorescent surfaces, i.e., reversal of the light path of the DK-2 instrument.

The Laboratory, therefore, compared three different methods of determining the tristimulus values of two nonfluorescent standard colors - Safety Red and Safety Aviation Orange - which were obtained from the National Bureau of Standards. These methods will be referred to herein as follows:

1. the Ward method employing the apparatus assembly designed by Ward (9), but substituting the DK-2 spectrophotometer for the Model DU as indicated;
2. monochromatic illumination in conjunction with the integrating sphere reflectance attachment for the DK-2 (normal light path; see Figs. 1 and 2);

3. monochromatic analysis of the reflectance spectrum, using achromatic illumination by Source C and the integrating sphere reflectance attachment (reversed light path; see Figs. 3 and 4).

Preparation of Fluorescent Test Panels

Inasmuch as this study was devoted solely to instrumentation, it was decided to limit the fluorescent paints to two colors, the fluorescent red-orange (Color No. 633) and the fluorescent yellow-orange (Color No. 634) of specifications Mil-P-21563. Furthermore, the test panels were prepared in strict conformity with these military specifications which, in brief, require the use of a suitable primer to obtain adhesion, a white lacquer undercoat to give high reflectance, a fluorescent color coat of thickness between 2.8 and 3.2 mils, and a 0.9 to 1.1 mil "clear" topcoat containing stabilizers and ultraviolet light absorbers to inhibit oxidation and photolysis. The same panels were used throughout the investigation and were protected against the action of light when not in use.

Figures 7 and 8 illustrate the spectral characteristics of both the fluorescent and nonfluorescent colors used in this study.

The results of the analyses of the nonfluorescent colors appear in Table 1 and do not indicate a significant difference in the tristimulus values as determined by any of the three experimental methods. The NBS photometric values are also shown in the table. It is to be noted that the diffuse reflectance rather than the total reflectance of these colors was measured by the machine. (Because of the diffuseness of fluorescently emitted energy, it is logical to analyze fluorescent colors only on the basis of their diffuse radiance. Therefore, the nonfluorescent colors also must be analyzed on the basis of diffuse reflectance in order that a valid comparison of methods of instrumentation can be made.) Significantly different tristimulus values were obtained when the colors were analyzed on the basis of total reflectance.

Table 2 shows a significant difference in the tristimulus values of the fluorescent paints dependent upon the method of instrumentation for color analysis. Particular note should be made of the Z values, which are indicative of the blue light seen by the instruments at their different angles of viewing the fluorescent surfaces. The amount of blue in the observed spectrum is indicative of degree of color purity - the more pure colors being those having the least amount of blue light in their combined reflected and fluorescent spectra. The relatively low proportion of blue detected at 45 degrees by the Ward-designed equipment explains the unusually high color-purity values obtained and appears attributable to the geometry of the system, which places a longer light path in the color coat itself (which is not opaque) at the 45-degree viewing angle than obtained with the NRL-designed equipment which views the color coat at 90 degrees.

Of equal, or greater interest, however, is the observation that there is a significantly greater intensity of red and yellow energy seen by the Ward-designed instrument. The cause of this phenomenon is not readily apparent. However, since there is close agreement between the two instrumental methods when analyzing colors that are not fluorescent, it must be presumed that the phenomenon of fluorescence itself is a significant factor. A possible explanation hinges on the finer resolution obtainable using the Ward method. When using the 1P21 phototube in the Beckman DK-2 spectrophotometer, it is possible to obtain excellent instrument sensitivity with the optical arrangement set up by Ward. This permits use of a constant slit width of 0.1 mm, or less, corresponding respectively, to effective bandwidths of 35A at 6000A wavelength, and 10A at 4000A wavelength. (It is to be noted that the Ward method specifies the use of a constant slit width of 0.5 mm, or less, when using the Model DU Beckman Spectrophotometer.) The authors have found that narrower slit widths (i.e., greater spectral resolution) produce higher peaks of the spectral radiance curve, therefore resulting in higher values of some of the X and Y tristimulus ordinates occurring between the wavelengths of 5700 and 6500A.

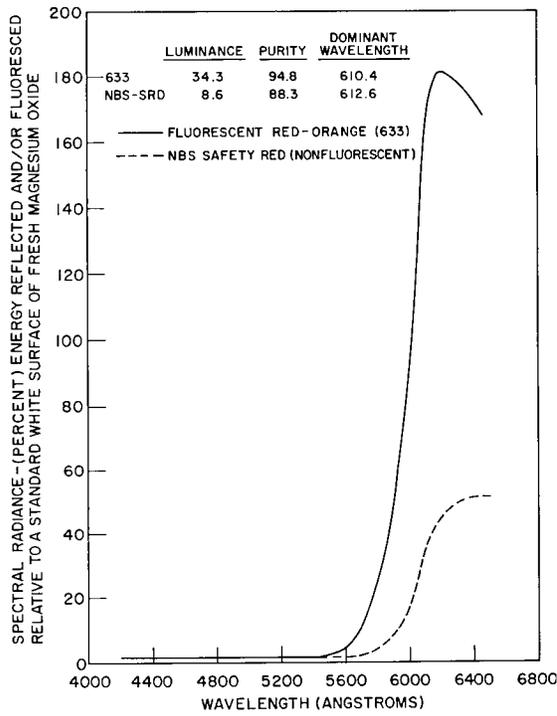


Fig. 7 - Spectral radiance of fluorescent red-orange and nonfluorescent Safety Red paints in the wavelength interval 0.40 to 0.68 μ

Fig. 8 - Spectral radiance of fluorescent yellow-orange and nonfluorescent Safety Aviation Orange paints in the wavelength interval 0.40 to 0.68 μ

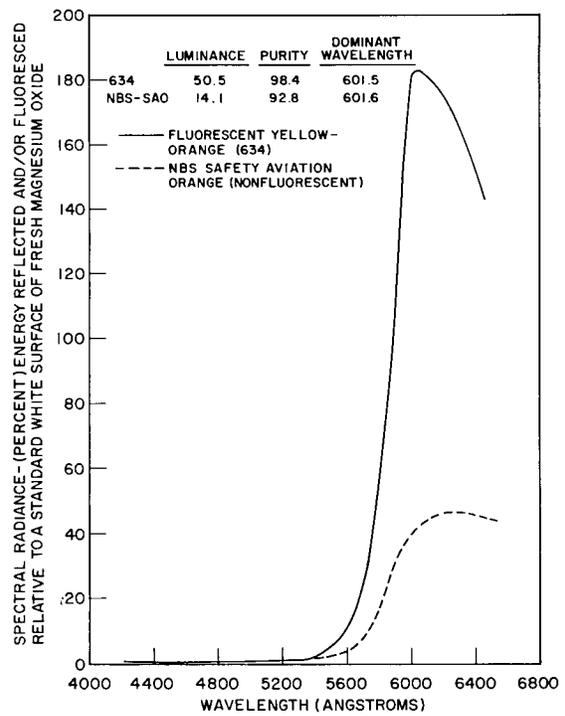


Table 1
Comparison of Color Measurements of Two Standard Nonfluorescent Colors
By the Use of Four Different Methods of Instrumentation

NBS SAFETY RED						
Method	Tristimulus Values*			Dominant Wavelength (m μ)	Excitation Purity (%)	Luminance (%)
	X	Y	Z			
Photometry †	0.175	0.090	0.012	612.6	88.6	9.0
Ward Method	0.163	0.084	0.011	612.6	88.0	8.4
Monochromatic Illumination and Detection (Normal Optical Path) ‡	0.174	0.088	0.011	613.3	89.3	8.8
Achromatic Illumination with Monochromatic (Detection Reversed Optical Path) ‡	0.167	0.086	0.012	612.6	88.3	8.6
NBS SAFETY AVIATION ORANGE						
Photometry †	0.244	0.147	0.013	600.9	91.6	14.7
Ward Method	0.231	0.139	0.0126	601.2	91.2	13.9
Monochromatic Illumination and Detection (Normal Optical Path) ‡	0.262	0.166	0.202	599.2	87.8	16.5
Achromatic Illumination with Monochromatic Detection (Reversed Optics) ‡	0.238	0.141	0.0105	601.6	92.8	14.1

*3rd significant figure is estimated.

†Determined by National Bureau of Standards.

‡Spectrally analyzed on the basis of diffuse reflectance.

Table 2
 Comparison of Color Measurements of Two Fluorescent Colors
 By the Use of Two Different Methods of Instrumentation

FLUORESCENT RED ORANGE (With Clear Topcoat)*						
Method	Tristimulus Values†			Dominant Wavelength (m μ)	Excitation Purity (%)	Luminance (%)
	X	Y	Z			
Ward Method	0.744	0.366	0.004	611.9	99.0	36.6
Achromatic Illumination with Monochromatic Detection (Reversed Optical Path)‡	0.669	0.343	0.020	610.4	94.8	34.3
FLUORESCENT YELLOW ORANGE (With Clear Topcoat)*						
Ward Method	0.904	0.518	0.0030	602.1	99.6	51.8
Achromatic Illumination with Monochromatic Detection (Reversed Optical Path)‡	0.828	0.480	0.0076	601.5	98.4	50.5

* Contains an ultraviolet light absorber.

†3rd significant figure is estimated.

‡Spectrally analyzed on the basis of diffuse reflectance.

When using the reflectance attachment with integrating sphere and the reverse light path, as in the NRL-instrument assembly, it is not possible to obtain 0.1-mm slit width resolution, even with the powerful RCA 7265 phototube. The reason for this, of course, is attributable to the lower efficiency of the sphere in illuminating the test surface with Source C energy as compared to direct illumination of the test surface by the source itself in the Ward method.

DISCUSSION OF RESULTS

The primary object of these studies has been to develop a rapid and accurate instrumental means for determining the color characteristics of daylight fluorescent paints conforming to military specifications (3,4). At an early stage in this research, it was concluded that reflectance spectrophotometry was the best method for determining the color characteristics of these new coatings because of the complete objectivity and good accuracy of the method.

The first fully satisfactory means for specifying these new colors by spectrophotometry was developed by Ward, as described in earlier sections of this report. It is the Laboratory's view that the instrument assembly used by Ward is the least expensive and most accurate equipment readily available for the color measurement of fluorescent paints. The Ward method of instrumentation has some disadvantages, which have been outlined, but its forte lies in its economy of equipment and the ability to give reproducible results from laboratory to laboratory. NRL is of the opinion that the accuracy and agreement of results between laboratories can be improved by utilizing a better reference, or working standard, than the magnesium carbonate block used by Ward. The Naval Research Laboratory has observed a wide variation in the reflectance of magnesium carbonate blocks secured from different sources. On the other hand, the Laboratory has experienced very satisfactory and reproducible results by using a reference standard of white Vitrolite. Such a standard seems preferable, after calibration, even to a freshly smoked magnesium oxide surface because of the difficulty of obtaining uniformity of these smoked surfaces when applied by different operator techniques.

The Laboratory has found that the detectors furnished with the Model DK-2 Spectrophotometers are unsatisfactory for the accurate specification of color of fluorescent paints by the reversed-light-path method. The reason for this is lack of detector sensitivity, resulting in very poor instrument resolution of the reflected and fluorescent spectrum of the coating. The only fully satisfactory solution was found in the use of the RCA 7265 photomultiplier, of much higher sensitivity than those furnished as standard equipment.

Until recently there has been virtually no demand for the precise measurement or specification of fluorescent colors. The demand for such measurements still are small compared to the extensive use of color measuring devices for the specification of non-fluorescent colors. However, the use of fluorescent colors is rapidly increasing, virtually assuring the need in the near future for better equipment with which to measure and specify these colors. It appears to be entirely practical to design a compact light source and reflectance accessory for any spectrophotometer such that it then can be utilized to determine the tristimulus values of fluorescent colors.

Finally, the accurate specification of tristimulus values demands excellent resolution in the analysis of any color. The apparatus designed by Ward made use of a fixed slit width not to exceed 0.5 mm. In the Beckman Model DU (and DK-2) this corresponds to an effective bandwidth of about 220A at 645.9m μ (the highest ordinate used in the calculation of tristimulus values by the ten-selected-ordinate method) and of 50A at 422.2 m μ (the lowest selected ordinate). The fact that this resolution cannot be obtained in the reverse-light-path setup with the 1P28 and lead-sulfide detectors furnished with the

Beckman DK-2 necessitated construction and assembly of the accessories which are described in this report. In no case should the requirements upon resolution be less than those prescribed by Ward, and better resolution (i.e., slit widths of 0.3 mm or less) appears highly desirable. The main advantage to be obtained from finer resolution is a more correct indication of the radiance of the color for all wavelengths. If, when using similar instrument assemblies, the specification of these colors is expressed in the subjective parameters of dominant wavelength, purity, and luminance, one would find that there is no significant difference between these values when they are determined for different degrees of spectral resolution, provided that at least the minimum condition (0.5 mm) recommended by Ward is observed. However, a sharper and higher peak radiance is obtained for the better orders of resolution. While the location and value of this peak reflectance may not be significant in the subjective specification of color for given tristimulus values, it is significant in quality control for purposes of military procurement.

CONCLUSIONS

The precise specification of fluorescent colors, particularly those of high luminance, can best be accomplished in terms of tristimulus values. If desired, tristimulus values can be converted to chromaticity coordinates (referring to the standard chromaticity diagram) and luminance, and these factors in turn can be expressed in the subjective parameters - dominant wavelength, excitation purity, and luminance.

There is no difference between any of the fundamental principals which form the basis of various instrument designs reported by prior researchers (7-9) and those used by the authors. However, since the instrument design, particularly relative to angle of illumination and viewing, influences the results obtained, it is desirable to standardize these treatments.

This Laboratory further concludes that calibrated Vitrolite, or equivalent, reference surfaces should be used by all laboratories having the need to specify the color of fluorescent materials. Magnesium carbonate varies too much in quality to make a good standard for comparing work between laboratories. Technique in the preparation of freshly smoked magnesium oxide surfaces is a significant factor in determining the quality of such surfaces and has been found to vary widely from operator to operator. Thus, while a properly prepared magnesium oxide surface is the best reference surface obtainable, it may prove very difficult to standardize the technique for the application and use of this surface.

Source C is a suitable and logical source of illumination.

There is need for a device specifically designed for the color measurement of fluorescent surfaces by spectrophotometry. Such a device should be a readily procurable accessory for one or more of the widely used standard spectrophotometers and should include provision for a standard source of illumination, specifically Source C.

The NRL instrument assembly described in this report is quite satisfactory for the spectrophotometric measurement of daylight fluorescent colors. However, its only advantages over the assembly designed by Ward, using the Model DU spectrophotometer, are speed and minimization of operator fatigue. This is important where a great many color measurements must be made. However, for a single determination, the equipment based on the manually operated Model DU probably is the more accurate. The authors believe that the shortcomings of the automatic recording spectrophotometer can be overcome if a special fluorescence-reflectance accessory is devised. The chief requirements of such a device are a standard light source, a very high sensitivity detector (at least equivalent to the RCA 7265), and a more compact optical system to reduce the length of the light path.

It is recommended that all government procurement specifications for daylight fluorescent paints express color requirements in terms of tristimulus values and, in addition, impose a requirement for the minimum peak spectral radiance at a desired wavelength. This latter requirement is a quality control feature and is not necessary to the subjective description of the fluorescent color itself.

REFERENCES

1. Cowling, J.E., and Noonan, F.M., "Development of High-Visibility Paints," NRL Memorandum Report No. 546, Dec. 1955
2. Noonan, F.M., and Cowling, J.E., "Methods of Accelerated Weather Deterioration for Fluorescent Paints," NRL Report 5027, Nov. 1957
3. Mil-P-21563; "Paint System, Fluorescent, for Aircraft Application," Aug. 4, 1958
4. Mil-P-21600; "Paint, Fluorescent, Removable, for Aircraft Use," Feb. 5, 1960
5. Mil-P-21698(Aer); "Paint, Fluorescent, for Aircraft, Process for Application of," Oct. 14, 1958
6. Hardy, A.C., ed., "Handbook of Colorimetry," Cambridge: The Technology Press, MIT 1936
7. Boardman, L.J., Dawson, L.H., Furlong, L.R., and Plymale, W.S., Jr., "Measurement of the Color Characteristics and Brightness of Fluorescent and Phosphorescent Material," NRL Report 3143, June 1947
8. Derr, A.J., "Spectral Requirements of Fluorescent Neon Red Fabric," Naval Air Material Center Report No. AML NAM AE 525108, Part I, July 1951
9. Ward, R.A., "The Day-Glo Color Specification System," Cleveland, Ohio: Switzer Bros., Inc., 1952
10. Beckman Instruments, Inc., Bulletin Number 19, Fullerton, Calif., 1957
11. RCA Tube Handbook HB-3
12. RCA Brochure 7265, Sept. 1958
13. Davis, R., and Gibson, K.S., "Filters for Reproduction of Sunlight and Daylight, and the Determination of Color Temperature," National Bureau of Standards Miscellaneous Publication 114, 1931
14. "Preparation and Colorimetric Properties of a Magnesium Oxide Reflectance Standard," NBS Ltr Circ LC-547, 1939
15. "Standards for Checking the Calibration of Spectrophotometers," NBS Ltr Circ LC-1017, Jan. 1955 (this report concerns the 200 to 1000 m μ wavelength region)

APPENDIX A

COMPOSITION OF DAVIS-GIBSON SOLUTION FILTERS FOR SOURCE C

Solution C₁

Copper Sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	3.412 gr.
Mannite ($\text{C}_6\text{H}_8(\text{OH})_6$)	3.412 gr.
Pyridine ($\text{C}_5\text{H}_5\text{N}$)	30.0 cc.
Distilled water to make	1000.0 cc. at 77° F

Solution C₂

Cobalt-ammonium sulphate ($\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$)	30.580 gr.
Copper Sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	22.520 gr.
Sulphuric acid (density 1.835)	10.0 cc.
Distilled water to make	1000.0 cc. at 77° F

APPENDIX B

DESIGN DETAILS OF THE PHOTOMULTIPLIER DETECTOR ASSEMBLY

The physical appearance and construction of the new detector assembly are shown in Fig. B1. The unit, fabricated of welded and dipped aluminum sheet metal, consists of a mounting plate (7) holding the tube socket clamp (6), and a housing (9) surrounding the tube (8) and coupling it to the spectrophotometer, as shown in Fig. B2. A box (2) is attached to the rear of the mounting plate supporting the connectors and containing the voltage-divider resistor board on which are mounted the focusing and accelerating electrode controls (1). This arrangement makes the latter readily accessible for adjustment from the rear of the box. (Since the focusing-electrode control is connected at the negative high-voltage end of the divider, it is important that it, in particular, be well insulated.) The anode load resistor is connected at the output connector (4), a type BNC, single-conductor, chassis-mounted receptacle designated UG-625/U (single-hole mounted). (The less-convenient type UG-290/U (Amphenol 31-003) may be substituted by drilling four additional small screw holes.) The high-voltage connector (3) is a single-conductor, chassis-mounted receptacle designated UG-560/U (Amphenol 82-805). The bypass condensers, C1 to C6, are connected to the indicated tube socket terminals. The socket (5) has twenty pins and is made by Alden Products Co. and designated as No. 220FT.

The tube housing (9) is notched at one end to conform to the dimensions of the Beckman instrument, and it is fitted with a black-felt gasket at the open end to provide a light-tight seal around the instrument aperture. Two bolts hold it in place against the Beckman mounting plate. They are enclosed in light-tight tubes welded to the sides of the housing. Two positioning lugs, which engage holes in the mounting plate, are also welded into the side of the housing notch. A flange is welded to the other end of the housing and this is fastened to the detector unit mounting plate by means of wing nuts on the bolts that are also used to hold the resistor board box to the other face of the mounting plate. The inside of the tube housing and the adjacent mounting-plate face are coated with flat-black paint, and the joint between the flange and the mounting plate is sealed with a black-felt gasket. The normal-light-path tube housing (10) is similarly constructed and treated, but it is provided with a flat flange at the outer end, instead of the notch, for attachment to the spectrophotometer above the integrating sphere.

The resistor box is provided with a flange for attachment to the mounting plate. A removable top plate on the box provides ready access to the internal connections. A collar or extension matches a small flange on the rear of the box (which is open at the back) and serves to hold the bakelite resistor board in place and also to house the resistors and control shafts. A black bakelite cover completes the component enclosure. It contains two holes opposite the control shafts so that the controls may be adjusted with a specially insulated screwdriver used for high-voltage electronic work. The tube socket is cushioned and light sealed in a strip of black felt inside the socket clamp. The tube itself is wrapped in a double layer of μ -metal sheet which contacts the metal collar connected to the focusing electrode operating at a high negative potential. This metallic shielding is held in place by a tight wrapping of black plastic tape which extends the full length of the tube and base. This treatment was considered necessary as a safety feature providing protection against stray light, high voltage, and stray electromagnetic fields, thereby contributing to stable operation of the tube.

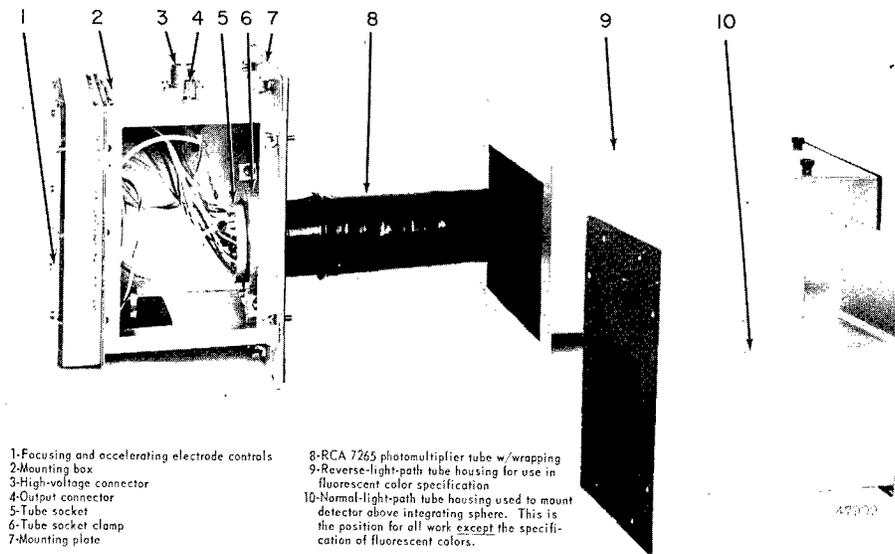


Fig. B1 - Major components of the photomultiplier detector assembly

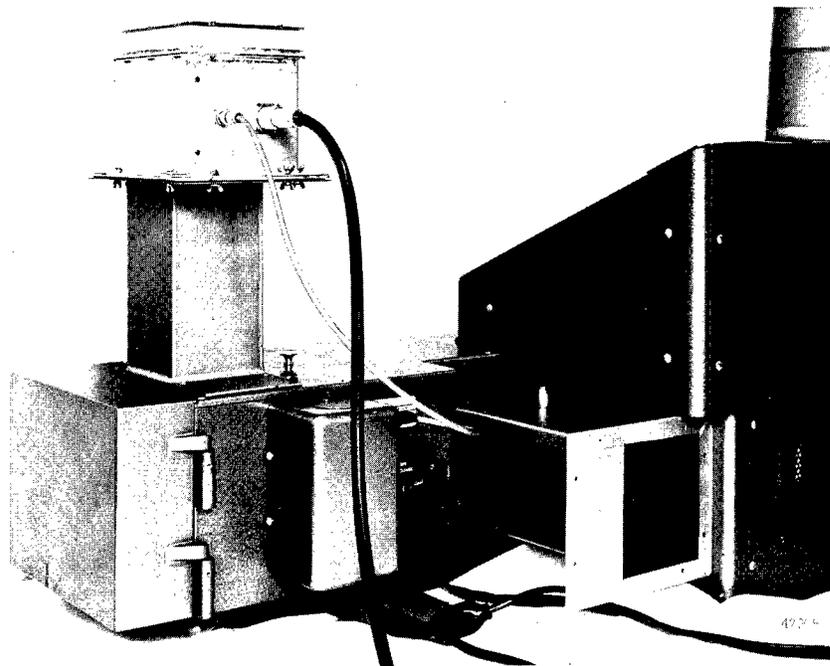
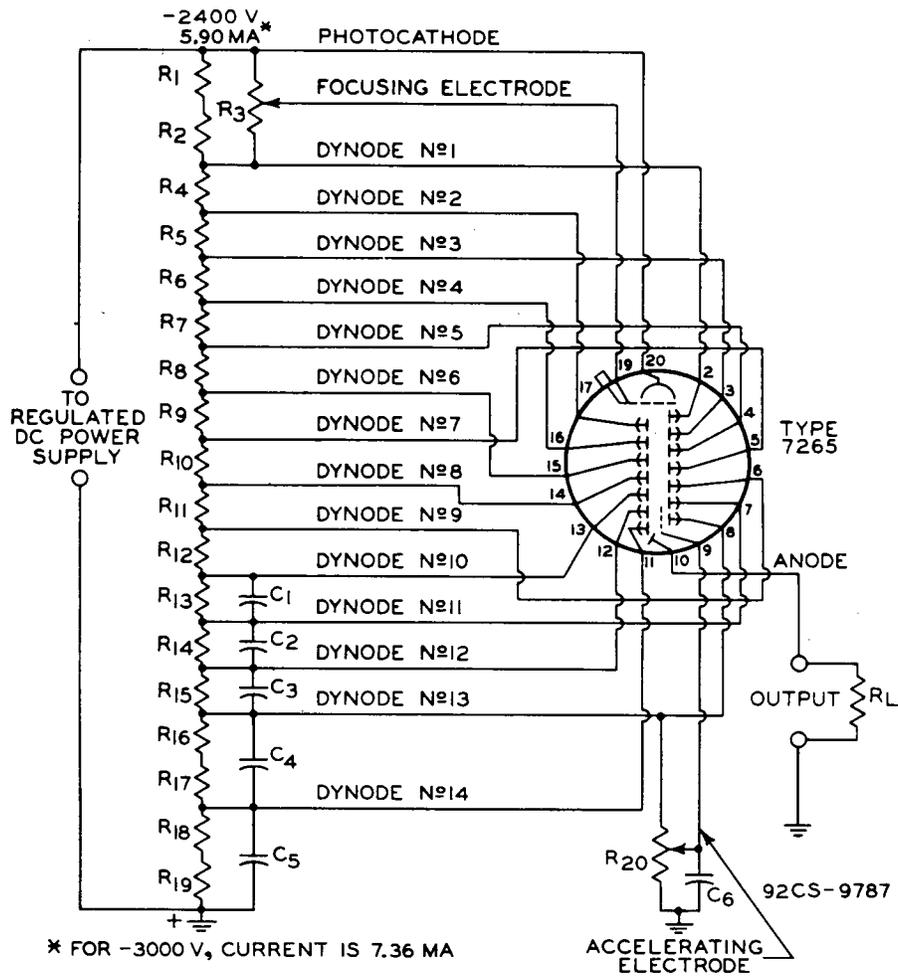


Fig. B2 - Reflectance attachment showing method of mounting both photomultiplier housings illustrated in Fig. B1. In actual use one or the other of these housings must be replaced by the light source.



* FOR -3000 V, CURRENT IS 7.36 MA

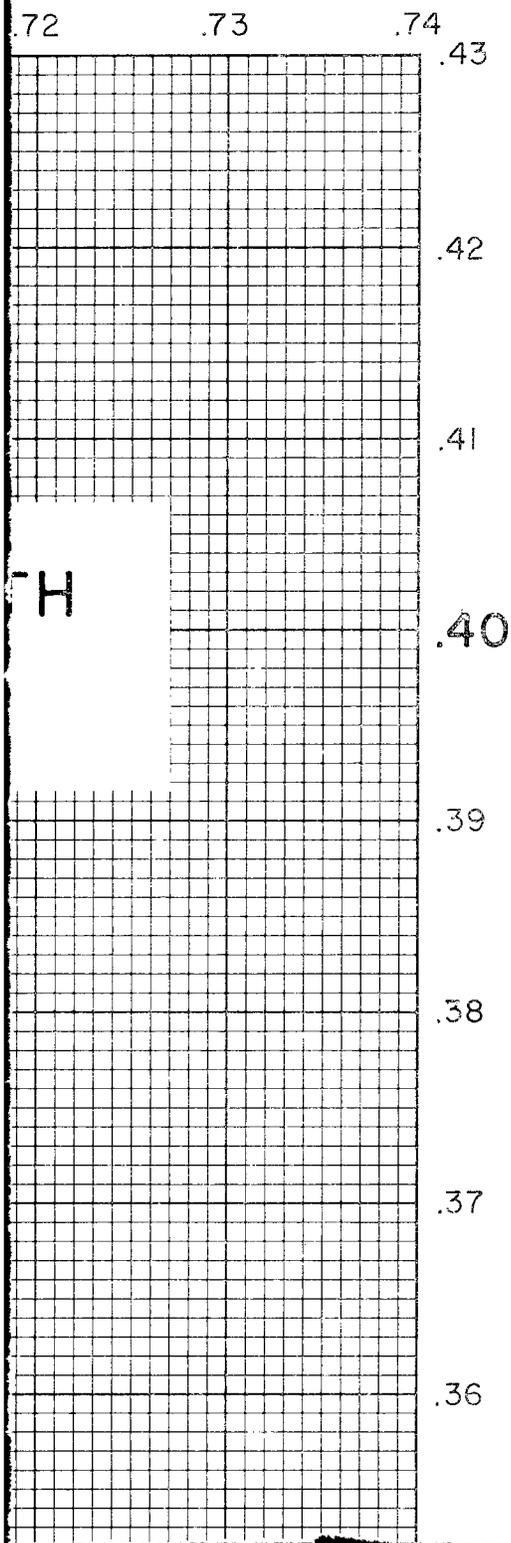
- | | |
|--|---|
| $C_1 = 25 \mu\mu\text{f}$, disk ceramic, 600 volts (dc working) | $R_{14} = 54000$ ohms, 2 watt |
| $C_2 = 50 \mu\mu\text{f}$, disk ceramic, 600 volts (dc working) | $R_{15} = 66000$ ohms, 2 watt |
| $C_3 = 100 \mu\mu\text{f}$, disk ceramic, 600 volts (dc working) | $R_{16} = 44000$ ohms, 2 watt |
| $C_4 = 250 \mu\mu\text{f}$, disk ceramic, 600 volts (dc working) | $R_{17} = 36000$ ohms, 2 watt |
| $C_5 = 500 \mu\mu\text{f}$, disk ceramic, 600 volts (dc working) | $R_{18} = 44000$ ohms, 2 watt |
| $C_6 = 100 \mu\mu\text{f}$, disk ceramic, 1000 volts (dc working) | $R_{19} = 44000$ ohms, 2 watt |
| $R_1 = 48000$ ohms, 1 watt | $R_{20} = 10$ megohms, 2 watt, adjustable |
| $R_2 = 44000$ ohms, 1 watt | $R_L = 10000$ ohms. Value will depend on magnitude of peak signal voltage desired, and characteristics of first stage of Beckman preamplifier |
| $R_3 = 2$ megohm, 2 watt, adjustable | |
| R_4 through $R_{13} = 44000$ ohms, 1 watt | |

Fig. B3 - Voltage-divider arrangement for the RCA 7265 photomultiplier tube

The phototube socket was wired to the resistor board and associated components in accordance with the circuit shown in RCA Brochure 7265 (see Ref. 12 and Fig. B3). However, since many high-voltage regulated supplies are limited to a 5-ma maximum output, it was decided to hold the current requirement of the detector unit under this value by doubling the RCA-recommended values of the resistors in the dynode bleeder stick, including the value of the focusing-electrode control R3. A 20-megohm control for R20, the accelerating electrode control, was not available so this value was left at 10 megohms on the assumption that a shunting resistance of over 50 times a given value should have a negligible effect. Low-noise, molded, boron-carbon resistors were used for the bleeder stick.

Referring to the preamplifier circuit of the Beckman model DK-2 spectrophotometer and to the recommended operating conditions for the 1P28 phototube in the RCA tube manual, it appears that a maximum stable output of approximately one volt is developed across the anode-load resistor network of the phototube. By the use of a 10,000-ohm anode-load resistor for the 7265 tube, the same output is developed by a current of $100\mu\text{amp}$, a value well below the limit recommended by RCA for stable, noise-free operation of the tube. The Laboratory obtained the most stable operation with adequate amplification when using an applied voltage of -1900V from a Fluke Model 405, regulated, dc power supply. (Other RCA 7265 phototubes might require slightly different optimum voltages.) The detector output was connected by a shielded cable to pins D and E of a plug matching the Beckman preamplifier input socket. (Pin D is connected to the cable shield.)

It was found that the tremendous amplification available with this circuit made it necessary to use every possible precaution to keep stray light from reaching the phototube. Liberal use of black masking tape around light-tight joints reduced the background substantially, and a black cloth draped over the entire unit further improved tube operation by excluding trace leaks of light.



UNCLASSIFIED

.35

.34

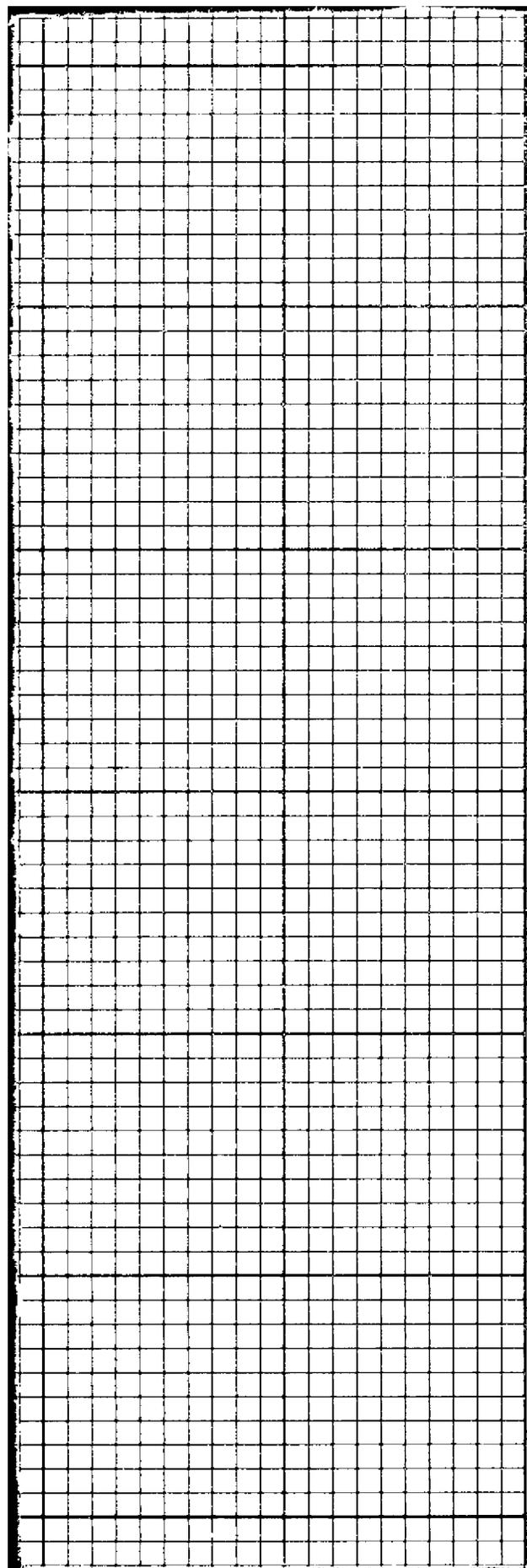
.33

.32

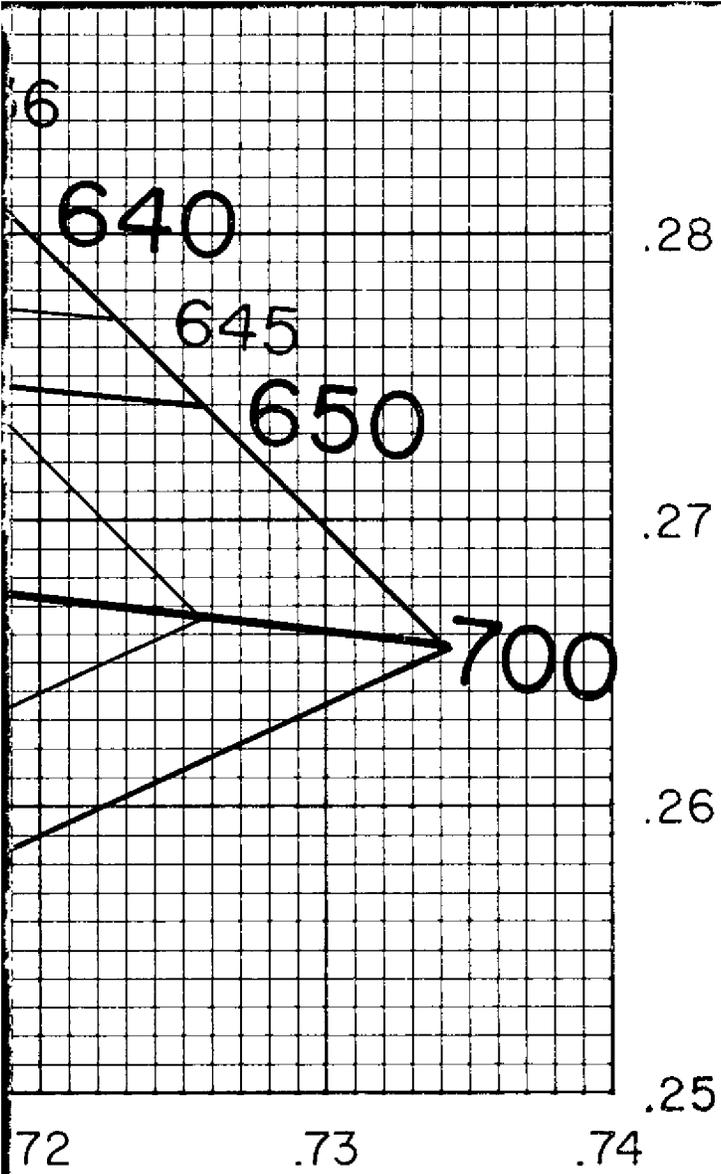
.31

.30

.29



UNCLASSIFIED



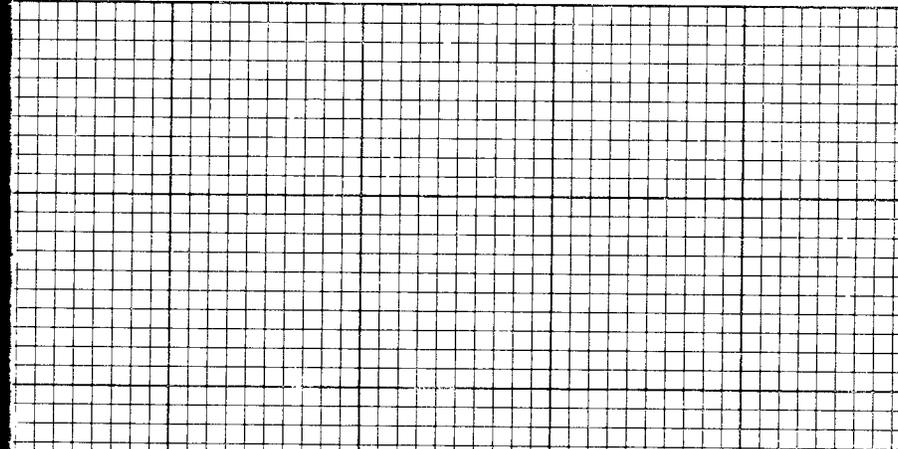
LABORATORY

.68

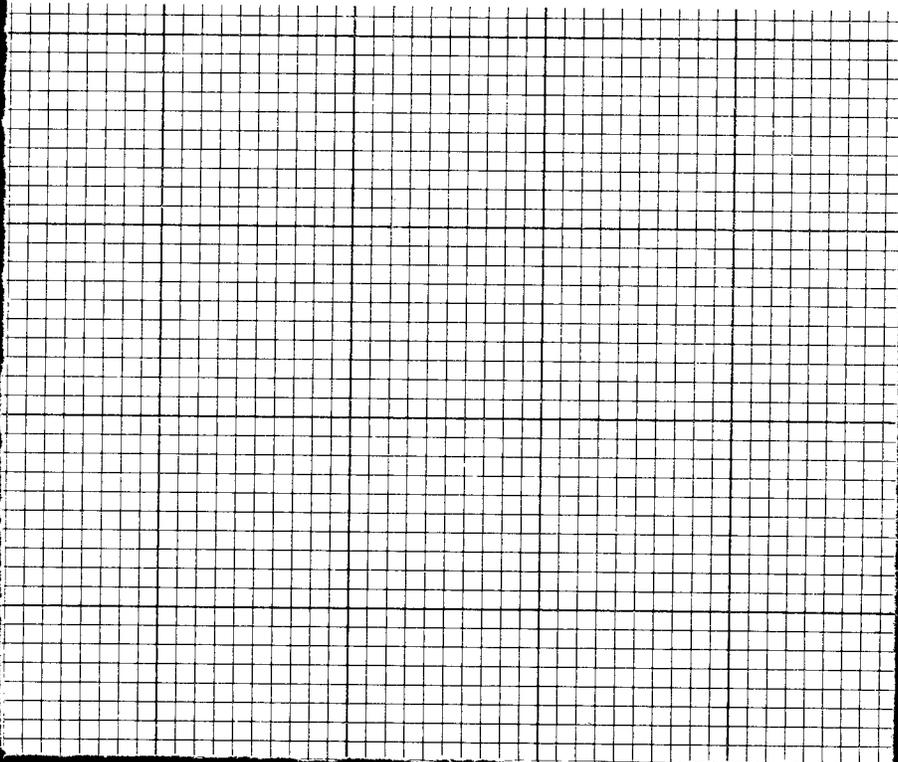
.69

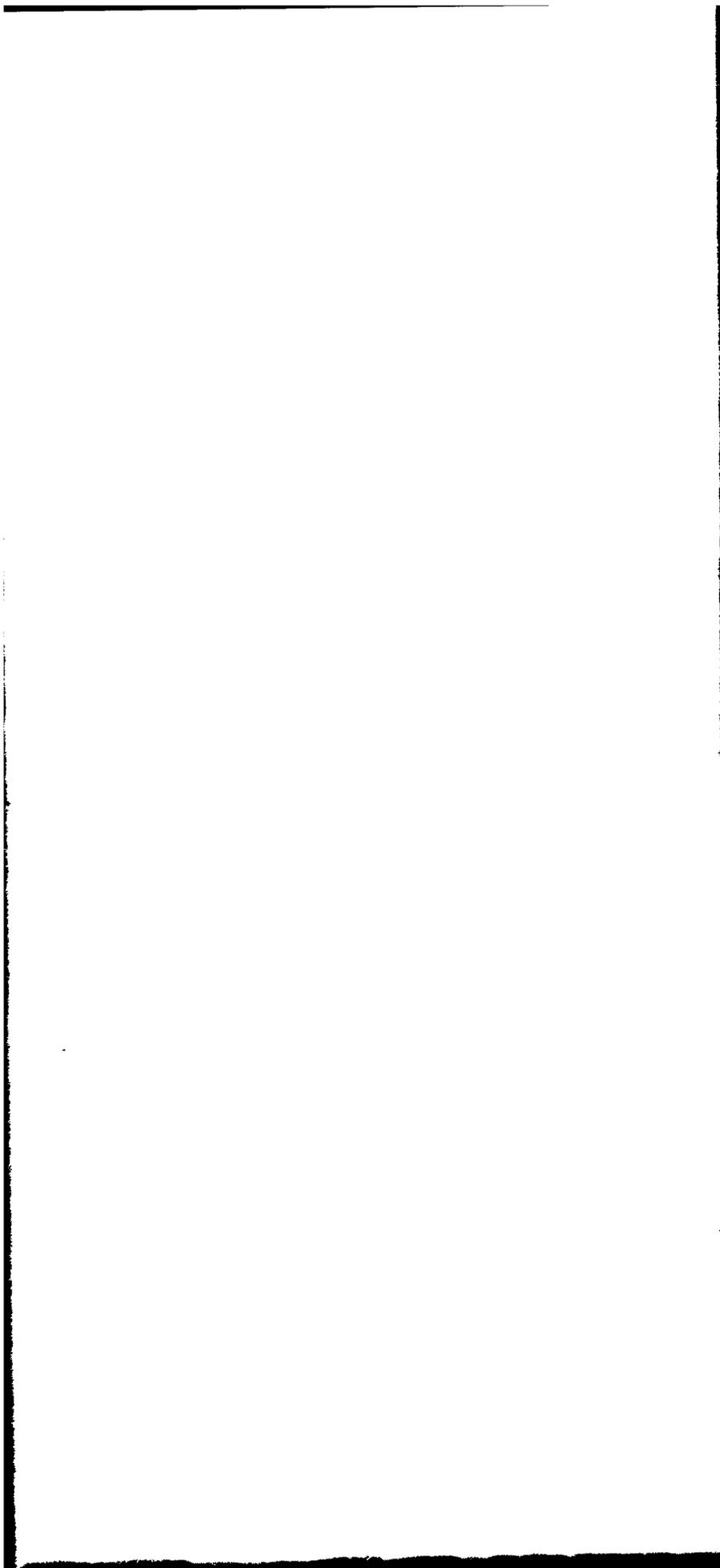
.70

.71



— DOMINANT WAVELENGTH
— EXCITATION PURITY





UNCLASSIFIED

612

613

614

615

616

617

618

619

620

622

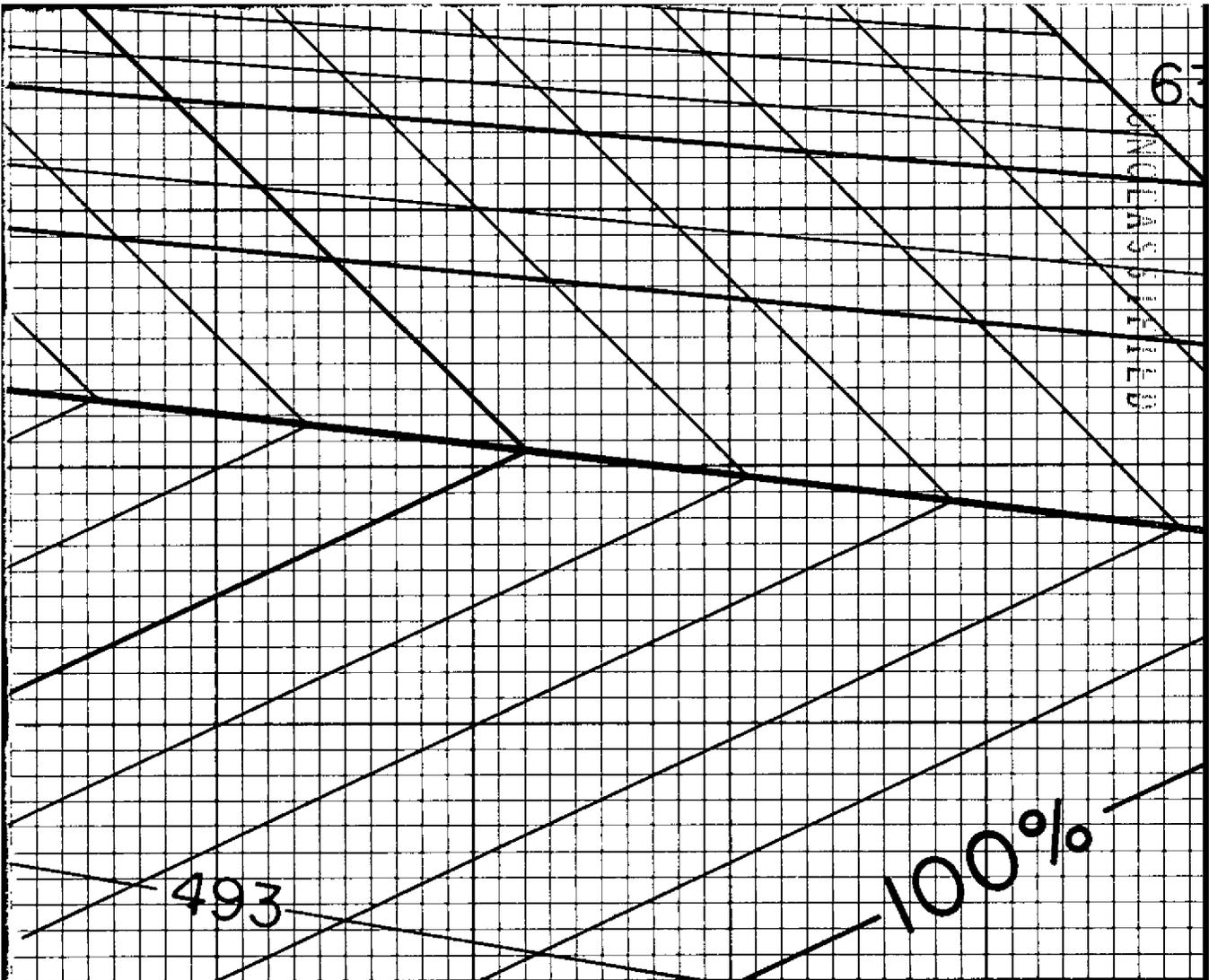
624

626

628

630

632



.68

.69

.70

.71

493

100%

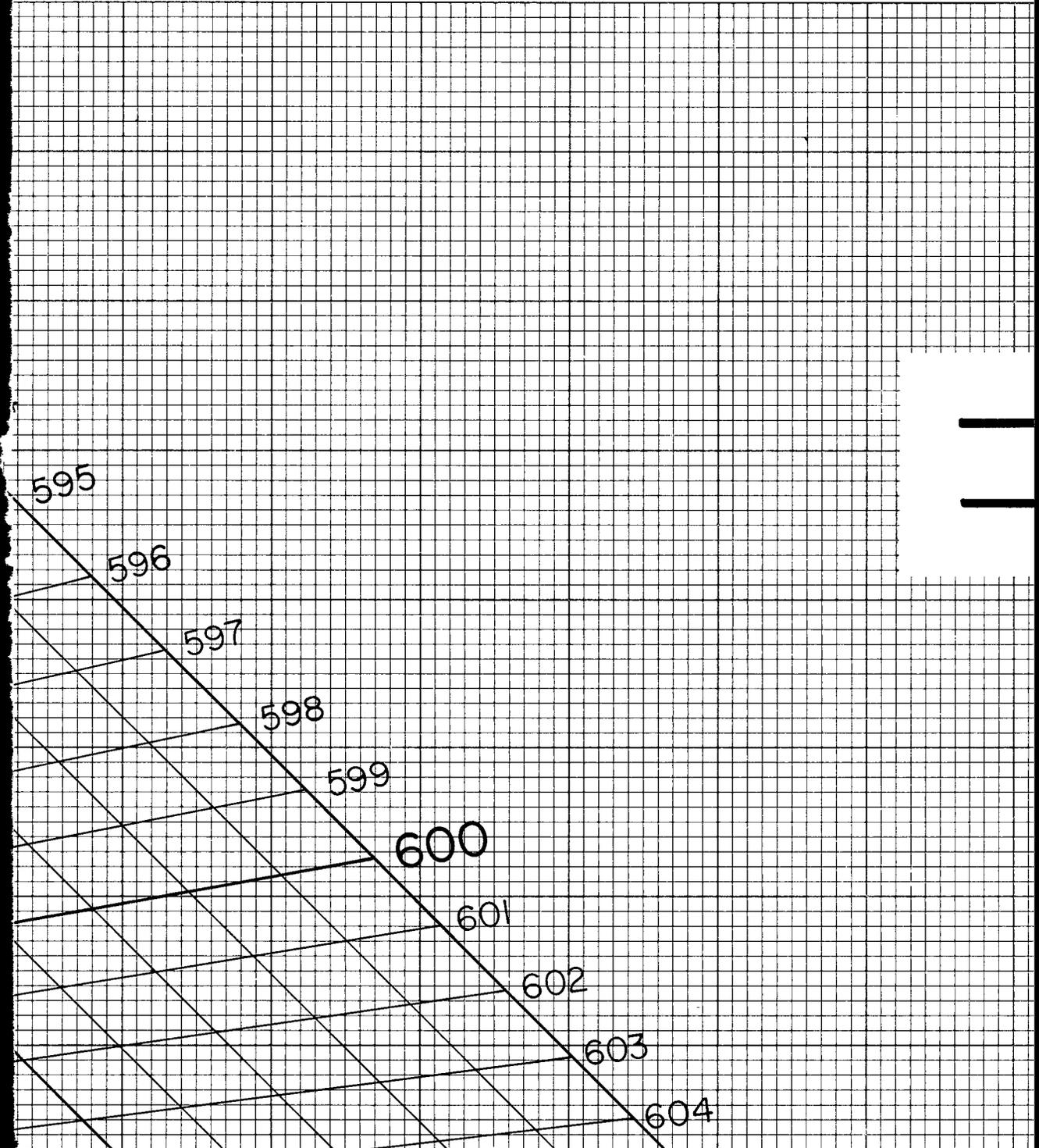
UNCLASSIFIED
63

CHEMISTRY DIVISION
U.S. NAVAL RESEARCH
WASHINGTON, D.C.

APPENDIX C

PORTION OF THE CHROMATICITY DIAGRAM

.61 .62 .63 .64 .65 .66 .67



605

606

607

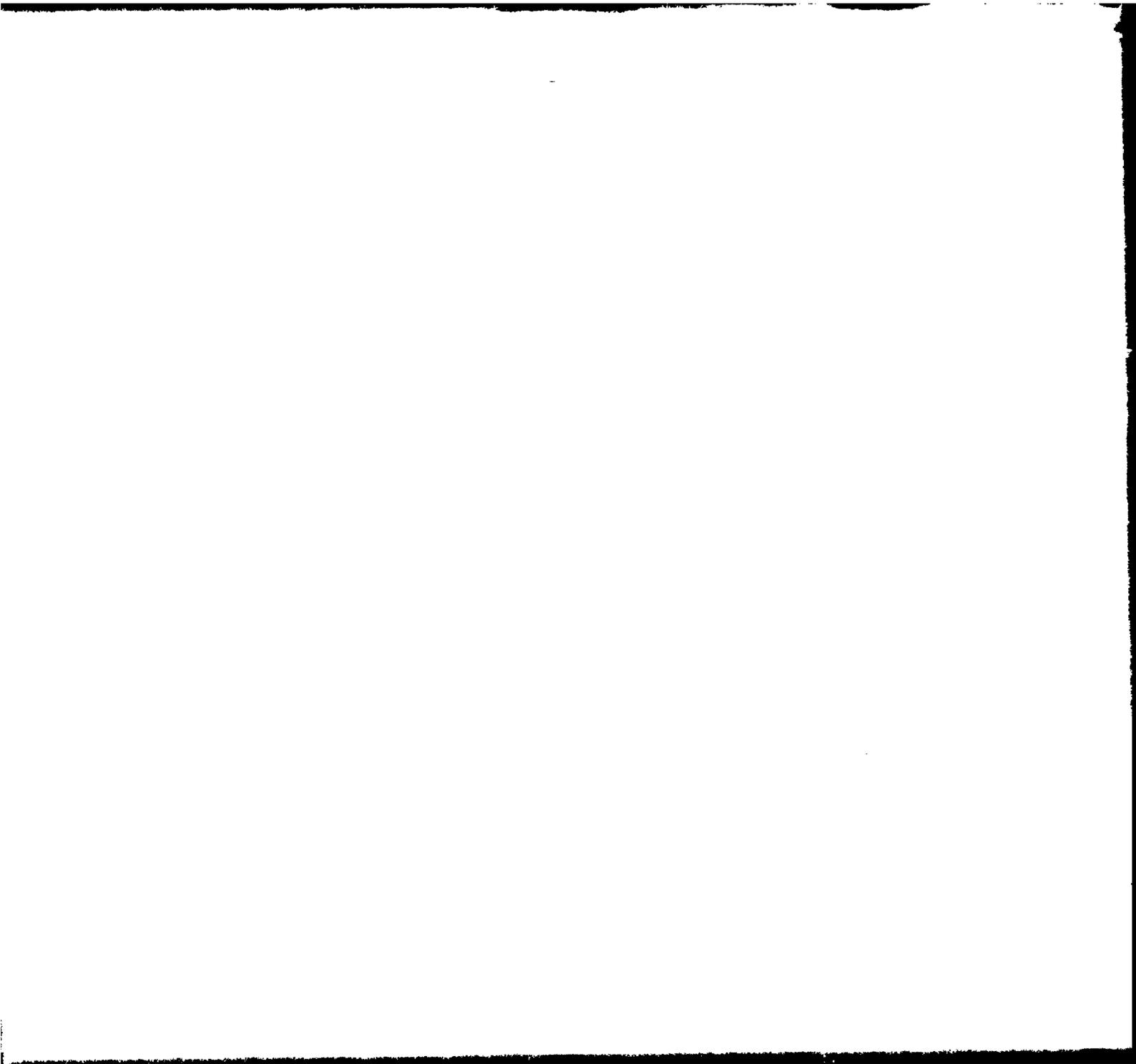
608

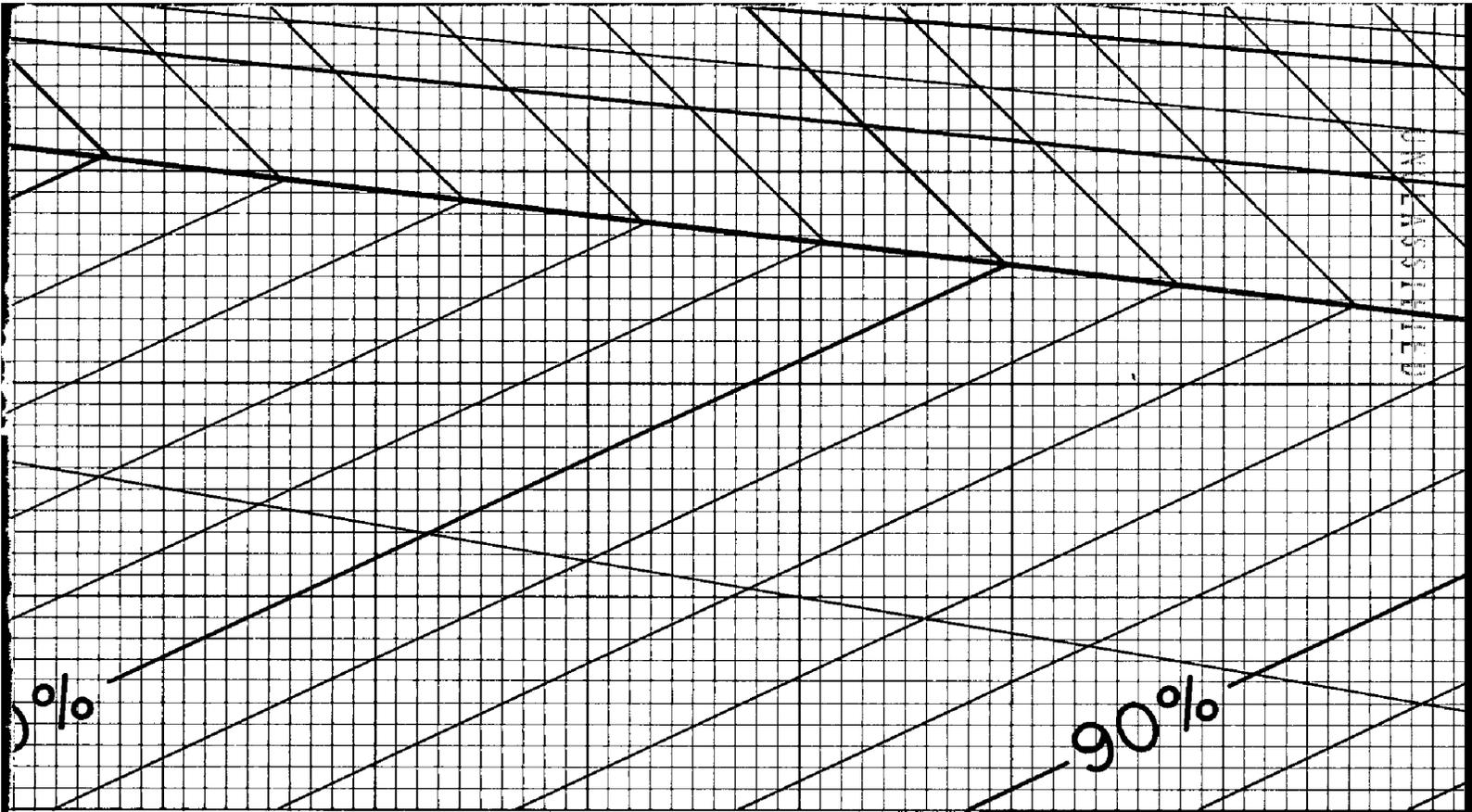
609

610

6

UNCLASSIFIED





.61

.62

.63

.64

.65

.66

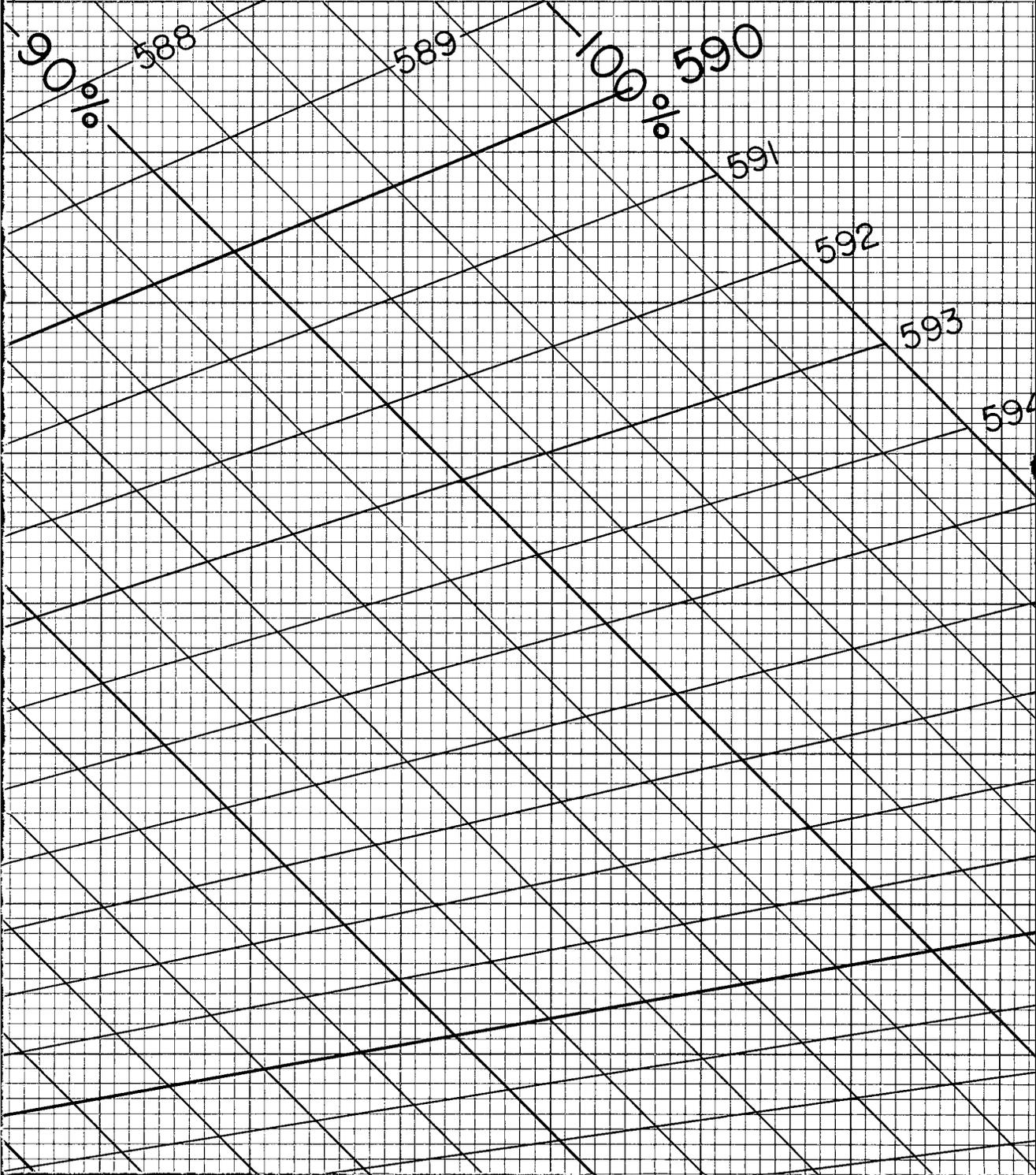
.67

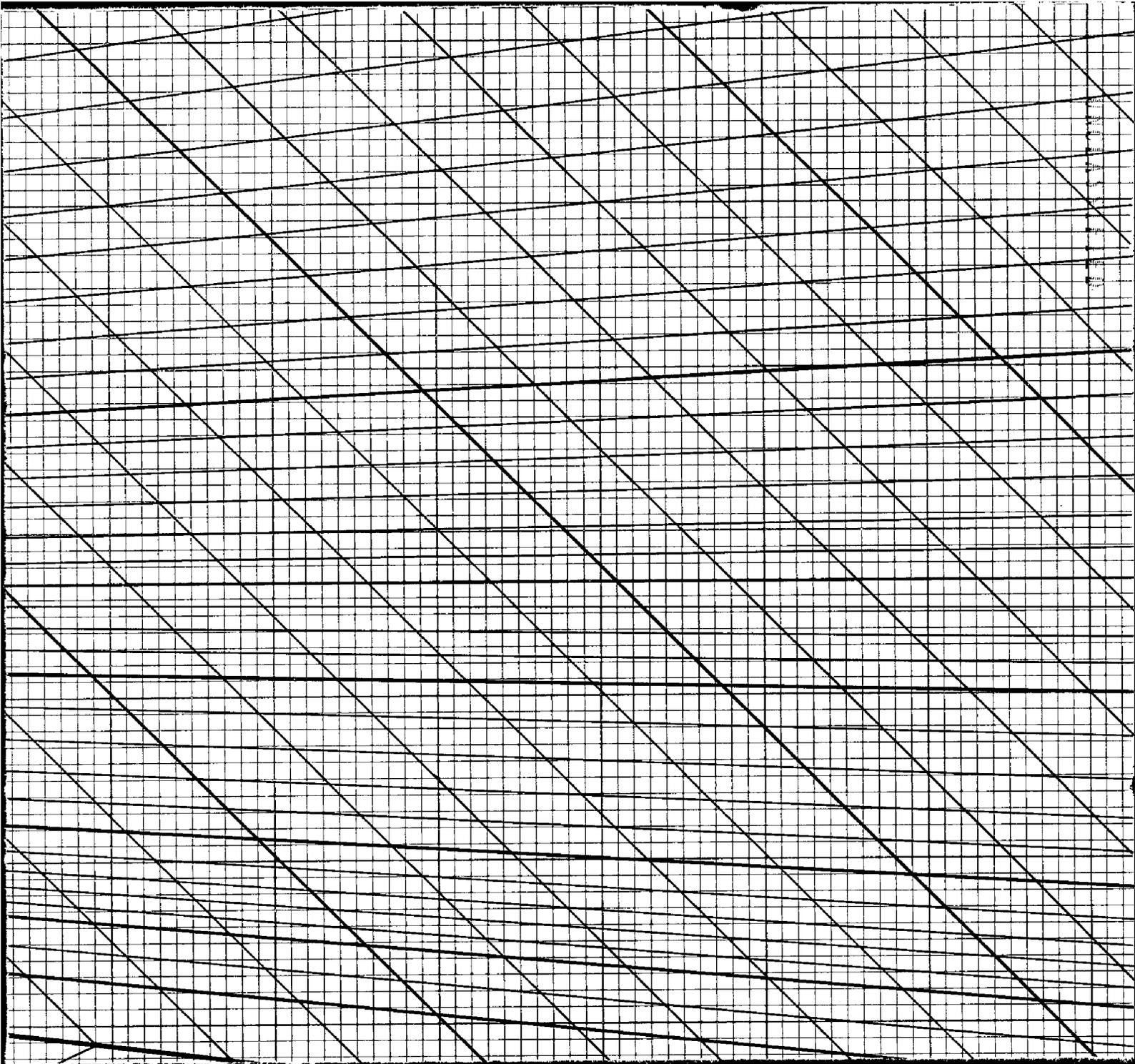
VALUES OF X

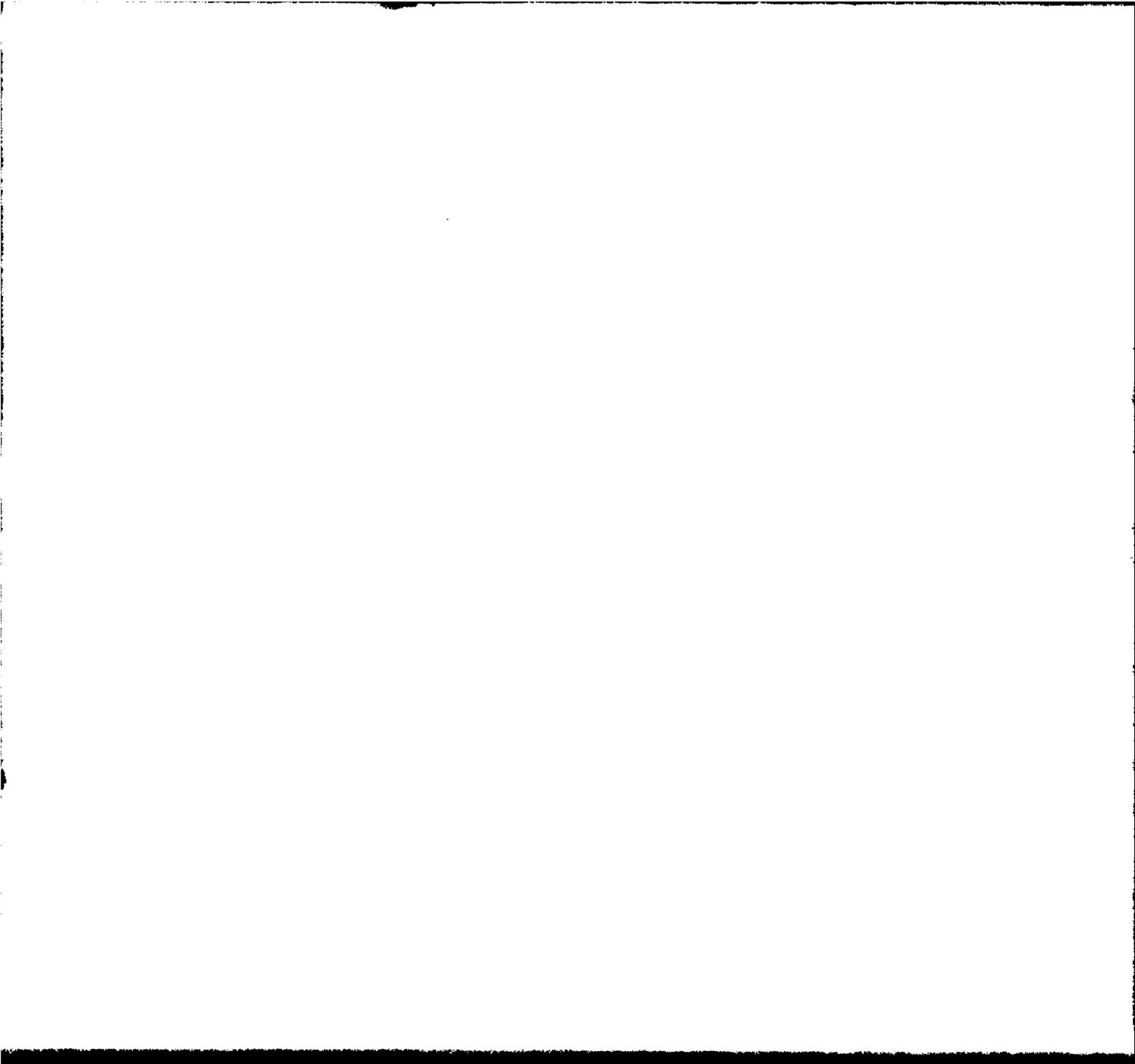
ATICITY DIAGRAM (PARTIAL)

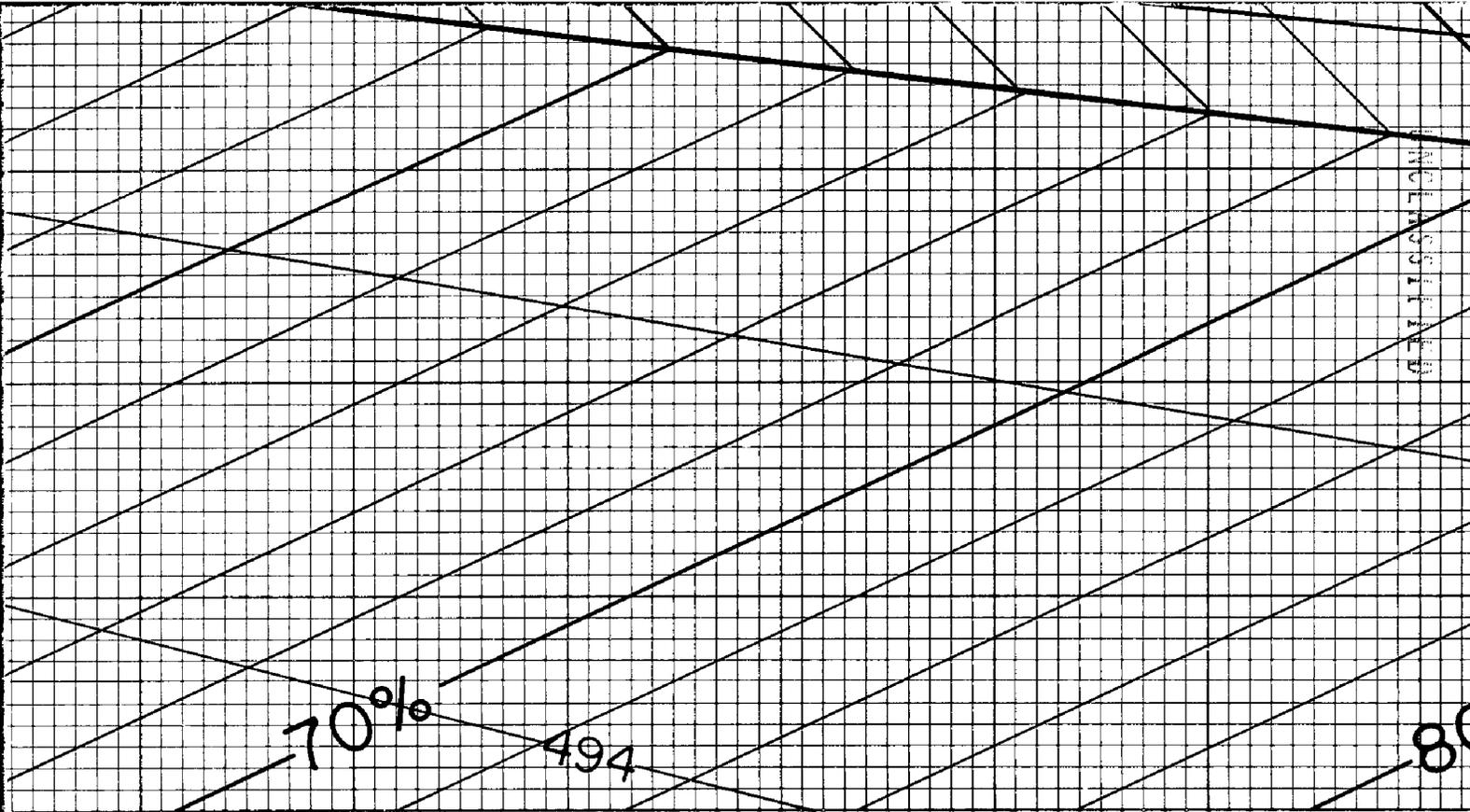
ENLARGEMENT OF A P

.54 .55 .56 .57 .58 .59 .60









.54

.55

.56

.57

.58

.59

.60

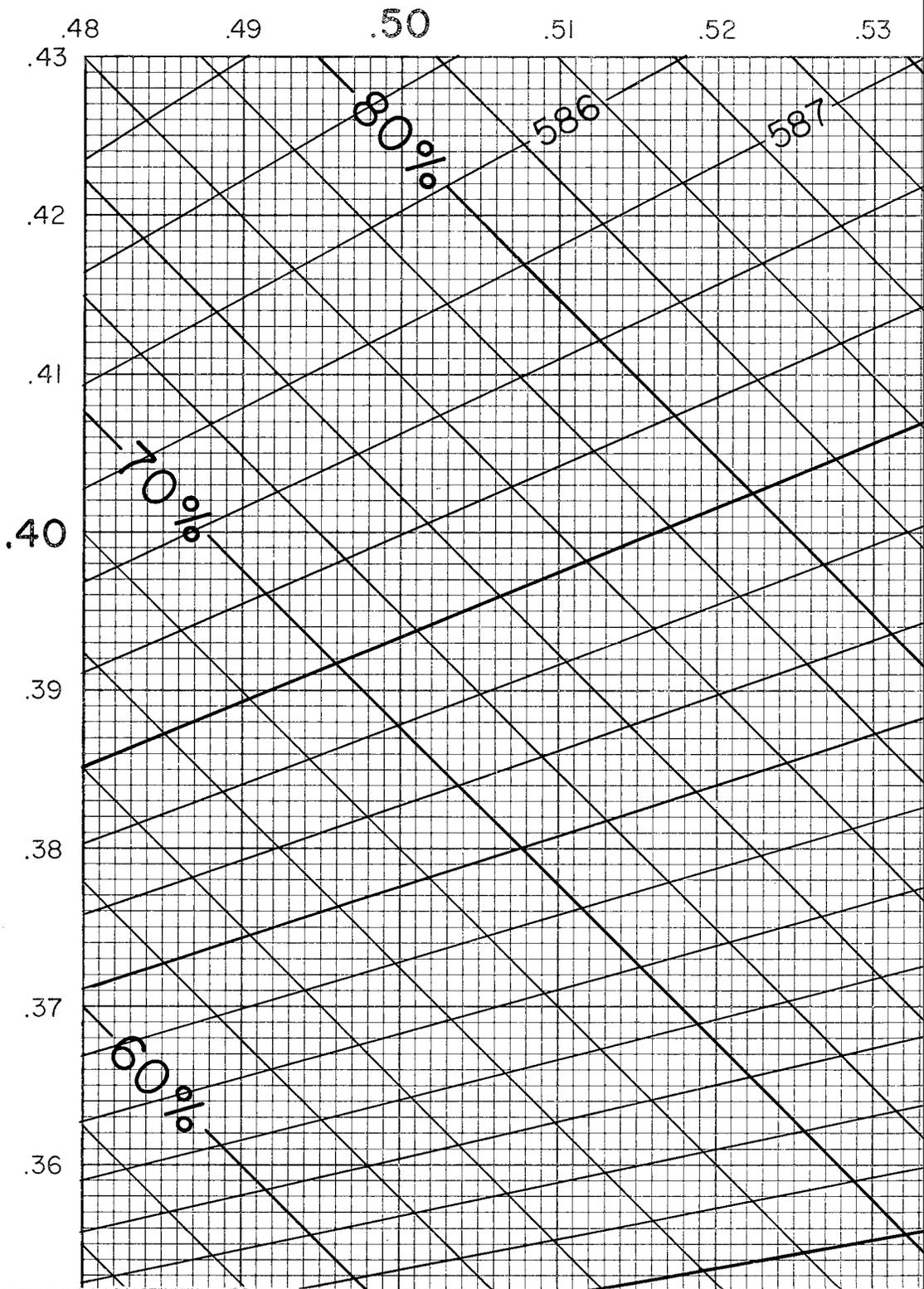
70°

494

80°

UNCLASSIFIED

CHROM

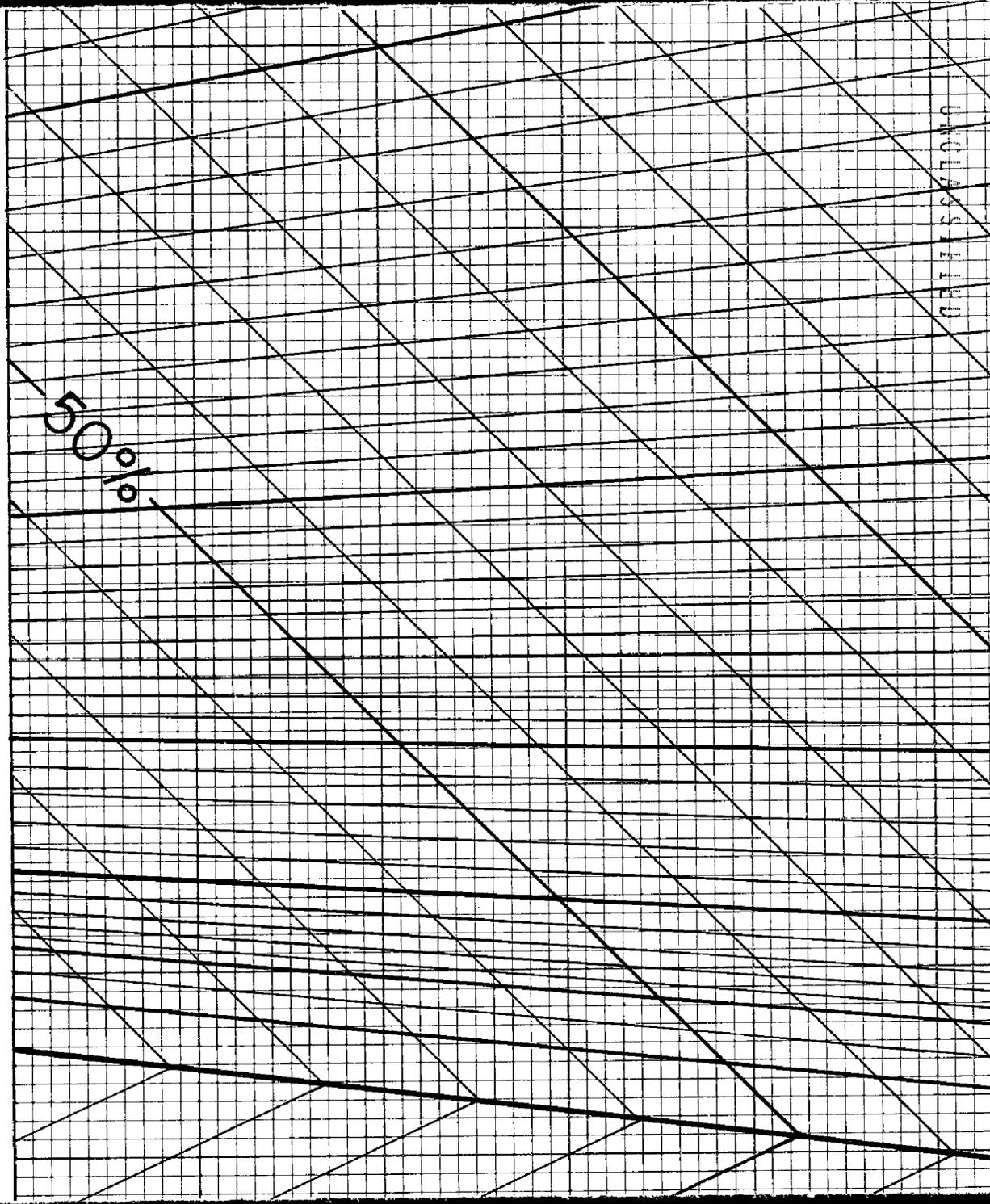


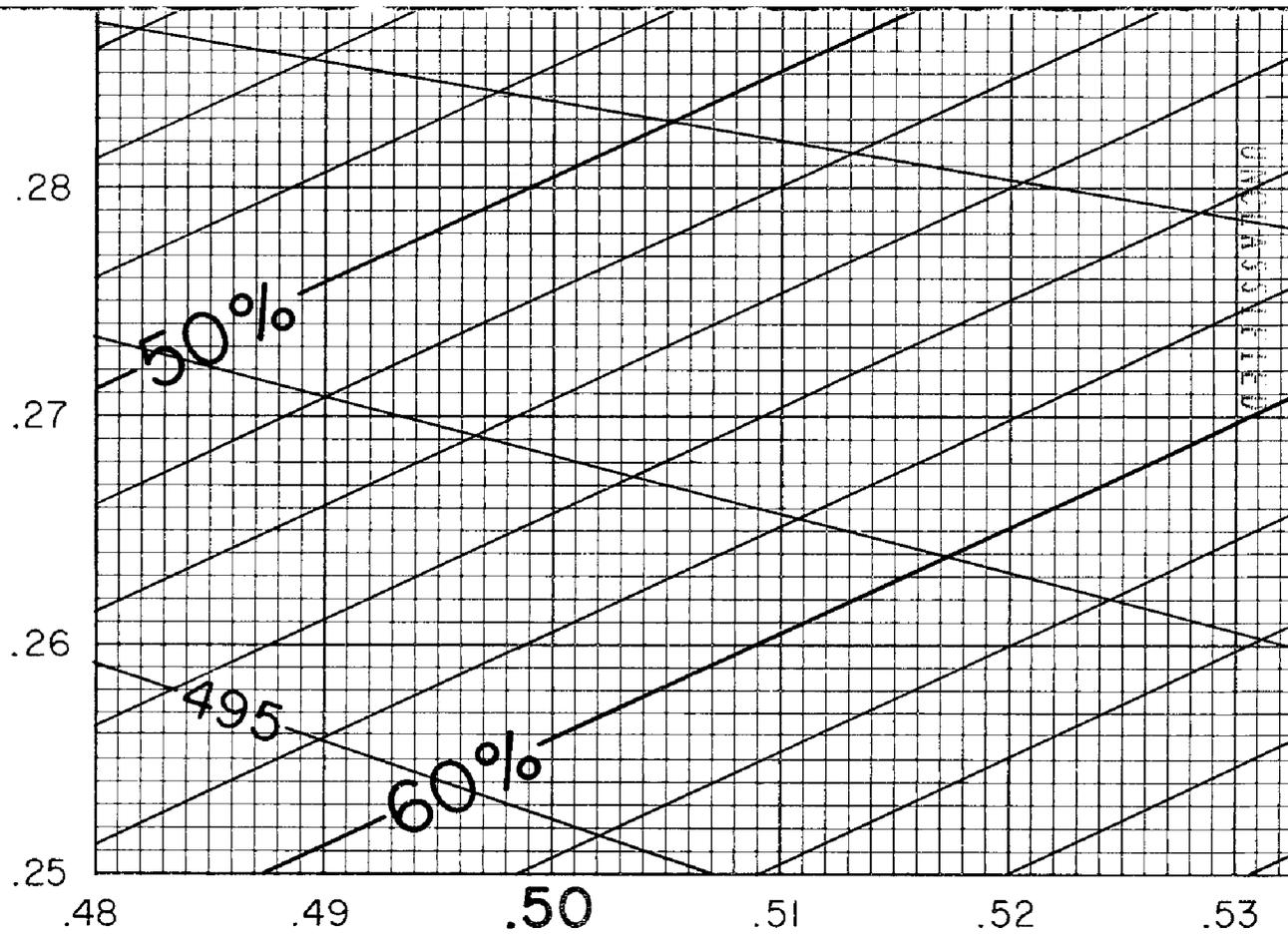
VALUES OF Y

.35
.34
.33
.32
.31
.30
.29

50%

U
T
I
L
I
T
Y





APPENDIX E

TRISTIMULUS VALUE CALCULATION SHEET FOR USE WITH THE NEW
SELECTED-ORDINATE CHART PAPER FOR I.C.I. ILLUMINANT C

Date _____
 Panel No. _____
 Vehicle _____
 Pigment _____
 Exposure _____
 Top Coat Yes No _____

Slit Width _____
 Phototubes _____
 Sensitivity _____
 Reference _____
 Source _____

	(X)	(Y)	(Z)
422.2 ... z
432.0 ... z
435.5 ... x
438.6 ... z
444.4 ... z
450.1 ... z
455.9 ... z
461.2 ... x
462.0 ... z
468.7 ... z
477.7 ... z
489.5 ... y
495.2 ... z
515.2 ... y
529.8 ... y
541.4 ... y
544.3 ... x
551.8 ... y
561.9 ... y
564.1 ... x
572.5 ... y
577.4 ... x
584.8 ... y
588.7 ... x
599.6 ... x
600.8 ... y
610.9 ... x
624.2 ... x
627.3 ... y
645.9 ... x

Sum

Multiplier (.098) (.100) (.118)

Tristimulus Value _____

X + Y + Z = _____ Luminance Factor _____

x = _____ Purity _____

y = _____ Dominant Wavelength (mμ) _____