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PROBLEMS IN SPECTROPHOTOMETRY

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PROBLEMS IN SPECTROPHOTOMETRY

The usual research program on colorants involves the measurement of uniformly coated test panels. However, in 1963 Miss Ruth Johnston and I suggested the possibility of measuring the spectrophotometric curves of colorants in paintings and in other museum objects (1). This is a more difficult problem than that of measuring well-prepared panels. For this reason, the chairman suggested that I review the requirements and limitations in spectrophotometric measurements and discuss some of the problems to be studied.

Colorimetry vs. Spectrophotometry

The use of the Lovibond Tintometer to measure color in paintings was suggested by Rawlins more than 25 years ago, but the measurement of color per se in artistic problems has not been widely exploited (2). There is a fundamental reason why this is so: colorimetry, the technique of measuring and specifying the visual experience of "color" in terms of three light sources (usually red, green, and blue) that may be combined to match a given color, is not a completely satisfactory way to describe the character of a colored object. Colorimetry deals with the interaction of three factors: the spectrophotometric character of (a) the illumination, (b) the colored object, and (c) the response of the eye. One of the key limitations to colorimetric specification is found in the problem of

2.

"metamerism," the phenomenon illustrated by the two Braden-Sutphin inks in Figure 1 (3,4). These two materials have much the same color when viewed under 7500°K daylight, yet they have different spectrophotometric curves (the result of their being based on different colorants) and appear as distinctly different colors under incandescent lamp light. This example clearly shows that specification of "color" does not define the reflectance characteristics of an object. Colorimetry is the descriptive tool, telling us what color will be seen. Spectrophotometry is the analytical tool.

Requirements for Spectrophotometric Studies

An abridged instrument such as the Color-Eye[®] (Instrument Development Laboratories, Division of Kollmorgan, Inc., Attleboro, Massachusetts) may be used to obtain a spectrophotometric curve. This instrument has 3 colorimetric filters and 16 narrow-band-pass filters. The latter permit the reflectance to be measured at selective wavelengths in the visible range (every 20 nanometers). Modestly priced spectrophotometers are also available which permit the spectrophotometric curve to be measured by selection of a desired wavelength and determination of the percentage reflectance first from a white reference sample and then from the colored sample.

More convenient than the above "single beam" instruments are recording spectrophotometers which automatically compare the reflectance of the sample relative to the standard. The latter are called recording "double beam" instruments. Reasonable precision in the shape of the

reflectance curves is required if the analysis of the color of pigment mixtures is to be made; a recording instrument offers advantages over the manually operated and the abridged instruments. One of the lowest priced recording double-beam instruments made in America is the Bausch and Lomb 505. This instrument and the Color Eye[®] are in roughly the same price class, about \$5,000 (about 1,800 pounds sterling). The price of the next more elaborate instrument, with increased capabilities, quickly reaches a figure of about three times this.

To measure small differences in color, the spectrophotometer must be capable of considerable precision, hence the considerable cost. Miss Johnston has pointed out that a difference of .5% in reflectance is often close to the minimum perceptible difference in ordinary samples. In the dark samples, the minimum perceptible difference may require measurement of reflectance to an accuracy of .1% (5). The instrument must also have high stability so that, as nearly as possible, the same readings can be obtained over long periods of time. This is particularly true if one wishes to record and study the slow changes that may take place under actual gallery conditions.

In order to record the precise change in the color of a painting after a period of 5, 10, or 20 years, measurements must be made on the same instrument. The reason for this is that the geometry of sample viewing and sample illumination is not identical in different instruments; and therefore, they will give different readings on the same standard. The data in Figures 2 (6) and 5 illustrate this point.

Since precision is needed, the laboratory undertaking such studies must make long- and short-term investigations of the repeatability of the instrument; it is necessary to know the minimum detectable difference in reflectance and in color that may be considered significant. To determine this, a set of stable reference standards must be maintained. Pieces of opaque colored glass are useful for this purpose, of sufficient thickness so that they are indifferent to the color of the backing placed behind them. If the glass has a high polish, this will facilitate easier maintenance of the surface condition (7). Miss Johnston has also pointed out that it is useful to have standards other than white, since these serve to check precision in the normal working range.

The standards should be calibrated by an instrument in a reliable color measurement laboratory and checked by the same laboratory over a period of years to determine if they have changed significantly. If one's own instrument is not the same as that in the reference laboratory, it will not give precisely the same color measurements on a given standard, as has been said. Nevertheless, the service of an outside laboratory is necessary so that a long-range check can be made on the stability of the working standards. If the standards are shown not to have changed, then the relative performance of one's own instrument can be evaluated and the size of the uncertainty in the measurements established.

It must be possible to include or exclude the specular reflectance from a sample at the operator's will. With dark colors, the specular reflectance can markedly effect the apparent color of a sample. On the other hand, it is necessary to include the specular component to describe the color of highly reflecting materials such as metals. In the study of chalking and other changes in gloss, two measurements are useful, one with the specular component included and another with it excluded (8).

Measurement of color in paintings requires that the painting be placed at the port in the instrument. Ways will be needed to hold the painting reasonably tight against the port and to locate the area to be measured. The Color-Eye[®] is so constructed that the wall of the instrument that contains the sample port is without obstructions, so that a paint sample of considerable area may be brought flush against the port opening. This instrument also comes with a periscope that can be used to inspect the sample while it is in position at the port. With a few minor changes, the General Electric Recording spectrophotometer can also be used to measure large panels. Others, however, do not lend themselves to this capability; therefore, this aspect of sample presentation is important to consider when purchasing an instrument.

As a last requirement, it is necessary to choose some way of calculating color change so that a "minimum perceptible difference" can be estimated. Unfortunately, there are any number of systems of color difference that can be used; no standard practice exists (9,10). The circles in Figures 2 through 5 represent color differences in MacAdam units (1945) estimated graphically on Simon and Goodwin charts (11). If many calculations must be made, an electronic color difference calculator can be helpful.

Limitations

It is wise to review the limitations of an analytical technique. The first requirement is to understand short- and long-term repeatability of one's instrument. A number of studies have recently been made regarding the repeatability and reproducibility of spectrophotometric measurements (12,13,14,15). The results have shown that even in the best of instruments and laboratories, there are differences to be expected on the order of 1% (95% confidence limits) in the measurement of C.I.E. tristimulus value, Y (12). In the case of dark colors of high chroma, the 95% confidence limit of the measurement is close to the minimum perceptible difference. Between laboratories, reproducibility on given standards varies more than this, from about 3 units of minimum perceptible difference to as high as 55 (14). It is for such reasons that the recommendation is made (a) to spend adequate funds for a reliable instrument, (b) to maintain good standards, and (c) to check the repeatability of the instrument regularly. The Color-Eye[®] is generally repeatable between different operators and different days within about 1 unit of perceptible color difference, as Miss Johnston has reported (15) and our data in Figures 3 and 5 show.

Ordinarily, it is necessary for the sample to touch the instrument. The contact area may be prepared with soft felt, however, so that there will be little danger of abrasion to the paint. More important, there is a need to be able to bring the painting into position at the port of the spectrophotometer in a repeatable manner. We have checked the

effects that gross misalignment of the sample may have on the measured color, both for a smooth surface glass standard (Figures 3 and 5) and for a rough surfaced painting (Figure 4). Considerable misalignment of uniform, light colored samples may not cause changes greater than about 2.0 units of minimum perceptible difference (diffuse reflectance, specular component rejected). On the other hand, if the paint sample has a highly patterned design (Figure 4) or if the color is dark (Figure 5), variations on the order of several units of minimum perceptible color difference can occur when the sample is not precisely positioned on repeated measurements.

As a general rule, measurements on dark colors are likely to be less reliable, let us say those with reflectance of less than 10%. Certain colors, particularly dark reds and maroons of high saturation, may introduce greater uncertainties than others (5).

The size of the area that must be viewed is another limitation. Some reduction of the viewing area can undoubtedly be made in one's own laboratory, but Robertson and Wright's survey indicates that the smallest port area in commercial instruments is about .8 cm x .5 cm in dimension (9). The standard viewing area is usually a circle or square of less than 2.2 cm in its greatest dimension. In the colorimeters that they examined, the illuminated area was generally larger than this, about 3 cm in the greatest dimension.

Test samples of rather uniform color are intentionally prepared in laboratory research. With paintings, rough surfaces and patterns of color are encountered. This places a premium on our ability to return to precisely the same spot. The results in Figure 4 show that this can

8.

sometimes be done reasonably well in spite of a highly patterned sample. In this particular sample, however, there was one small area of blue which was "lost" from the viewed area when the sample was tilted, causing a serious loss of precision. Ordinarily, one may avoid choosing an area that will present such a marked problem. The example is included here, however, as a warning.

Patterned samples also may occasionally present problems in interpretation if only one of the colors changes. For example, a yellow varnish may fade over the entire surface or a yellow pigment may fade in only one particular area of the design. The change measured by the instrument will not distinguish between the two.

One final limitation must be mentioned: color is only one aspect of appearance (16). The first step in evaluating the change in a sample is, in fact, simply to look at it (6,17). The word "validity" is used to refer to the extent to which the instrumental measurements conform to what we see (14). Appearance is the result of a complex combination of a number of factors. Such factors as changes in surface roughness, transparency, and gloss often require additional measurements. Nevertheless, with judgment and understanding of the limitations of the spectrophotometer it is possible to record the essential change in appearance that has taken place over a long period of exposure and to make an intelligent analysis of the reasons for the change.

Problems to Be Studied by Spectrophotometry

The spectrophotometric curves of the color of materials can be used as a means of identification of the pigments (18). This is a

nondestructive method of analysis, which often can be facilitated by the use of differential curve analysis (1). The related field of absorption spectrophotometry is also of considerable value in museum problems. Saltzman, for example, has reviewed the identification of dyestuffs by their absorption curves in solution (19,20,21).

Miss Johnston and I have pointed out that reflectance spectrophotometry should be of considerable assistance in the study of glazes (8). Colors of the highest possible saturation are obtained in transparent glazes over white when little scattering occurs in the glaze. When considerable scattering occurs, interesting and sometimes unexpected colors develop in glazes over dark substrates, such as the green appearance of chrome yellow over black (8). Colored lacquers applied over metals may also be profitably studied, as well as the color of the metals themselves, of textiles, ceramics, and ceramic glazes. When discolored varnish is stripped from a painting, spectrophotometric measurements may provide evidence that a glaze has not been removed.

Since an instrument can remember the original color far better than the human eye, spectrophotometry is obviously of value in the study of color change. Investigations of fading measurements will determine if it has taken place and whether, in a mixture, one component or another has changed.

Some colors darken rather than fade. Toishi has studied the darkening of vermilion as well as other color changes in pigments exposed to light (22). We have found that the darkening of emerald green in oil takes place primarily as a decrease in the principal reflectance peak

(Figure 6). On the other hand where a change has perhaps been made in the way that the oil and pigment system scatters the light, the absorption curve changes in a uniform manner throughout the entire spectrum, as in the case of green earth in Figure 7. This is a type of alteration that may lead to pentimenti.

The change in the curve during the darkening of green earth in Figure 7 has been shown to be not completely constant across the spectrum. The displacement in the shorter wavelengths is assumed to be due in part to a bleaching of the linseed oil. Spectrophotometry thus can be useful in the study of yellowing and bleaching of the varnish or vehicle under various conditions of exposure. The shape of a "vehicle" yellowing curve is generally a gradual increase in absorption as one approaches the ultraviolet. This may, in many cases, be distinguished from the specific curves of yellow substances that might be found in a glaze, such as we see the curve shapes of many yellow pigments, particularly in the short wavelengths of the visible spectrum (4). Miss Johnston has given examples in which the shift in spectrophotometric curve can be used to distinguish color changes (a) that may be due to a change in the principle absorption band of the pigment and (b) that come about through alteration in the color of the vehicle (4).

There is another aspect of identification by spectrophotometry which has not been exploited: the analysis of the fluorescence of pigments and dyestuffs. Although this requires a spectrofluorometer for greatest precision and utility, many spectrophotometers can be adapted to measure fluorescence. The data on the fluorescence of Indian yellow and the natural madder in Figures 8 and 9, for example, can be used to identify these pigments. Determination of the reflectance of a fluorescent pigment usually requires

special precautions, however, as the curves in Figure 10 indicate. A study of the fluorescence of resins, oils, glues, and waxes is in progress.

As a last point: spectrophotometry can increase the precision in the monitoring of fading standards. The fading of the International Standards Organization's standard blue wool cloths (ISO Recommendation R105, British Standard 1006:1961) is usually rated visually, as are the similar standards of Germany (DIN), the United States (AATCC), and others. Small frames containing BS 1006:1961 standards 1 to 4 are currently being used to monitor exposure on museum walls (23). As our observations in Figure 11 (24) and those of others (25) have shown, the visual rating of these can give satisfactory results, as good as may be expected with only 5, or at best 10, "steps" in the rating scale of the change (the geometric grey scale, British Standard 2662:1961). Instrumental measurements can increase the precision of the measurements considerably. Any number of measurements of the color change can be used to establish an empirical scale. We have used the Munsell Value Function in Figure 12, but Berger and Brockes have used color difference (MacAdam units) for the same purpose (26). The National Bureau of Standards' light sensitive papers have been rated by reflectance measurements through an amber filter (27); the recently issued standard sheets of yellow dyed plastic, by the change in transmittance at 418 or 420 nanometers (28).

Summary

I have attempted to review the requirements of a spectrophotometer if one intends to measure changes in color in actual paintings. The need to make long-term measurements on the same instrument has been emphasized

as well as the need for an instrument of high quality. Some of the limitations have been pointed out, for it is only by the proper understanding of these that the measurements can be used to good advantage. In view of the variety of problems that can be studied by reflectance, transmittance, and fluorescence, the purchase of an instrument with a certain degree of versatility is a wise investment.

Unless the intention is to become deeply involved in spectrophotometry, the average museum technical laboratory can explore the usefulness of these measurements effectively by taking their samples to laboratories which have well-calibrated instruments and extensive experience in the techniques and limitations of the measurements. Colleagues who may wish to consider the applications of spectrophotometry in further detail, however, will find that an excellent series of publications has appeared in the last 5 years. The basic publications have been noted. Reference to these will lead readily to an extensive bibliography.

Acknowledgment

The measurements and calculations on repeatability were made by Mr. William Fettes; those on the darkening of green pigments and the fading of the BS 1006:1961 standards, by Mr. Joseph Matous.

Samples of natural madder and Indian yellow were kindly supplied by Winsor and Newton. The Indian yellow agreed by fluorescence, microscopic examination, and infrared analysis (Figure 13) with 50-year-old samples kindly supplied by Mr. Stephen Rees Jones of the Courtauld Institute of Art and Miss Elizabeth Jones of the Fogg Art Museum.

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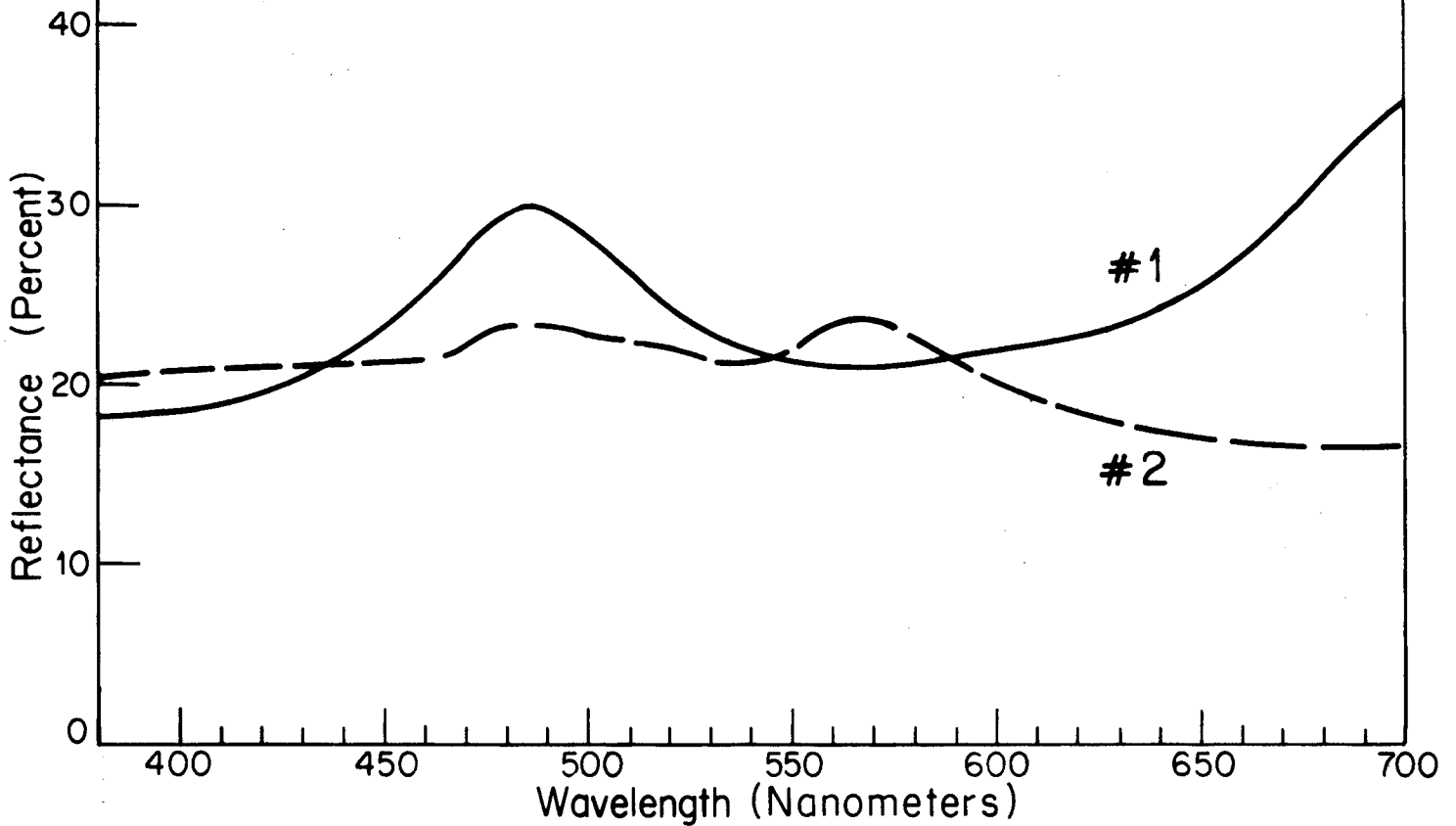
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FIGURE 1 - Metameric Green Inks
Comparison: BaSO₄

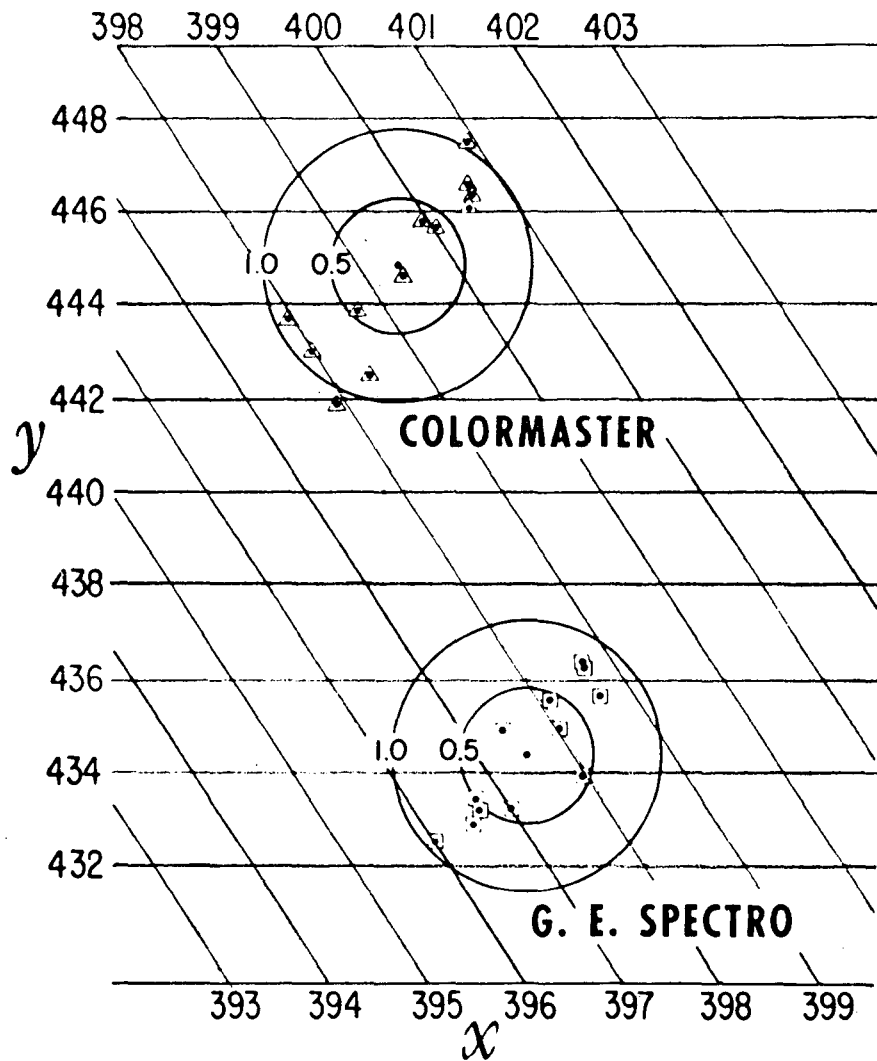
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 Y= 22.77 y=.3094 # 1
 Z= 28.71 z=.3901
 "A" _____
 X=24.95 x=.4429
 Y=22.49 y=.3992 # 1
 Z= 8.89 z=.1578

"C" _____
 X= 20.20 x=.2999
 Y= 21.54 y=.3198 # 2
 Z= 25.62 z=.3803
 "A" _____
 X=21.95 x=.4317
 Y=21.11 y=.4152 # 2
 Z= 7.78 z=.1530

Data of R. M. Johnston



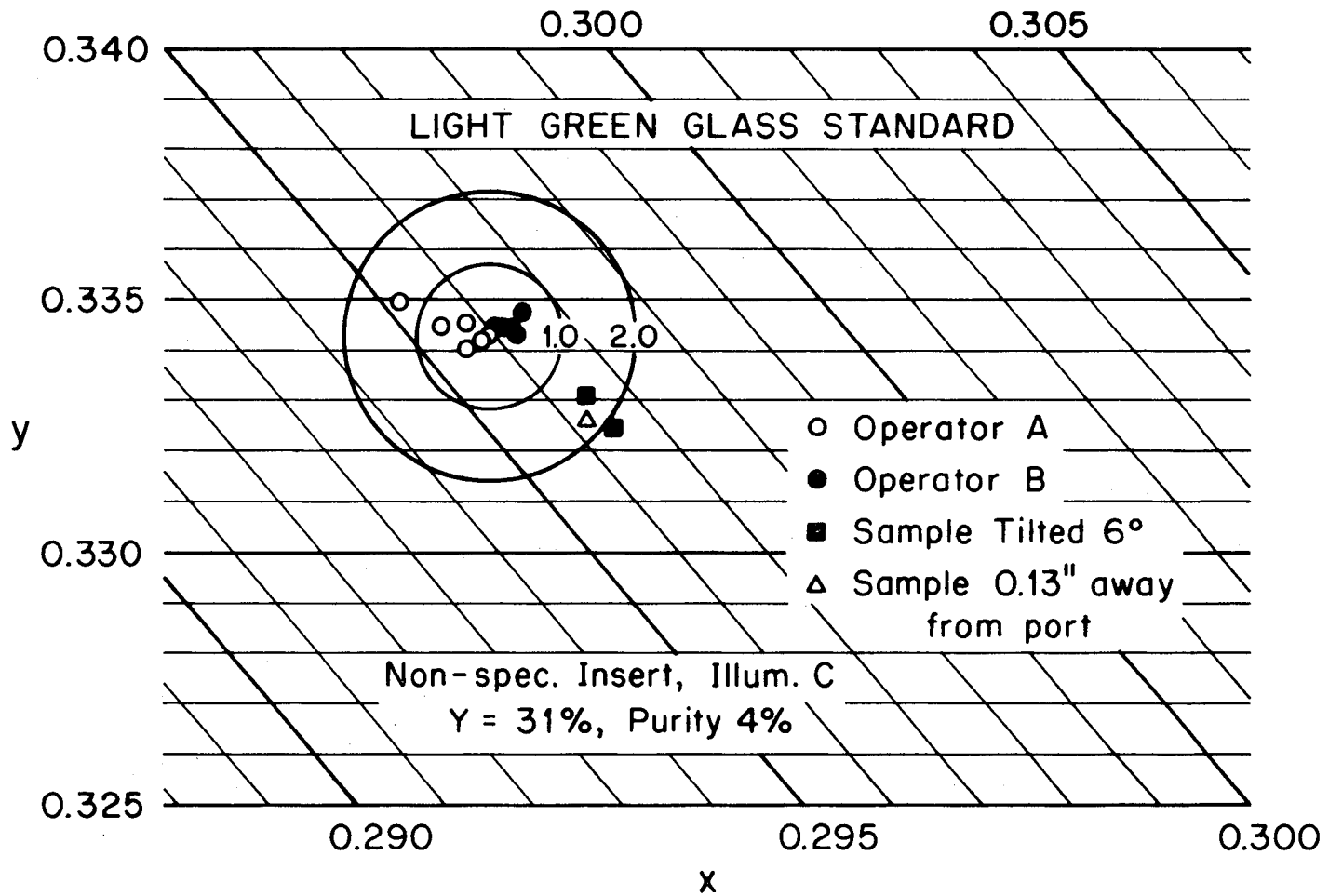
Circles in Figures 2 through 5 represent MacAdam (1945) units of color difference.



CIE readings by GE Spectrophotometer and Color Master Colorimeter differ, and are not interchangeable.

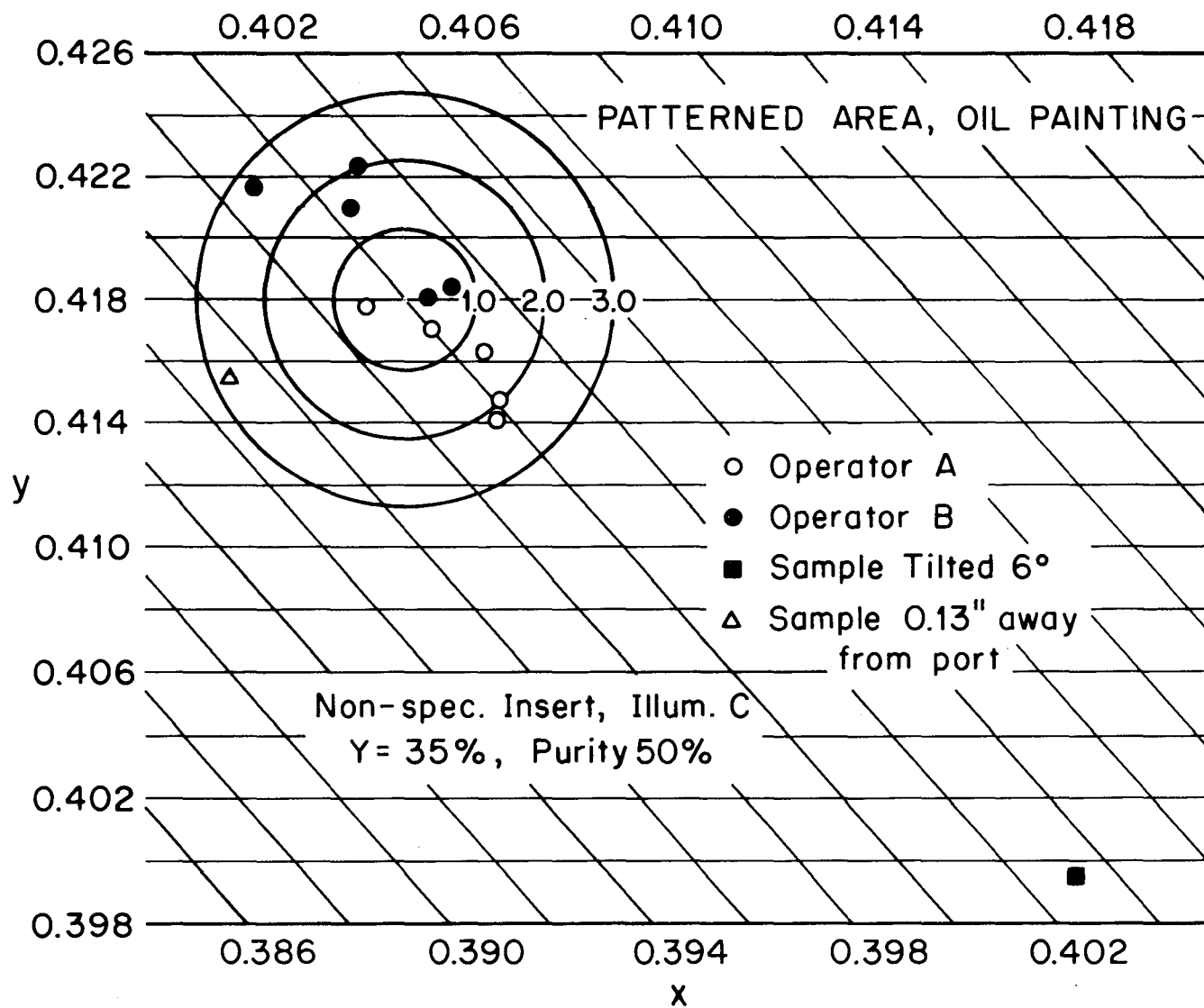
FIGURE 2

From: Saltzman, M., "Color Measurement with the Eye and Other Instruments," Color Eng., 1, No. 4 (1963), p. 18.



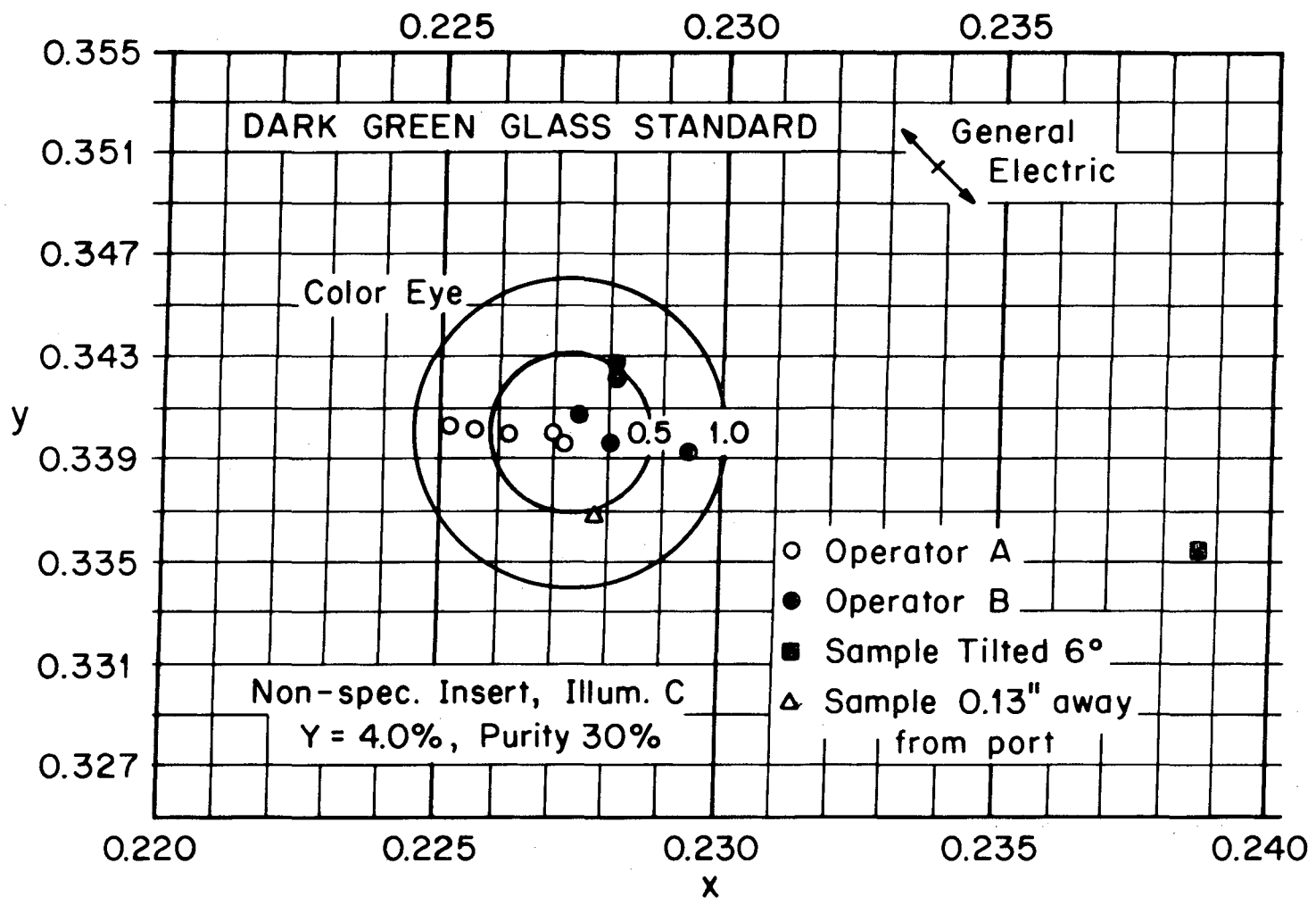
REPEATABILITY OF COLOR-EYE®

FIGURE 3



REPEATABILITY OF COLOR-EYE[®]

FIGURE 4



REPEATABILITY OF COLOR-EYE®

FIGURE 5

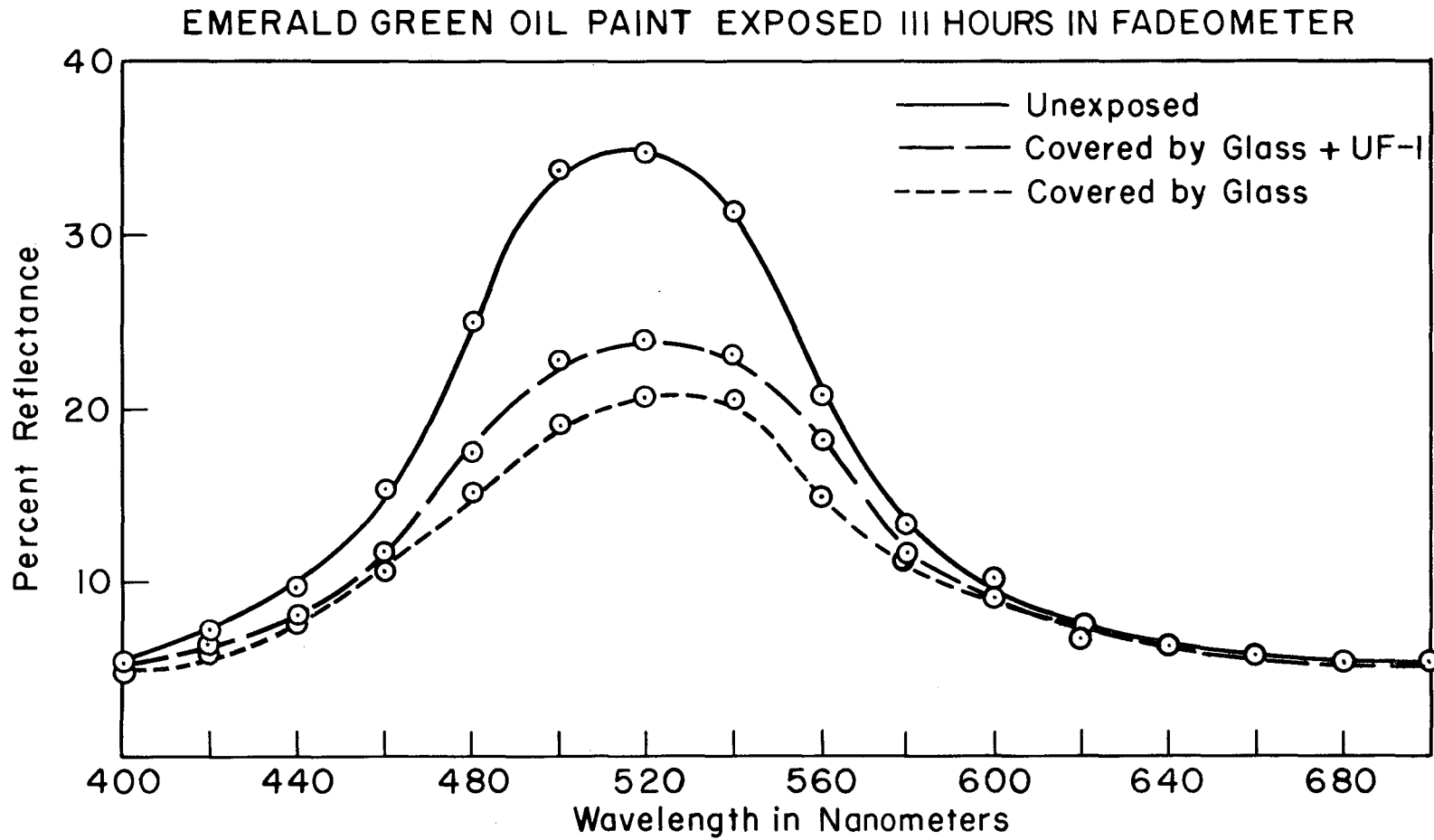
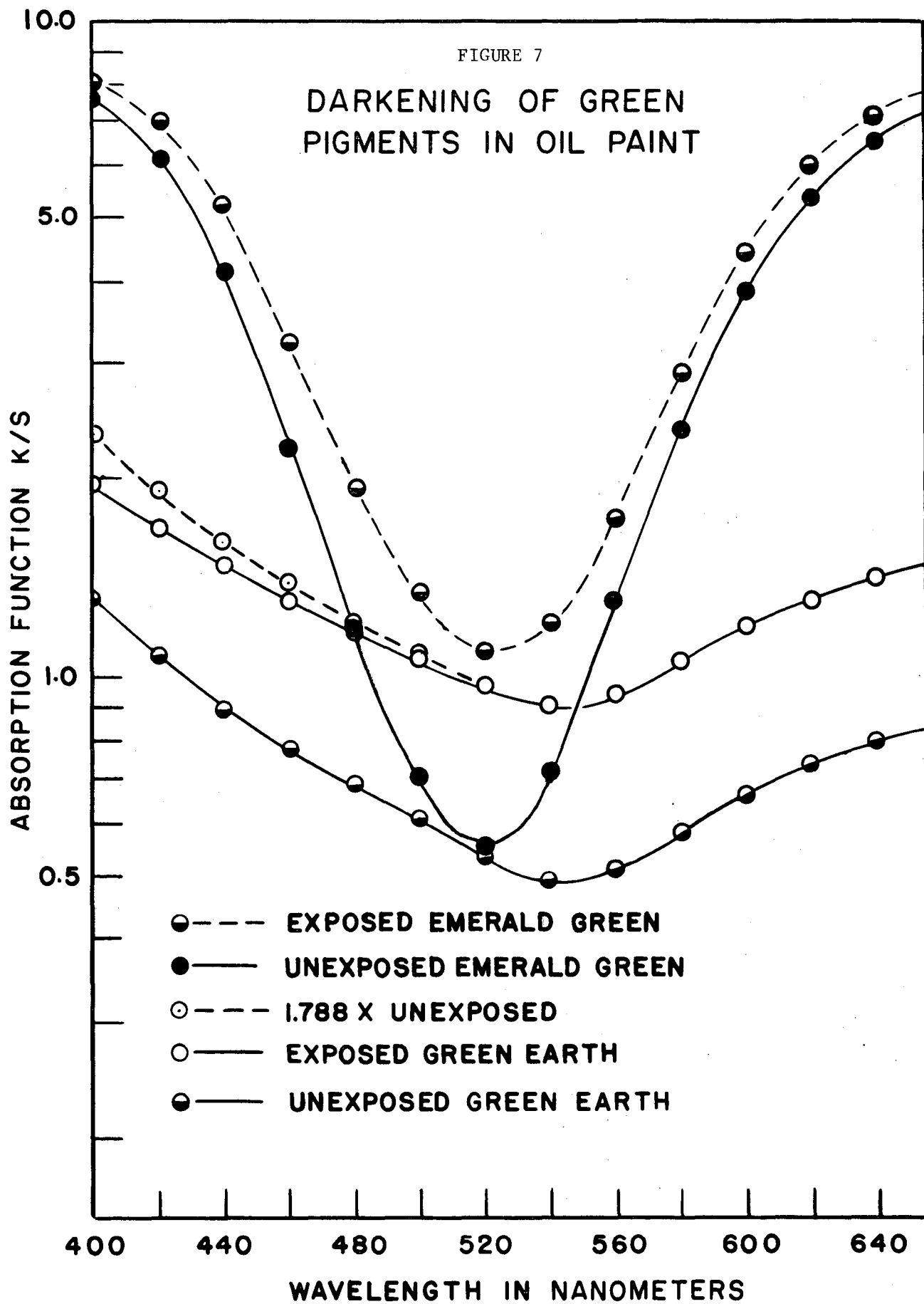


FIGURE 6



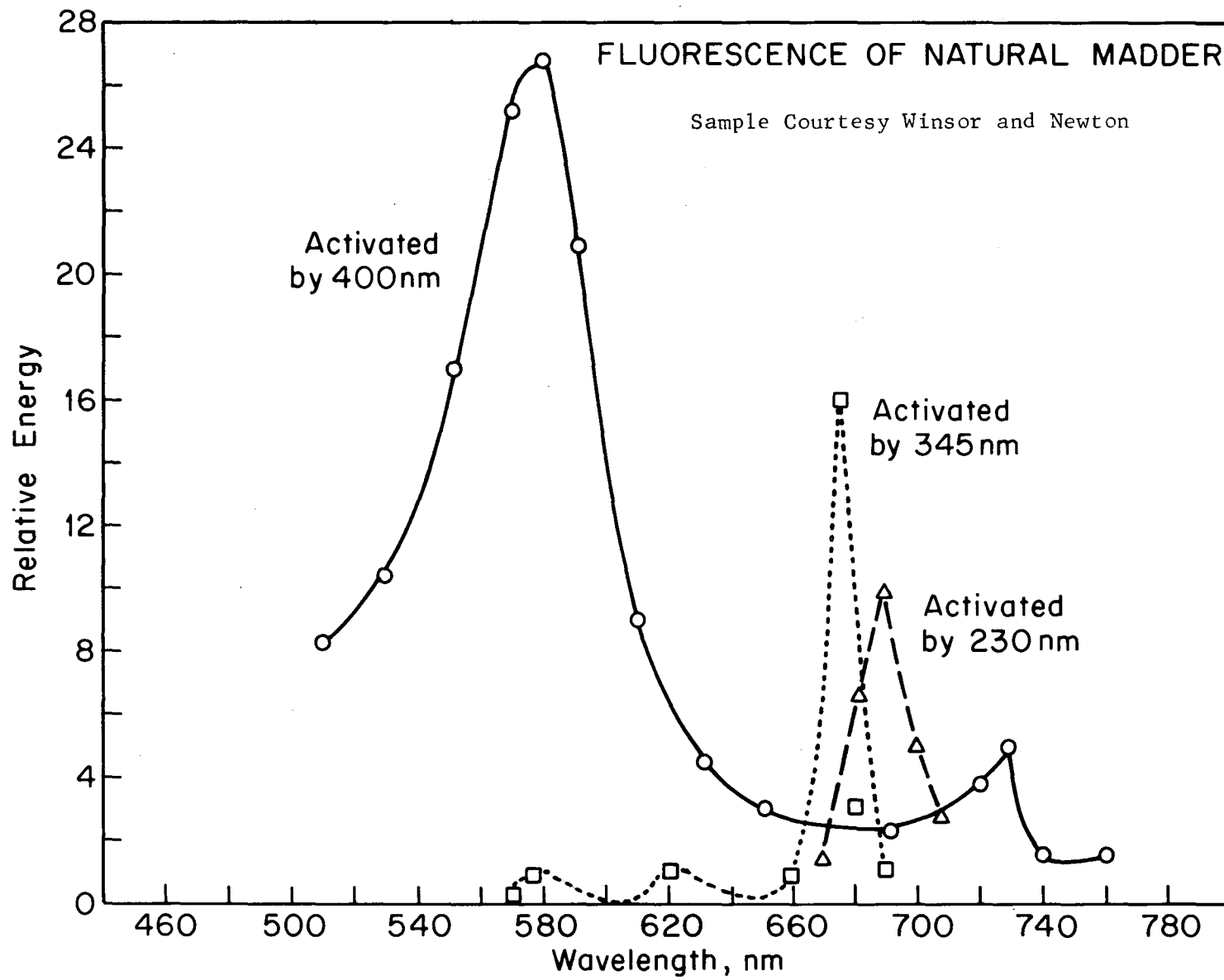


FIGURE 8

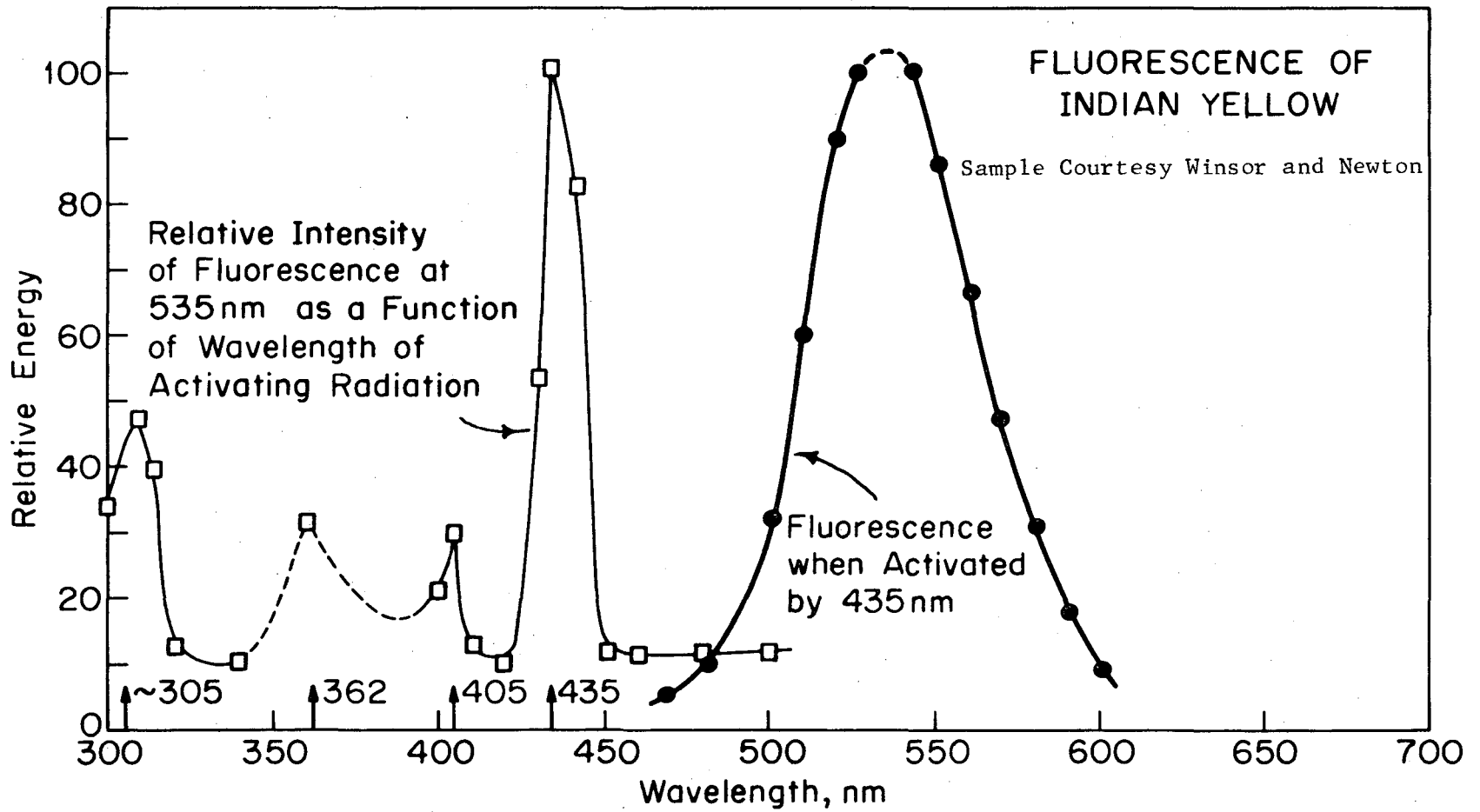


FIGURE 9

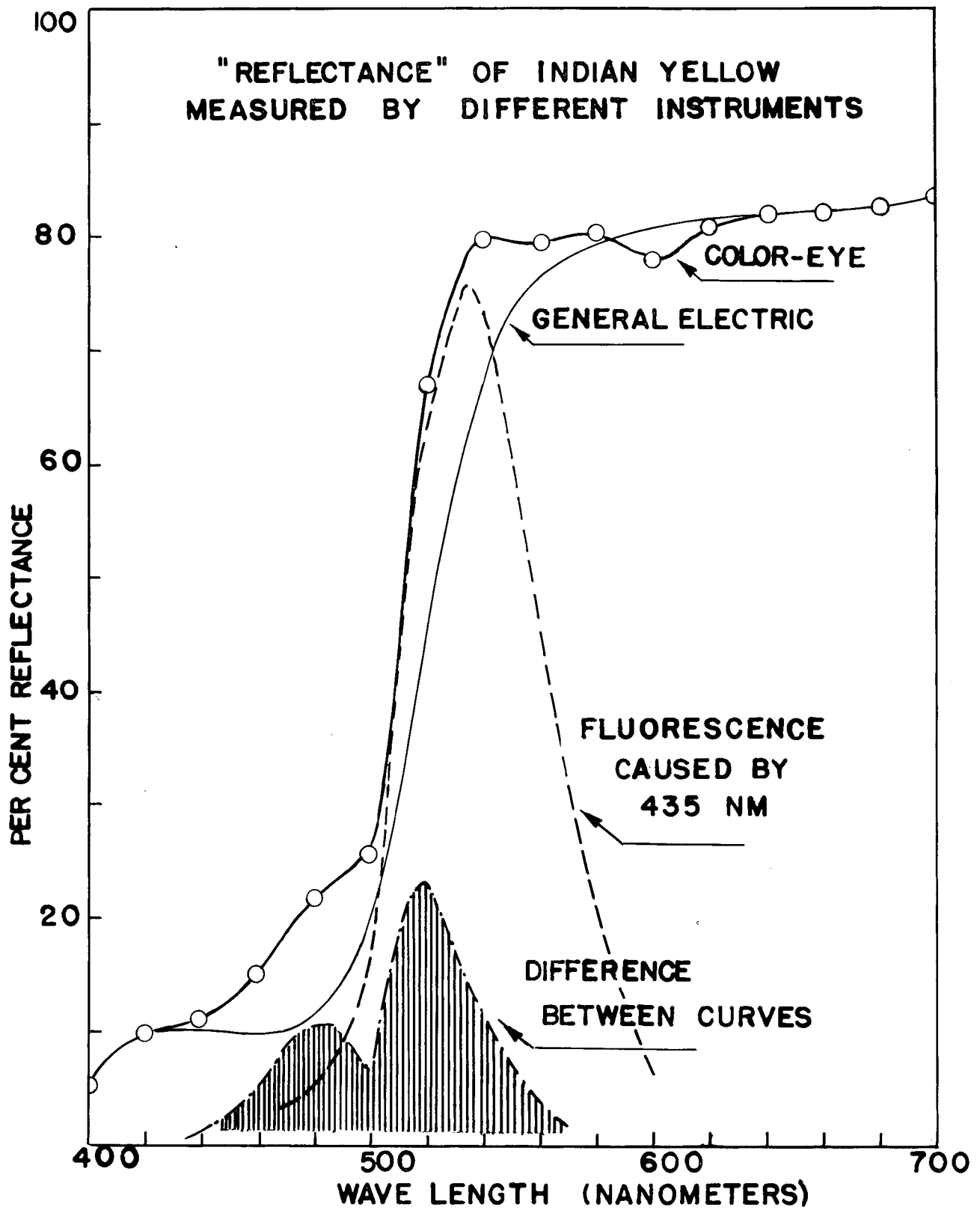
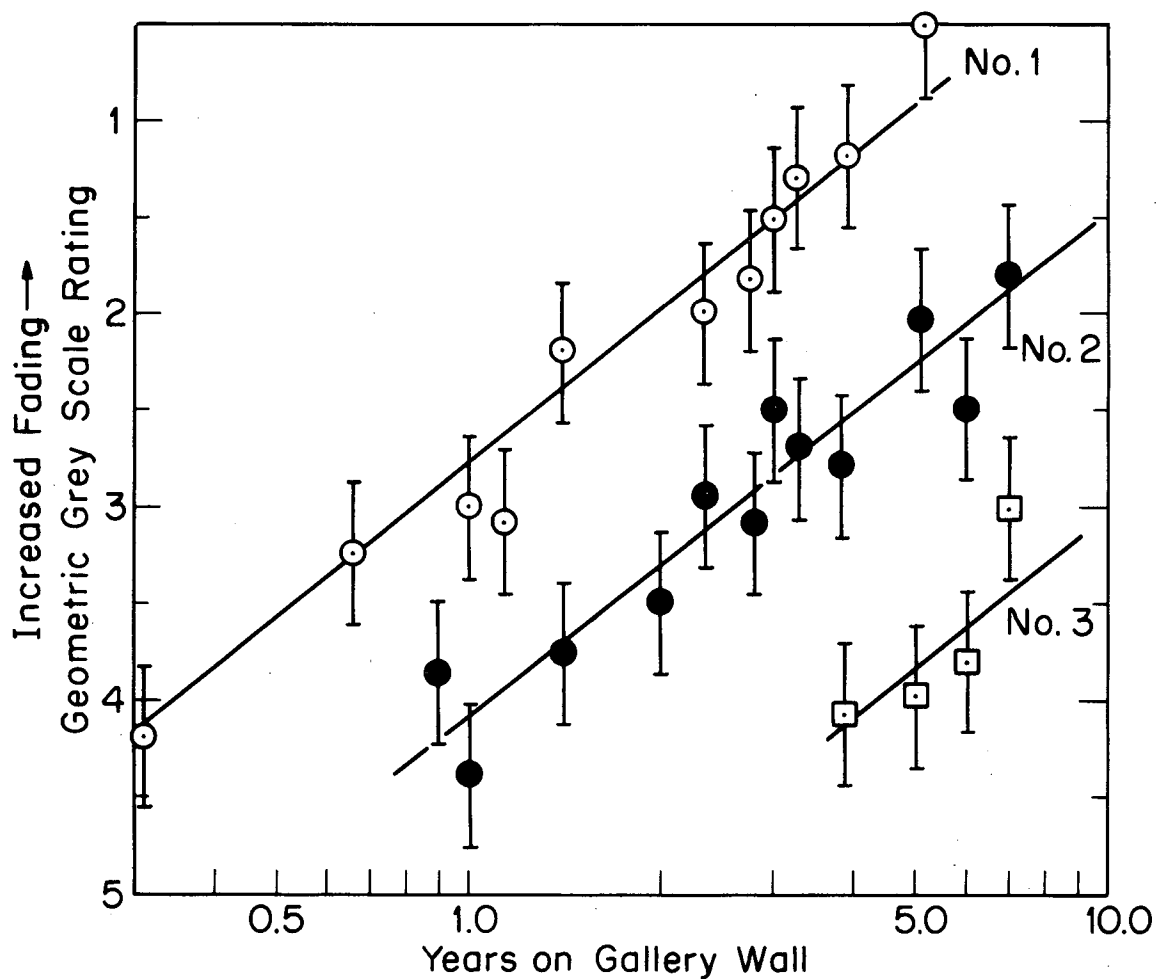


FIGURE 10



FADING OF BRITISH STANDARD 1006:1961
 BLUE-CLOTH STANDARDS 1, 2 AND 3 ON
 NORTH WALL OF DAY-LIGHTED GALLERY

FIGURE 11

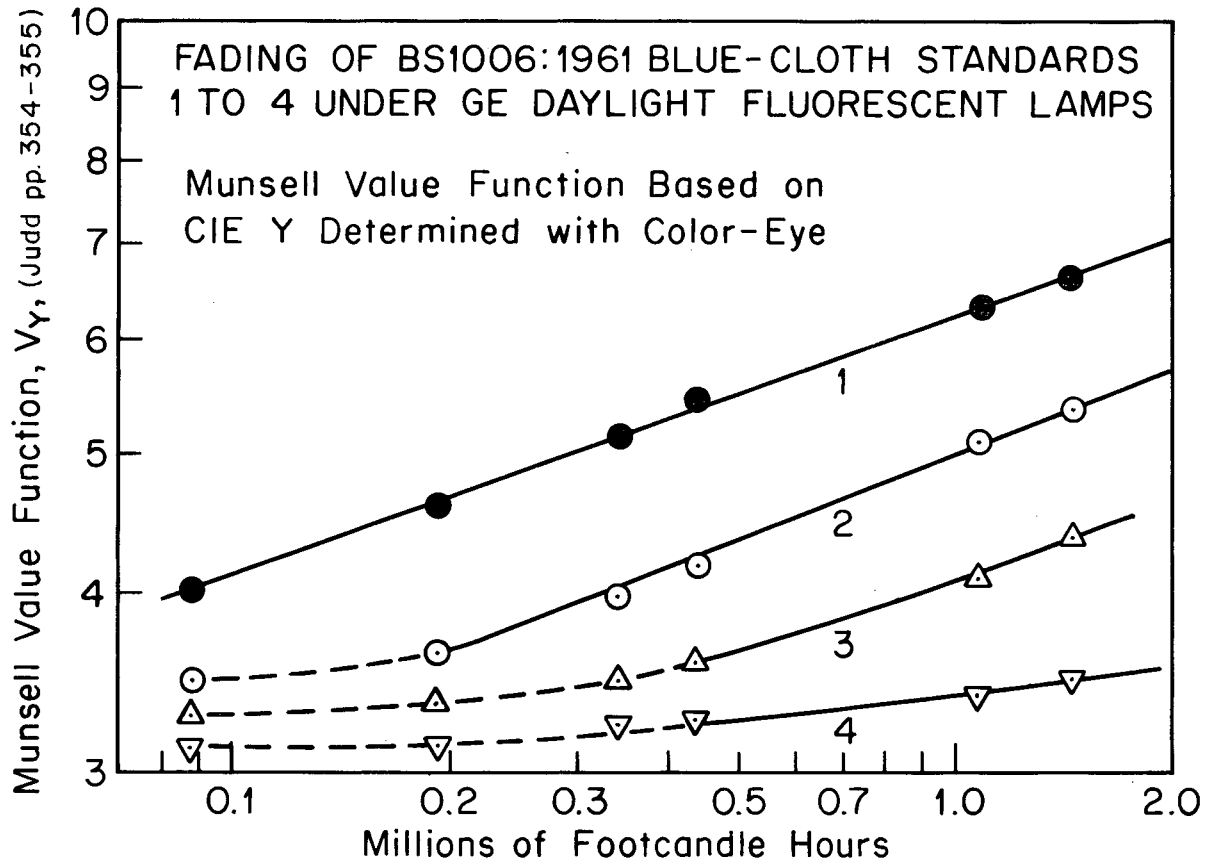


FIGURE 12

INFRARED SPECTRUM OF INDIAN YELLOW (PURRÉE)

SAMPLE COURTESY WINSOR AND NEWTON

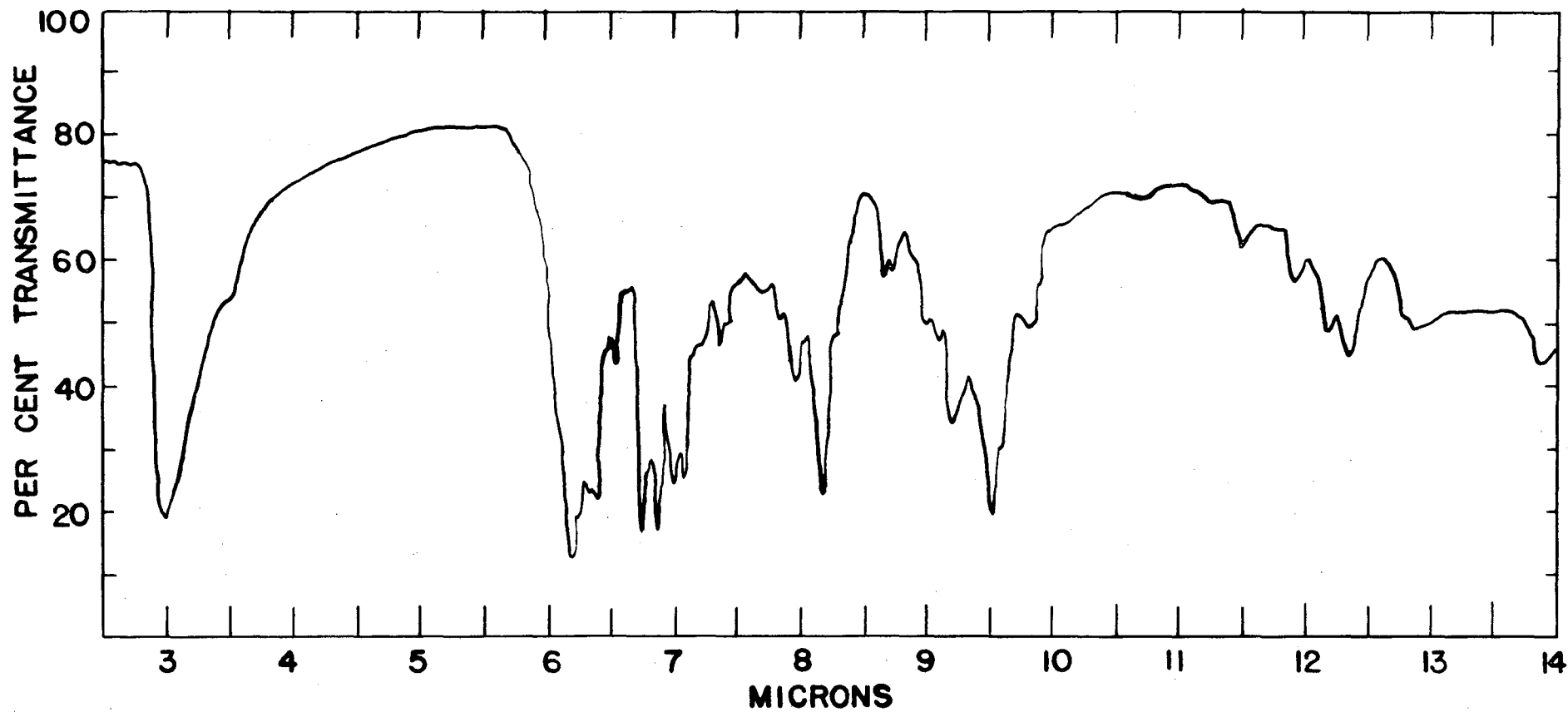


FIGURE 13