







# NBS TECHNICAL NOTE **594-9**

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

*Optical Radiation Measurements:*

**Describing  
Spectrophotometric Measurements**

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*Optical Radiation Measurements:*

**Describing Spectrophotometric Measurements**

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William H. Venable, Jr. and  
Jack J. Hsia

Heat Division  
Institute for Basic Standards  
National Bureau of Standards  
Washington, D.C. 20234



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U.S. DEPARTMENT OF COMMERCE, Frederick B. Dent, *Secretary*  
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, *Director*

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## Preface

This is the ninth issue of a series of Technical Notes entitled OPTICAL RADIATION MEASUREMENTS. The series will consist primarily of reports of progress in, or details of, research conducted in radiometry, photometry, and spectrophotometry in the Optical Radiation Section of the Heat Division.

The level of presentation in OPTICAL RADIATION MEASUREMENTS will be directed at a general technical audience. The equivalent of an undergraduate degree in engineering or physics, plus familiarity with the basic concepts of radiometry and photometry [e.g., G. Bauer, Measurement of Optical Radiations (Focal Press, London, New York, 1965)], should be sufficient for understanding the vast majority of material in this series. Occasionally a more specialized background will be required. Even in such instances, however, a careful reading of the assumptions, approximations, and final conclusions should permit the non-specialist to understand the gist of the argument if not the details.

At times, certain commercial materials and equipment will be identified in this series in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Any suggestions readers may have to improve the utility of this series are welcome.

Henry J. Kostkowski, Chief  
Optical Radiation Section  
National Bureau of Standards

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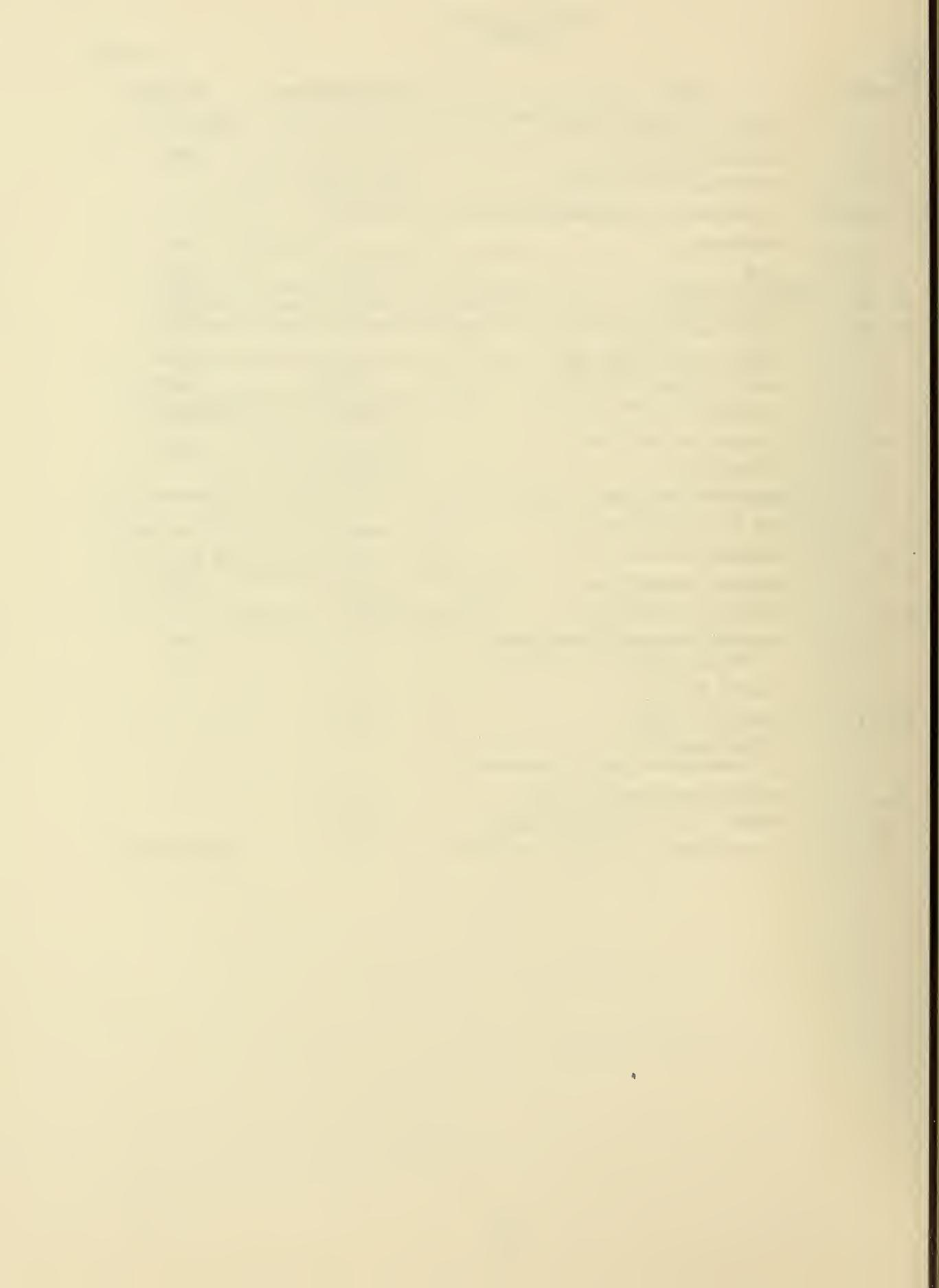
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## Symbols

Symbol	Name	Best Reference	Dimension
L	Spectral radiance input	p. 6	$[W\ m^{-2}sr^{-1}m^{-1}]$
$\vec{P}, \vec{p}$	Position vectors	p. 9, 11	[m]
$\vec{U}, \vec{u}$	Directional unit vectors	p. 9, 11	
$\vec{1}, \vec{2}, \vec{3}$ and $\vec{4}$	Directions of polarization	p. 13	
$\Lambda, \lambda$	Wavelength	p. 9	[m]
T, t	Time	p. 9	[s]
$d\vec{A}, d\vec{a}$	Area element	p. 9	$[m^2]$
$d\Omega, d\omega$	Solid angle element	p. 9	[sr]
$\Gamma$	Angle between $\vec{U}$ and $d\vec{A}$	p. 9	[rad]
$\gamma$	Angle between $\vec{u}$ and $d\vec{a}$	p. 30	[rad]
E	Irradiance	p. 9	$[W \cdot m^{-2}]$
$\phi_i$	Incident radiant flux	p. 11	[W]
C	Probability	p. 13	
S	Scattering function	p. 11	$[m^{-2}sr^{-1}m^{-1}s^{-1}]$
$\delta(\ )$	The Dirac delta function	p. 13	
$L_e$	Emergent radiance	p. 15	$[W\ m^{-2}sr^{-1}m^{-1}]$
$\phi$	Emergent radiant flux	p. 15	[W]
R	Relative responsivity	p. 17	
$\phi'$	Response (responsivity-weighted emergent flux)	p. 17	[W]
K	Scaling function	p. 17	
$N(t', \phi')$	Numerical readout	p. 18	
$G_x$	Output-input ratio (transmittance and reflectance)	p. 19	
$F_{xy}$	Relative measurement ( $G_x/G_y$ )	p. 20	
$F_x$	Factor (e.g. reflectance factor)	p. 21	
$S_k$	Characteristic scattering function	p. 22	$[m^{-2}sr^{-1}m^{-1}s^{-1}]$



William H. Venable, Jr. and Jack J. Hsia

A general method is presented to describe spectrophotometric measurements mathematically. All space is divided into instrument space or sample space. Idealized absolute and relative measurements are defined at the boundary between the instrument and sample space by four descriptors: a radiance input  $L$ , a scattering function  $S$ , a relative responsivity  $R$ , and a scaling function  $K$ . Real measurements are also defined at the boundary and described by these four descriptors, and general expressions for fractional error are derived. A 45-degree, 0-degree reflectance measurement is used as a specific example to illustrate an application of this method to describing measurements and performing an error analysis.

Key Words: Accuracy; appearance; colorimetry; definition of spectrophotometry; error analysis; photometry; radiation transfer; reflectance; scattering; spectrophotometry; transmittance.

## 1. Introduction

### 1.1 Purpose and Scope

Improving the accuracy and usefulness of spectrophotometric measurements made throughout the scientific and industrial community is a fundamental purpose of the spectrophotometry group of the Optical Radiation Section of NBS. In order to move intelligently toward accomplishing this purpose, it is essential that we have a clear understanding within the context of each type of measurement of just what is being measured and of just what is meant by accuracy and error. The lack of such clear definitions and understanding has played a major role in causing uncertainty and confusion in these measurements in the past. In this Technical Note we would like to present an orderly general method for developing mathematical descriptions of spectrophotometric measurements by which these measurements can be defined, instrument calibrations can be described, and error analyses can be performed in a very precise manner. This method will be used in our future work on specific measurement classes.

It is not within the intended scope of this Technical Note to define specific spectrophotometric measurements, as this will be done in later publications. Although some nomenclature must be introduced in order to describe the mathematical method being presented, it is not our intention to propose here a specific set of nomenclature for general use. Every effort has been made to avoid conflict with customary usage and to conform with CIE nomenclature [1]<sup>1</sup> in general, but this Technical Note should be regarded as an effort to organize concepts rather than as an effort to promote a particular symbolism or nomenclature. In the spirit of the authors of the recently proposed Chinese Restaurant Nomenclature [2], we will carefully label our concepts with as many words as necessary and then, for convenience, will introduce short names for concepts which are mentioned often in the text.

### 1.2 An Overview

In our present context, a spectrophotometric measurement involves three elements: a well-defined input flux of radiation, a sample with which the flux interacts, and a well-defined output flux resulting from the interaction. The object of the measurement is to determine as a function of wavelength, and sometimes of other optical parameters, the ratio of the outgoing flux to the incoming flux in order to evaluate certain optical properties of the sample. (These optical properties may, in turn, be correlated with other properties

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<sup>1</sup>Figures in brackets indicate the literature references at the end of this paper.

of the sample such as its chemical composition or its structure, but such correlations are outside the scope of this Technical Note.) As one attempts to describe the fluxes of radiation, the sample, and their interaction, it becomes obvious that each is very complex. A mathematical framework for expressing the descriptions must allow for the complexity, and, therefore will itself be quite involved. For this reason, we will use the remainder of this section to describe the approach we intend to use in common words and as generally as possible. The details of the approach will then be given in the sections which follow.

In sections 2. and 3., we break a measurement down into several component parts in a very general way. In section 2., the principal object is to locate the sample in space. Real samples, particularly those with rough surfaces, are nearly impossible to describe in detail. Often, as in the case of atomic absorption measurements, the surface of the sample is of no interest except as it impedes getting the desired information. To uniquely locate the sample, we surround it with a closed mathematical boundary surface and say by definition that everything inside the boundary is the sample. Of course, such a boundary is chosen to closely match (in shape and extent) what is intuitively regarded as the physical sample, and, if the measurement is to be meaningful, the allowed motion of the physical sample within the imposed boundary should have a negligible effect upon the results.

By using boundaries such as a nearly contiguous plane to represent a rough surface, one can often greatly simplify the mathematics involved in describing a measurement, but a far more important advantage to enclosing the sample with a mathematical boundary is that the measurement can be defined at the boundary in terms of radiances and a function to represent the sample itself. Section 3. deals with the way in which this will be done. The incident flux upon the sample can be calculated from the radiance at the boundary which is directed into the space occupied by the sample, and the outgoing flux can be calculated from the radiance at the boundary directed outward from the space occupied by the sample. Since the sample is completely enclosed in the boundary, all of the flux will automatically be taken into account, and, since all quantities are defined only on the boundary, the tendency to count a portion of flux twice will be eliminated. The sample itself is represented by a function, called the scattering function, which is defined on the boundary and which establishes a relationship between the incoming flux and the outgoing flux which results from it. The scattering function takes into account transmission, absorption, fluorescence, and reflection in addition to what is customarily called scattering, i.e. the entire interaction of the incoming radiation with the sample. An additional function is introduced on the boundary to describe the relative effect on the instrument response of the radiation which is leaving the sample from a particular point, at a particular time, at a particular wavelength, and in a particular direction. Thus, the entire radiometric part of the measurement can be described uniquely on the boundary. A final function, not defined on the boundary, is introduced to express the relationship of the flux calculated from the response weighted integral of the outgoing radiance to the numbers obtained as data from the instrument. This function would take into account electronic gain and time constants and digitalization of the data, among other things.

Upon the foundations laid in sections 2. and 3., a means for defining measurements is built in section 4. A definition is based upon an ideal distribution of incoming radiance and an ideal distribution of response weighting, both defined at the boundary. These, taken with the description of the boundary itself, serve to define a property of whatever is contained within the sample boundary at a given time. If a sensible choice of boundary, incident radiance, and response weighting has been made, the property can reasonably be attributed to the sample itself. In this case, we speak of such things as the reflectance of a piece of tile or the transmittance of a filter.

Finally, in section 5. we deal with real measurements. After a measurement has been carefully defined, and only then, it is possible to discuss such things as calibration of instruments, measurement errors, and correction for systematic errors, which are the topic of that section.

Even from the overview, an idea of the complexity of these measurements can be gained. It is important that a standardization laboratory such as NBS be aware in detail of the workings of the measurements with which it deals, and it is as a guide to such understanding that this Technical Note is directed. It is equally important that spectrophotometric measurements be useful in science and industry. This requires that the user be able to perform the measurements to within the accuracy that he desires with a minimum number of

standards for calibration and the simplest procedures possible. It is our intention to use the concepts presented here to help provide the users with such a capability, and it is our hope that this Technical Note will be put to similar use by instrument makers, secondary standards laboratories, and consultants serving this portion of the measurement system.

## 2. Instrument Space, Sample Space, and Boundary

### 2.1 Intuition

Some of the radiation from the source which supplies the input flux for a spectrophotometric measurement can go where it was not intended to go. Furthermore, radiation from other sources than the intended one can get to the detector and contribute to the output signal from the spectrophotometer. In order that all radiation can be accounted for in an orderly fashion, it is important to account for all space in accurately describing a spectrophotometric measurement, even though it will usually work out that most space will be classified as too remote to be of importance. In a measurement, we are intuitively aware of the presence of an instrument with which the measuring is done and a sample which is being measured. In setting up a frame of reference for describing spectrophotometric measurements, we will simply extend this intuition by connecting the remaining parts of space, which one usually tends to ignore, either with the instrument or with the sample.

### 2.2 Mathematical Partition

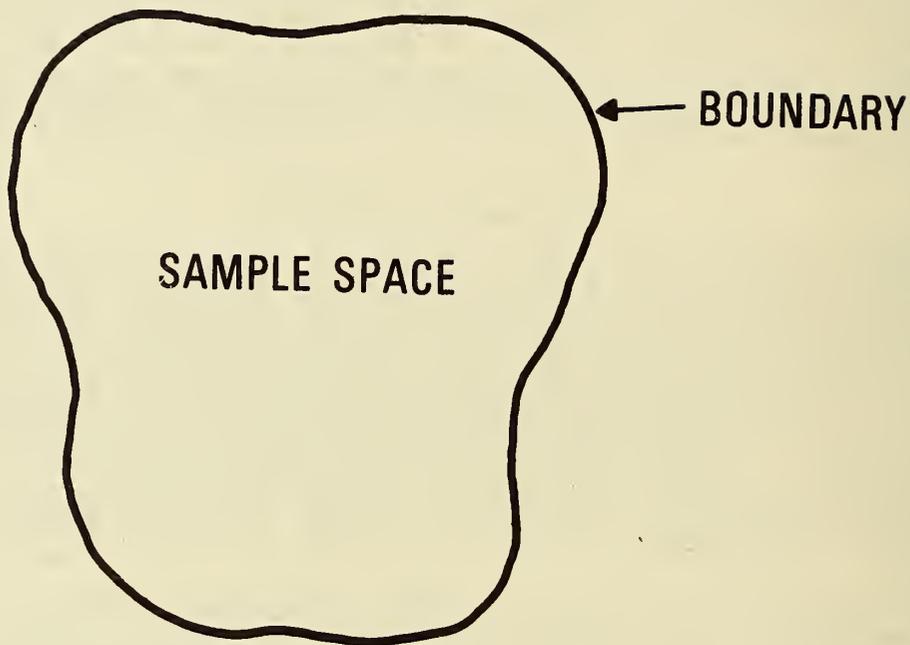
The foregoing intuitive feeling can be more formally expressed by imbedding the entire measurement in a three-dimensional Cartesian space. Each point in the space will then be assigned to one of three sets: the instrument space, the sample space, or the boundary between the two spaces. In this way all space will be accounted for. Since the measurement involves comparing radiation transferred from instrument space into the sample space (input flux) to that transferred from the sample space back into the instrument space (output flux), it will be quite natural to define measurements on the boundary between the spaces. Of course, in order to consider details of instrument performance one must also involve instrument space, and to consider details of the optical behavior of the sample one must work in sample space as well as on the boundary, but the measurement can be defined on the boundary alone.

The instrument space and sample space are to be regarded as volumes in the ordinary sense and the boundaries will be ordinary two-dimensional surfaces. In order to illustrate points in the remainder of this paper, we will generally use drawings such as that in Fig. 1. This shows, in cross section, the sample as a single simply connected region surrounded by instrument. This type of drawing, which is used because of its simplicity, is reminiscent of a number of common real-life situations in which a small object such as a filter is being examined in a laboratory. However, in other cases such as in remote sensing from an airplane or satellite the instrument space can be a relatively small region surrounded by sample. In still other cases, it may be useful to divide the instrument space, the sample space, or both into two or more completely unconnected regions. For example, in an atmospheric transmittance measurement in which the incoming flux is from a searchlight on the ground and the outgoing flux is measured with a radiometer in an aircraft, it might be convenient to regard the instrument space as divided in two as illustrated in cross section in Fig. 2. In the case of the dual beam absorption spectrophotometers common in chemical work, it is often useful to regard the unknown and reference samples as occupying two separate portions of sample space which are surrounded by instrument space. Although the approach to be developed in this Technical Note is intended to apply to every possible case, as a matter of convenience, simple illustrations such as Fig. 1 will be used to represent a general case.

### 2.3 Basis for Dividing Space

Beyond the obvious superficial resemblance of the sample space to the sample itself, the details of dividing the space are quite arbitrary. Since several equally precise definitions of a sample space can generally be made for a particular sample, the choice of the boundary must involve other considerations. The principal basis for the choice of the

**INSTRUMENT SPACE**



**INSTRUMENT SPACE**

ig. 1 The type of drawing which will be used to illustrate in general the division of all space into instrument space and sample space



**SAMPLE SPACE**



**INSTRUMENT SPACE**

**Fig. 2** A drawing illustrating a specific measurement in which the instrument space is in two disconnected regions

detailed description of the sample space will be its suitability to the purpose for which the measurement is intended. Determining which division of space is most suitable is often accomplished by choosing a likely division and seeing what difficulties are encountered under that division. Such factors as ease of sample preparation, simplifying the calculation of desired results, and facilitating error analysis may influence the choice of division. As an example, consider a liquid sample contained within a glass container as depicted in cross section in Fig. 3. If the purpose of the measurement is to determine absorption of radiation in the liquid, then the left and right sample boundaries should probably be chosen as planes within the liquid, parallel to and very close to the interior glass surfaces as indicated by the dimension A in the illustration. In such a case, the glass surfaces would be regarded as part of the instrument and allowance would be made for reflections between them as is done, for example, by Burnett [3]. If on the other hand, one is dealing with the liquid and the container together as a "liquid filter", then the left and right boundaries would probably be chosen as planes in the surrounding air parallel to and very close to the exterior glass surfaces as indicated by dimension B in the illustration. In this case, the interreflections between the glass surfaces are included as part of the sample behavior. In either case, if the liquid is not fluorescing or scattering, and if the radiation passes through reasonably close to normal as indicated, all that is required of the edge boundary which remains is that it completely surround the portion of the sample through which the radiation passes. As a second example, consider a circular, translucent plastic disk with a reflective coating painted on its edge as shown in Fig. 4. Light striking this material is scattered within it. If the purpose of the measurement is to determine the characteristics of the plastic itself and the reflective coating is used to avoid light loss at the edge, then the coating should not be included in the sample space. The coating would be considered as part of the instrument in that it would affect the ability of the instrument to simulate an infinite sheet of the material. On the other hand, if the disk is considered as a standard of diffuse transmittance, the coating should be included as part of the sample.

### 3. Four Descriptors

Once the sample and instrument spaces and their separating boundaries have been established, four mathematical expressions will be used to describe the measurement: one to describe the radiation coming in, a second to describe its interaction with the sample, a third to describe the relative distribution of instrument sensitivity to emerging radiation, and a fourth to describe the relationship between the detected radiation and the numerical reading of the instrument.

#### 3.1 The Radiance Input

##### 3.1.1 Definition

The first descriptor, which will be denoted by  $L$ , is the one used to describe the radiation incident upon the sample. As used here,  $L$  is to be regarded as defined only on the boundary between the sample and the instrument. With regard to units of radiation, we will use  $L$  in one or the other of only two ways. When we refer to radiation in energy units,  $L$  will be, in the Chinese Restaurant Nomenclature [2], the incident spectral power radiance upon the sample. In this case  $L$  will have the dimensions of energy per unit time per unit area per unit solid angle per unit wavelength interval. In terms of the CIE vocabulary [1], the sample can be regarded as a receptor and  $L$  is then the spectral radiance incident upon the receptor.\* On the other hand, when we refer to radiation in photon units,  $L$  will be, in the Chinese Restaurant Nomenclature, the incident spectral photon radiance upon the sample. In this case, the dimensions of  $L$  would be photons per unit time per unit area per unit solid angle per unit wavelength interval. For the aid of those not thoroughly conversant with the concept of radiance in general, a discussion of this concept is given in Appendix A of this paper. From here on, the descriptor  $L$  will be called the "radiance input function", or the "radiance input" for short.

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\*The subscript  $\lambda$  in the usual CIE notation  $L$  has been dropped. The functional dependence on wavelength will be denoted by  $\Lambda$  in parenthesis as in Equation (1).

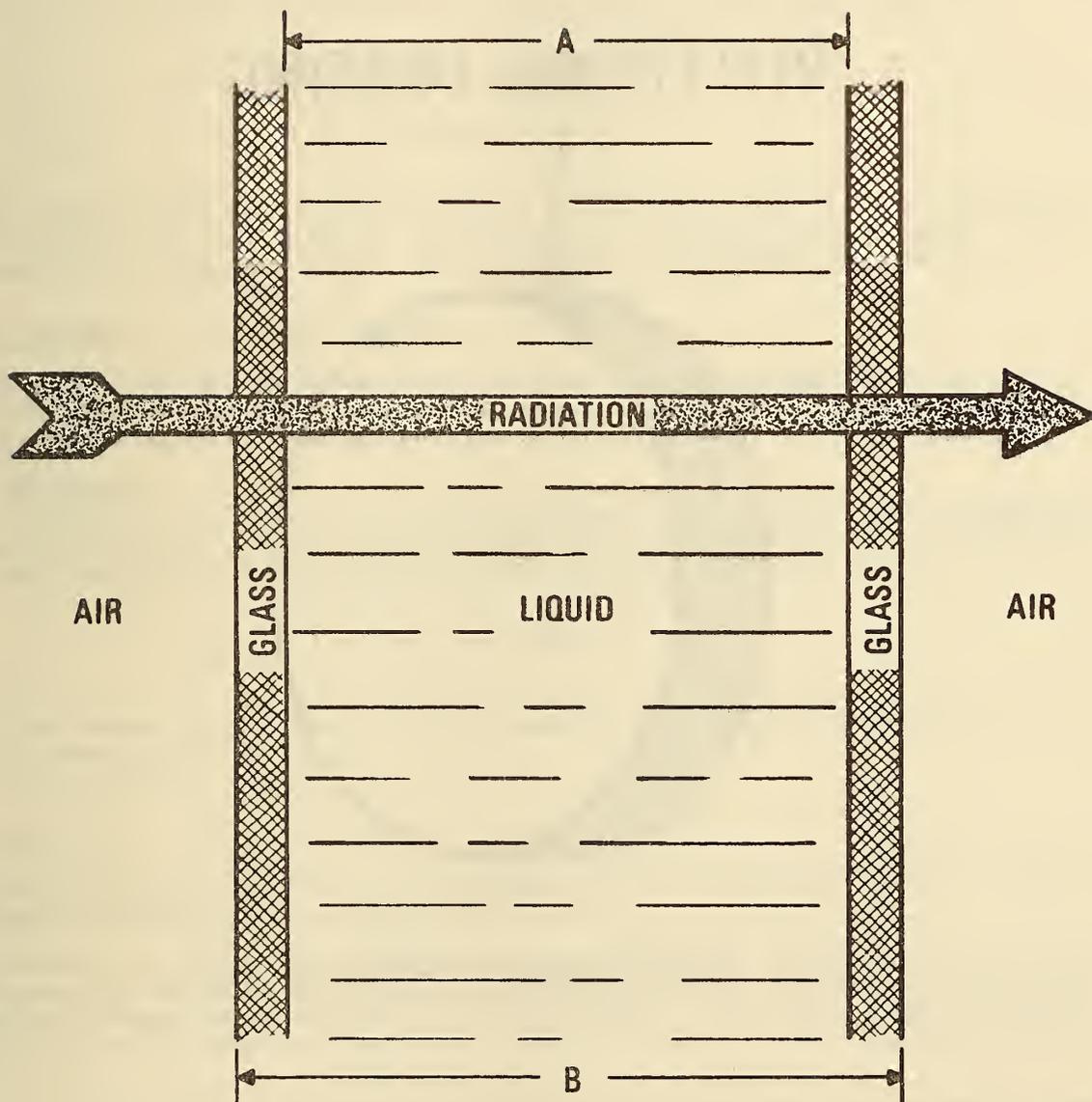


Fig. 3 Cross section of a liquid sample contained in glass

# REFLECTING COATING

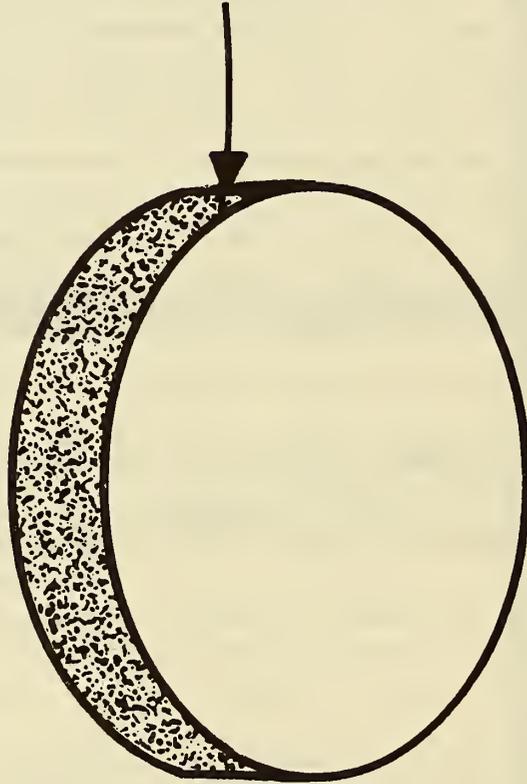


Fig. 4 Disk with reflective coating on the edge

The geometrical entities involved in the radiance input are illustrated in Fig. 5.  $L$  is a function of position on the surface, which will be represented by a position vector  $\vec{P}$ ; a direction, represented by a unit vector  $\vec{U}$ ; wavelength<sup>†</sup>,  $\lambda$ ; and time,  $T$ . (Note that upper case letters are used to represent quantities that relate to the incident radiation. The corresponding lower case letters will be used to represent the corresponding quantities that relate to the outgoing radiation.) The input radiance has a dual vector character, one aspect of which is the direction of travel of the incident radiation indicated by the vector  $\vec{U}$ . The second aspect of the vector character of  $L$  is the polarization of the radiation. To represent this aspect when needed, we will resolve  $L$  into two separate functions corresponding to two mutually perpendicular directions of polarization, each of which we choose to be perpendicular to the direction of propagation. Such directions might be represented by the vectors  $\vec{I}$  and  $\vec{J}$  in Fig. 5, and the corresponding two functions by  $L_1$  and  $L_2$ . If the radiation is to be considered to be a flow of energy, then the quantity given by

$$\begin{aligned} dW_1 &= L_1(\vec{P}, \vec{U}, \lambda, T) \vec{U} \cdot d\vec{A} \, d\Omega \, d\lambda \, dT \\ &\equiv L_1(\vec{P}, \vec{U}, \lambda, T) \cos\Gamma \, dA \, d\Omega \, d\lambda \, dT^* \end{aligned} \quad (1)$$

is the energy passing into the sample through the element of area  $d\vec{A}$  at  $\vec{P}$ , within the element of solid angle  $d\Omega$  oriented in the direction  $\vec{U}$ , within the elemental range of wavelengths  $d\lambda$  at  $\lambda$ , during the element of time  $dT$  at  $T$ , and polarized in direction  $\vec{I}$ .

### 3.1.2 Derivation of Related Quantities

When  $\vec{P}$ ,  $\vec{U}$ ,  $d\vec{A}$ , and  $d\Omega$  are expressed in terms of an appropriate coordinate system, integrals of the radiance input can be used to calculate certain related radiometric quantities, some examples of which follow:

#### IRRADIANCE

Irradiance, as specified by the CIE nomenclature (reference [1], item 45-05-160), can be expressed using  $L$  as a power radiance and integrating over solid angle and wavelength. Thus the irradiance  $E$  at point  $\vec{P}$  on the sample boundary at time  $T$  is given by:

$$E(\vec{P}, T) = \int^2 L(\vec{P}, \vec{U}, \lambda, T) \cos\Gamma \, d\Omega \, d\lambda^{\ddagger} \quad (2)$$

where the integral in  $\Omega$  is over the entire incident hemisphere and the integral in  $\lambda$  is over all wavelengths.

<sup>†</sup>We use wavelength arbitrarily as the spectral parameter, but frequency, photon energy, and wavenumber are also used to represent this parameter.

\* $\Gamma$ , as used here, is the angle between the vectors  $\vec{U}$  and  $d\vec{A}$ . Because  $\vec{U}$  gives the direction associated with the solid angle element  $d\Omega$ , the quantity  $\cos\Gamma \, d\Omega$  is often called the projected solid angle and represented by a single symbol. In the present context, however, we wish to express the angular dependence explicitly by using notation involving the dot product or  $\cos\Gamma$ .

‡The superscript 2 on the integral sign indicates integration over two generalized dimensions (in this case solid angle and wavelength) of the four involved. In general, the symbol  $\int^n$  will indicate integration with respect to  $n$  such generalized variables. In actual computation, the calculation of an integral over the solid angle might in itself involve integration over two variables, but in this presentation it will be represented as a single integration in order to keep the notation simple.

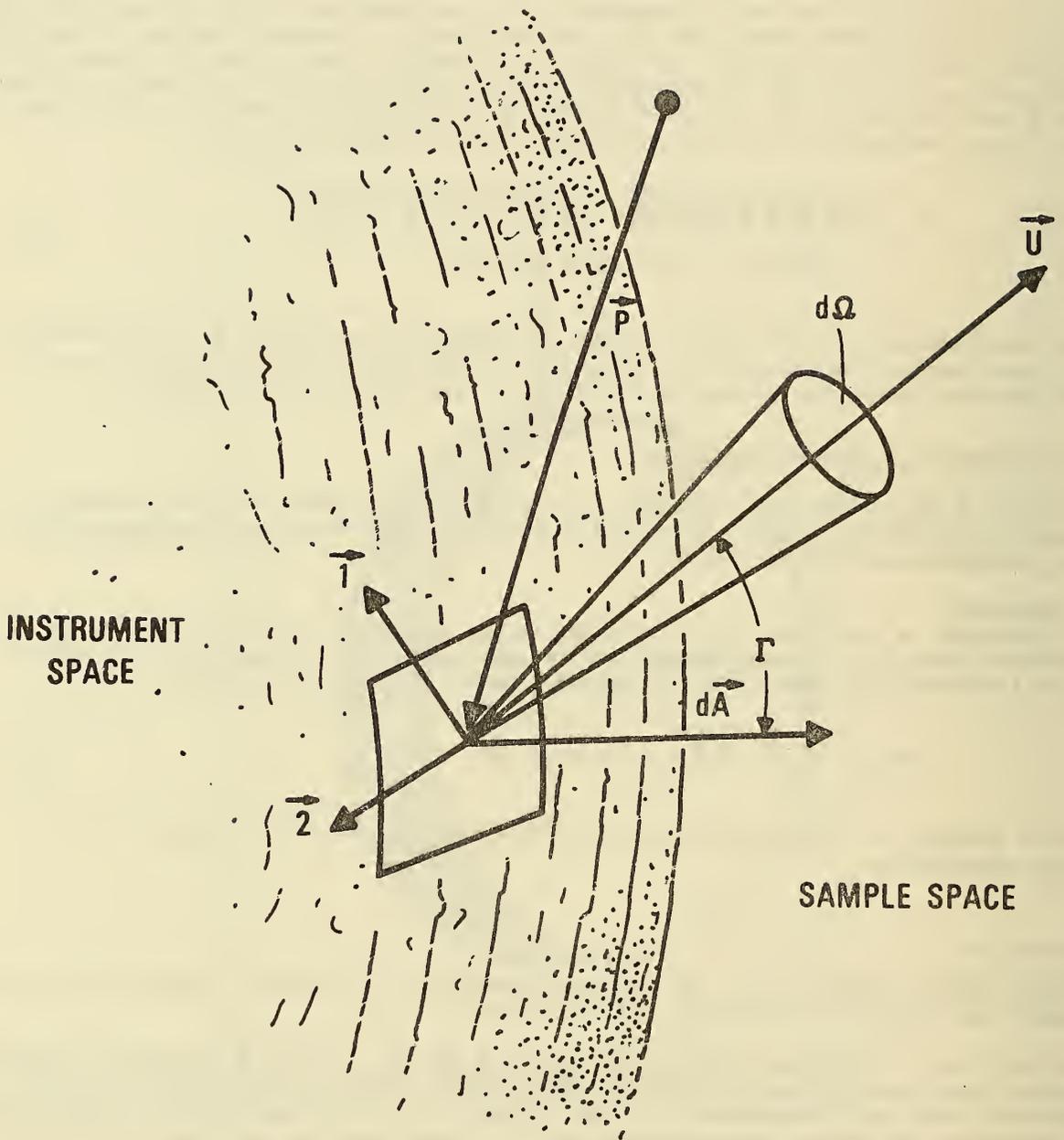


Fig. 5 A diagram for description of the radiance input. (Note that since this arrangement is used to describe radiation entering the sample space  $d\vec{A}$  is defined as positive when directed into sample space.)

## INCIDENT RADIANT FLUX

As specified by CIE (reference [1], item 45-05-135), radiant flux is the power emitted, transferred or received in the form of radiation. The radiant flux  $\phi_i$  into the sample is given by:

$$\phi_i(T) = \int^3 L(\vec{P}, \vec{U}, \Lambda, T) \vec{U} \cdot d\vec{A} \, d\Omega \, d\Lambda \quad (3)$$

where the integral in A is over the entire sample boundary surface, the integral in  $\Omega$  is over the entire incident hemisphere, and the integral in  $\Lambda$  is over all wavelengths. Unless otherwise specified, we will include all incident radiance, including that from light leaks and reflections within the instrument, as part of the radiance input in calculating quantities such as incident radiant flux. Since radiation coming through the boundary out of the sample space can be reflected back into the boundary, the radiance input can be influenced by what is in the sample space. One example of the sample's influencing the radiance input occurs in hemispherical reflectometers using an integrating sphere. In such instruments, the sample becomes part of the sphere wall and strongly influences the radiance input.

### 3.2 The Scattering Function

#### 3.2.1 Definition

The second descriptor is called the scattering function. This descriptor is used to indicate the way in which radiation moving into the sample space emerges from it. The name "scattering function" arises intuitively in the case of samples which are diffuse reflectors or translucent. In such materials, a photon of radiation entering the sample can be thought of as being deflected by a number of particles in the material before it emerges. Since this process results in a more or less random distribution of directions of emergence for photons incident in a given direction, the incident photons can truly be regarded as being scattered by the sample. We will generalize the meaning of scattering to include interaction of the incoming radiation with material in any way, including specular reflection and regular transmission, in which case, of course, the direction of emergence of a "scattered" photon can be predicted by the laws of reflection and refraction. With this general meaning of scattering in mind, we have chosen to give the name "scattering function" to the descriptor which gives the interaction of the radiation with any sample. This function will be denoted by the upper case letter S.

The scattering function describes the way in which radiation interacts with the contents of the sample space. Care should be taken to distinguish between the concept "interacts with the contents of the sample space" and the less well-defined "interacts with the sample". The difference between the two arises chiefly from the fact that the sample space boundary can be chosen in a way which allows the radiation entering and leaving it to be described in a tractable manner, whereas the "real" boundary of the sample is difficult to define and could be highly irregular, rendering calculations impossible. In a well-designed measurement, the position of the sample within the sample space is not critical or else means are provided for aligning the sample carefully, but in either case, the outcome of the measurement can be well defined and is characteristic of the way in which radiation interacts with "the sample itself".

The scattering function will be an explicit function of the variables  $\vec{P}$ ,  $\vec{U}$ ,  $\Lambda$ , and T used to describe the incoming radiation and of the variables  $\vec{p}$ ,  $\vec{u}$ ,  $\lambda$ , and t used to describe the outgoing radiation. In addition, in the case of materials in which the radiative interaction is non-linear, the scattering function can also depend implicitly upon the variables  $\vec{P}$ ,  $\vec{U}$ ,  $\Lambda$ , and T through the radiance input. This dependence will be indicated by including L among the variables indicating functional dependence. The cross section diagram, Fig. 6, illustrates the geometrical aspects of S. The dimensions of S are per unit area, per unit solid angle, per unit wavelength interval, and per unit time. In terms of photon radiance, the quantity

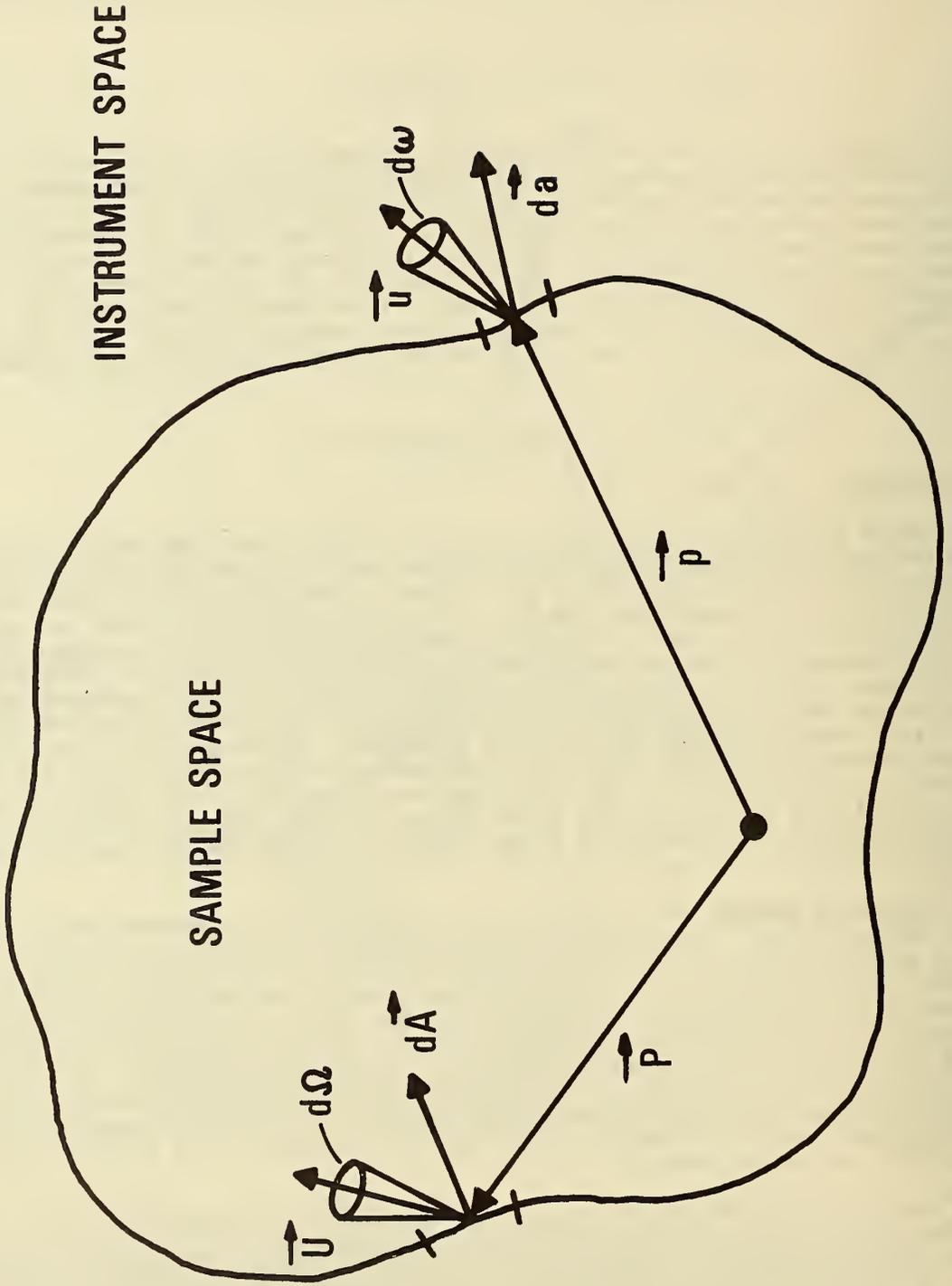


Fig. 6 A diagram for the description of the scattering function

$$C(\vec{P}, \vec{U}, \Lambda, T) = S(\vec{P}, \vec{U}, \Lambda, T; \vec{p}, \vec{u}, \lambda, t; L) \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda \, dt \quad (4)$$

is the probability that a photon of wavelength  $\Lambda$  entering the sample at location  $\vec{P}$  in direction  $\vec{U}$  and at time  $T$  will cause a photon to emerge from the sample through the element of area  $d\vec{a}$  located at  $\vec{p}$ , within the element of solid angle  $d\omega$  in the direction  $\vec{u}$ , within the elemental wavelength range  $d\lambda$  containing the wavelength  $\lambda$ , and during the time interval  $dt$  at time  $t$ . If power radiance is used to describe the radiation,  $C$  would be interpreted as the fraction of the energy put in at  $\vec{P}$  in direction  $\vec{U}$  at wavelength  $\Lambda$  and at time  $T$ , which emerges within the output elements of area, solid angle, wavelength, and time.

When polarization is involved, the scattering function will be resolved into four parts identified by two subscripts each, the first subscript denoting the incident polarization and the second indicating the emerging polarization. Thus if the incoming radiation is resolved into two mutually perpendicular directions of polarization  $\vec{1}$  and  $\vec{2}$ , as in Fig. 5 and the emerging radiation is similarly resolved into two polarizations  $\vec{3}$  and  $\vec{4}$ , then  $S_{13}$  would be used to describe the contribution that radiation entering the sample with polarization 1 would make to the emerging radiation with polarization 3, and similar interpretations apply to other possible combinations  $S_{14}$ ,  $S_{23}$ , and  $S_{24}$ . It may also be necessary to include in  $S$  a way of accounting for relative phase shifts if such things as elliptical polarization are involved.

The scattering function, being a function of nine variables, appears quite complex even in the general form which has been presented so far. There are three ways in which the functional dependence, and hence the notation, can be simplified. The first is the recognition of the linearity of most radiative interactions, the second is a means of reducing the number of variables representing a given dimension such as time, and the third is recognition of uniformity in one or more dimensions. We will present a more detailed discussion of these simplifications before giving illustrative examples of the use of  $S$  in calculating quantities of interest in spectrophotometric measurements.

### 3.2.2 Linearity

The scattering function  $S$  is indicated as an explicit function of  $L$ , since the way in which the radiation is transferred is affected by the density of the radiation flux itself. This effect can be quite strong in the case of phosphorescence where depopulation of the ground state can be considerable, and it can become evident in the case of ordinary reflection and transmission at very high levels of flux such as that from high powered lasers. However, since the effect is negligibly small in a large majority of the cases ordinarily encountered,  $S$  will usually be considered to be independent of  $L$  and the functional dependence of  $S$  on  $L$  will be indicated only when non-linearity is of particular interest.

### 3.2.3 Reduction

Care has been taken to distinguish between the variables used to describe incoming radiation (upper case letters) and those used to describe outgoing radiation (lower case letters). In some situations, there is a definite need for this distinction, while in others the distinction is not important and certain simplifying assumptions can be made. For example, in the case of long-lived phosphors it is usually necessary to distinguish between the time of entry of the exciting radiation and the time at which the resulting radiation leaves the sample space. In most other cases, however, the outgoing radiation emerges a very short time after the entrance of the radiation which causes it, the only delay being due to the finite speed of light as it passes through the sample space or perhaps the decay of very short-lived excited states. In most instrumentation, this very small delay will be of no consequence to the measurement so that we can consider the interaction to be instantaneous and write the scattering function in a reduced form as:

$$S(\vec{P}, \vec{U}, \Lambda; \vec{p}, \vec{u}, \lambda, t) \equiv \delta(T-t) S(\vec{P}, \vec{U}, \Lambda, T; \vec{p}, \vec{u}, \lambda, t) \quad (5)$$

The notation for S on the left will be said to be "reduced in time", and in calculations it will be handled as containing a delta function in T-t as indicated on the right.

Similarly, in fluorescence and phosphorescence, incoming radiation of a given wavelength may cause outgoing radiation having a quite different wavelength. However in many cases, the outgoing radiation has very nearly the same wavelength as the incoming radiation which caused it, the only shift being due to slight energy losses or gains in the scattering processes. In such cases, the scattering function can be reduced in wavelength, the notation then simplifying to:

$$S(\vec{P}, \vec{U}, T; \vec{p}, \vec{u}, \lambda, t) \equiv \delta(\Lambda - \lambda) S(\vec{P}, \vec{U}, \Lambda, T; \vec{p}, \vec{u}, \lambda, t) \quad . \quad (6)$$

In a similar fashion, S can reasonably be reduced in position on the surface (i.e., in the variables  $\vec{p}$  and  $\vec{P}$ ) in the case of highly opaque materials in which the only significant outgoing radiation occurs very close to the entry point of the incoming radiation which caused it. Reduction of S in direction would make sense only for nearly perfect retro-reflecting materials which are seldom encountered.

Of course it is quite possible for S to be reduced in more than one dimension at once. Thus for a highly opaque non-fluorescing material, one might represent S by:

$$S(\vec{U}; \vec{p}, \vec{u}, \lambda, t) \equiv \delta(\vec{P} - \vec{p}) \delta(\Lambda - \lambda) \delta(T - t) S(\vec{P}, \vec{U}, \Lambda, T; \vec{p}, \vec{u}, \lambda, t) \quad . \quad (7)$$

CAUTION: Reduction represents an approximation to reality. One should always be sure that for a given instrument and sample the assumptions leading to reduction are valid before proceeding with an analysis based on it.

#### 3.2.4 Uniformity

In the case in which S represents a sample which is uniform in one or more of its dimensions, a further simplification in the functional dependence can be recognized. If, for example, the material giving rise to S is stable in time, then the time dependence between the incoming and outgoing radiation will only involve elapsed time, i.e., t-T. In this case one can write S as:

$$S(\vec{P}, \vec{U}, \Lambda, T; \vec{p}, \vec{u}, \lambda, t - T) \quad . \quad (8)$$

Similar simplifications based on uniformity can be recognized in the other dimensions. One which often occurs in treating diffuse reflectance from translucent materials is a simplification in position in which the amount of radiation emerging from a given point from the sample depends only on its displacement from the point of entry of the incoming radiation which causes it. In this case S becomes

$$S(\vec{U}, \Lambda, T; \vec{p} - \vec{P}, \vec{u}, \lambda, t) \quad (9)$$

or, in cases when the material is also homogeneous,

$$S(\vec{U}, \Lambda, T; |\vec{p} - \vec{P}|, \vec{u}, \lambda, t) \quad . \quad (10)$$

In cases of uniformity in a given dimension in which reduction also applies, no variable need be retained to represent that dimension at all. As an example, time dependence can be dropped entirely from the notation for S in the case of linear, stable, non-phosphorescing materials.

### 3.2.5 Derivation of Related Quantities

Use of the scattering function allows us to express the derivation of several radiometric quantities which will be of interest in the definition and analysis of spectrophotometric measurements. In these examples, the complete functional dependence will be used with no simplifications.

#### EMERGENT RADIANCE

In all cases except that of a black body, some of the incident radiant flux causes radiation to emerge from the sample boundary into the instrument space. This emergent radiance  $L_e$  is given by:

$$L_e(\vec{p}, \vec{u}, \lambda, t) = \int^4 L(\vec{P}, \vec{U}, \Lambda, T) S(\vec{P}, \vec{U}, \Lambda, T; \vec{p}, \vec{u}, \lambda, t) \vec{U} \cdot d\vec{A} \, d\Omega \, d\Lambda \, dT \quad (11)$$

where the integral in  $A$  is over the entire sample boundary, the integral in  $\Omega$  is over the incident hemisphere above each surface element, the integral in  $\Lambda$  is over all wavelengths and the integral in  $T$  is over all past time up to and including  $t$ .

A great deal of care must be taken in defining  $S$  and interpreting quantities such as  $L_e$ . Unless specifically noted, we will attempt to define  $S$  in such a way that  $L_e$  includes all emergent radiance caused by  $L$  and no other. For example, thermal emission fed by energy entering the sample by means other than the radiance input, such as by electrical heating, chemical reaction, or by heat transfer by conduction, would not be included in  $L_e$ , but thermal emission fed by heating caused by the incident radiant flux would ordinarily be included, and would represent a case of non-linearity. This type of radiation transfer process could be strongly affected by the temperature of the sample in the cases in which it is important, which serves to illustrate that  $S$  quite often depends upon parameters other than those explicitly indicated by the functional dependence in the definition in section 3.2. In the ordinary applications of spectrophotometry, only radiation in the past is included as the cause of radiation in the present. In order to simplify the expressions for  $S$ , this causality will usually be taken into account in the limits of integration for  $T$  as described in the preceding paragraph.

#### EMERGENT RADIANT FLUX

In this case we are dealing with the CIE defined concept of emitted radiant flux, but only that part which is caused by the incident radiant flux (see 3.1.2). This flux, which we will call the emergent radiant flux and will designate by  $\phi$ , is given by the expression:

$$\phi(t) = \int^7 L S \vec{U} \cdot d\vec{A} \, d\Omega \, d\Lambda \, dT \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda \quad (12)$$

where the usual functional dependences apply for  $L$  and  $S$  and where the integrals in  $A$  and  $a$  are over the entire sample boundary, the integrals in  $\Omega$  and  $\omega$  are over the incident and emergent hemispheres respectively, the integrals in  $\Lambda$  and  $\lambda$  are over all wavelengths, and the integral in  $T$  is over all time in the past up to and including  $t$ .

## 3.3 Relative Responsivity

### 3.3.1 A Receiver Model

In order to describe how data from the measurements is related to the emergent radiance (see 3.2.5), we will use an idealized receiver model illustrated schematically in Fig. 7. Although it is not perfectly general, this model can represent the response of most useful spectrophotometric instruments to the emergent radiance. It should be emphasized that this is an idealization of the behavior of the instruments and it may be that a simple analogy between the blocks in the diagram and specific physical portions of the instrument itself cannot be made. The first block will be treated in the present section (3.3) and the remaining part will be treated in section 3.4.

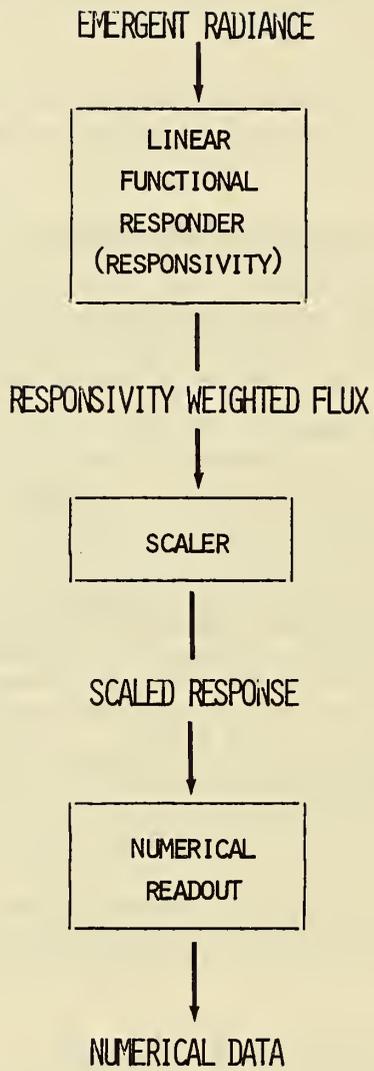


Fig. 7 Block diagram of receiver model used in a general description of spectrophotometric measurements

### 3.3.2 Relative Responsivity

The first portion of the receiver model will be represented by a descriptor which will be called the relative responsivity. The relative responsivity in this context provides a geometrical weighting function which describes the relative contribution to the instrument output by the radiance leaving the sample space at a particular point and in a particular direction. The relative responsivity will be defined on the boundary between the instrument and sample space in terms of the emergent geometrical quantities and will be denoted by the letter R, i.e.:

$$R \equiv R(\vec{u}, \vec{p}, \lambda, t) \quad (13)$$

Since R is a relative weighting function, it will be determined only to within a multiplicative constant, so that in order to make R unique in any particular situation, one must impose a scale on R. Since R is being used strictly as a weighting function, we will define it to be dimensionless. The functional dependence expressed above implies that R is linear, i.e., that the relative response of the instrument does not depend significantly in any way upon the emergent radiance. This assumption is consistent with good practice in spectrophotometric measurement, since the results of a measurement would be quite unpredictable if non-linearity of this type existed. This condition does not rule out the possibility of non-linearity with respect to responsivity-weighted emergent flux as defined in the next paragraph. This latter type of non-linearity will be included in the scaling function defined in section 3.4.

### 3.3.3 Response

The principal quantity calculated directly through the use of R will be the responsivity-weighted emergent flux which will be designated by the symbol  $\phi'$  and which is defined as:

$$\phi'(t) = \int^3 L_e R \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda \quad (14)$$

where the emergent radiance  $L_e$  is defined in expression (11). This responsivity-weighted emergent flux, which we will call the response for short, provides a measure of the impact of the emergent radiance upon the instrument's receiver. This relationship between response and emergent radiance (the response is a linear functional of the emergent radiance) is one of the major assumptions of the model we are using. Under this assumption,  $\phi'$  depends only on the current level of the radiation received by the instrument, and not on its history, and, furthermore, such effects as "cross-talk" between portions of the flux entering the instrument in different ways and localized saturation of the detector for radiation entering at specific angles and from specific locations are ruled out.

## 3.4 The Scaling Function

### 3.4.1 Definition

The remaining descriptor, which we will call the scaling function and denote by the letter K, takes into account any time dependence or non-linearity which is either intentionally or unintentionally introduced into the receiver. The scaling function determines the connection between the response and the numerical output of the instrument and may be used to account for anything from simple logarithmic scaling or simple time constants to the more complex behavior of a phase-sensitive demodulator. Any units required for associating the scale units on the numerical readout (volts, amperes, etc. or simply numbers) to the units of the quantity involved in the emerging flux (energy, photons, etc.) would be included in K, and the adjustable scale factors which are often included in an instrument for purposes of calibration would also be included in K. In general, K takes into account all of the behavior of the instrument except the relative sensitivity distribution which is described by R.

### 3.4.2 Datum Calculation

The final output of the instrument is a number. This number, which will be denoted by  $N(t', \phi')$ , can be determined from

$$N(t', \phi') = \int_0^{t'} K(t, \phi'(t)) dt \quad (15)$$

where  $\phi'(t)$  is given by expression (14). Here the assumption is made that  $N$  is independent of the distribution of the emergent radiance giving rise to the response  $\phi'$ , an assumption which is not entirely general, but which covers almost all good spectrophotometric practice. Note that although no descriptor is associated with the Numerical Readout portion of the receiver model, one aspect of this portion of the model must be taken into account, i.e., the resolution of the readout. It should be remembered that the resolution of the readout places an upper limit on the number of significant figures which appear in each datum and thus an upper limit on the significant figures in related quantities which are calculated from the data. Since  $N$  and  $K$  depend on details of the specific instrument which is used, they will not be further discussed in this Technical Note.

### 3.5 Remarks

It has been our intention to provide a mathematical framework within which to place the description of spectrophotometric measurements which allows a maximum of flexibility in accounting for individual variations of measurements while still providing a precise means of communicating descriptions of these measurements. Certain points about the descriptors should be reemphasized. The radiance input  $L$  is defined on the boundary between the sample and instrument and includes all incident radiation, even including radiation which may have entered the sample space, left it, and been reflected back into it. The scattering function  $S$  is defined twice on the entire boundary, once for incoming geometry and once for outgoing. The relative responsivity  $R$  is defined on the boundary also, and not somewhere else in the instrument such as at a detector.  $R$  is a dimensionless weighting function which describes the geometrical, spectral, and temporal distribution of the sensitivity of the receiver. All other description of the receiver, including non-linearity, scale changes and adjustments of units, will be included in the scaling function  $K$ .

## 4. Defining Measurements

An essential part of analyzing a measurement for systematic errors is to have the measurement well defined. The scheme just presented for dividing space and representing measurement with descriptors is well suited for defining measurements. Because of the complexity introduced by finite decay times and dual wavelength dependence in phosphorescence and fluorescence, we will restrict ourselves in illustrating how measurements are defined to scattering functions which are reduced in wavelength and are completely time-independent. Such scattering functions still are sufficiently general to cover all reflectance and transmittance measurements.

### 4.1 Approach to Definition

A practical way to define a measurement on a given boundary is in terms of a specific radiance input  $L$ , which we will call the defining  $L$ , and a specific relative responsivity  $R$ , which we will call the defining  $R$ . For example, in a specific case, the radiance input  $L$  might have a constant value for specific ranges of angles of incidence and points of incidence and be zero elsewhere. Similarly, the relative responsivity  $R$  used to define the measurement might be unity over a particular range of wavelengths, exit points, and angles, and be zero for all others. The scaling function  $K$  would usually be chosen for purposes of definition so that the instrument output is numerically equal to the response as defined in expression (14). One usually tries to choose the defining boundary in such a way that the response does not depend strongly on a small displacement of the sample. Once the defining boundary, defining  $L$ , and defining  $R$  have been chosen, the measurement of a particular

sample will depend upon the sample being measured, and the scattering function S represents the properties of the sample space in the expressions for the definitions.

#### 4.2 Defining Output-Input Ratio ( $G_x$ )

The fundamental spectrophotometric measurement consists of taking a ratio of a portion of the outgoing flux to the incoming flux which caused it. The particular class of measurement will depend upon the defining boundary, L, and R. For example, if the defining boundary is a plane, and L and R are non-zero only on the same side of the plane (the instrument space side), the measured quantity would generally be called a reflectance. If the boundary were a parallel pair of planes with the sample space between them and L non-zero only on one side of the sample space and R non-zero only on the other side, the measured quantity would normally be called a transmittance. In the case of more complicated samples and boundaries, the distinction between transmittance and reflectance becomes less clear and the measurement becomes more difficult to classify. However, we will sidestep such problems in nomenclature by using the letter G to represent all such output-input ratios.

Specifically,  $G_x$  is the ratio of a specific portion of the emergent flux to the flux which caused it. As indicated in 3.1.2, the incident flux is:

$$\phi_i = \int^3 L(\vec{U}, \vec{P}, \lambda) \vec{U} \cdot d\vec{A} \, d\Omega \, d\lambda \quad (16)$$

where the lower case variable for the wavelength anticipates the consequences of reduction with respect to wavelength (see 3.2.3), and the corresponding response-weighted emergent flux would be

$$\phi'_e = \int^5 L(\vec{U}, \vec{P}, \lambda) S_x(\vec{U}, \vec{P}; \vec{u}, \vec{p}, \lambda) R(\vec{u}, \vec{p}, \lambda) \vec{U} \cdot d\vec{A} \, d\Omega \, \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda \quad (17)$$

where integration is over the entire range of each variable involved. The defined G associated with the particular choice of defining L and R would be:

$$G_x \equiv \frac{\phi'_e}{\phi_i} = \frac{\int^5 L S_x R \vec{U} \cdot d\vec{A} \, d\Omega \, \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda}{\int^3 L \vec{U} \cdot d\vec{A} \, d\Omega \, d\lambda} \quad (18)$$

A variation on the definition above which is commonly encountered is the spectral reflectance or transmittance in which the integral over the wavelength is not taken. If we denote such a quantity by  $G_x(\lambda)$ , it would be defined as:

$$G_x(\lambda) = \frac{\int^4 L S_x R \vec{U} \cdot d\vec{A} \, d\Omega \, \vec{u} \cdot d\vec{a} \, d\omega}{\int^2 L \vec{U} \cdot d\vec{A} \, d\Omega} \quad (19)$$

where again, L and R are appropriate defining quantities.

In those cases in which L and R are constant with respect to the geometrical parameters  $\vec{P}$ ,  $\vec{U}$ ,  $\vec{p}$  and  $\vec{u}$  over specific ranges and zero elsewhere,  $G_x(\lambda)$  is often defined as

$$G_x(\lambda) = \frac{\int^4 S_x \vec{U} \cdot d\vec{A} \, d\Omega \, \vec{u} \cdot d\vec{a} \, d\omega}{\int^2 \vec{U} \cdot d\vec{A} \, d\Omega} \quad (20)$$

where the integrals are now taken over the specific ranges (the same ranges for the incident variables, of course, in both the numerator and denominator integrals). The expression (20) is formally equivalent to (19) under these conditions on L and R, and expressions such as (20) are commonly used as defining relations. However, since (19) is more stimulating to insight into how to analyze an instrument with which one is attempting to approximate the conditions of definition, expression (19) is the form we will use to develop definitions.

The ranges over which L or R are non-zero can be vanishingly small in one extreme or can cover the whole allowed range of a variable in the other extreme. As an example involving both extremes consider SPECTRAL DIRECTIONAL/HEMISPHERICAL REFLECTANCE. In this case, the universe is divided in two by the boundary plane, on one side of which is instrument space and on the other side of which is sample space. The L of definition is non-zero L( $\lambda$ ) only over a small area A' surrounding the P' and within a small solid angle  $\Omega'$  surrounding the direction  $\vec{U}'$ , where A' and  $\Omega'$  are allowed to become vanishingly small. The defining responsivity is R=1 over the entire boundary and in all directions from the boundary into instrument space. Using these in expression (19), we have for the directional/hemispherical reflectance

$$G_x(\lambda) \vec{U}' \vec{P}' / h = \int^2 S_x(\vec{U}', \vec{P}'; \vec{u}, \vec{p}, \lambda) \vec{u} \cdot d\vec{a} \, d\omega \quad . \quad (21)$$

This expression could have been obtained formally from expression (20) by simply not integrating over the incident solid angle, but the former approach is more suggestive of a means of treating attempts to meet the definition with real measurements in which the solid angles  $\Omega'$  and the area A' do not vanish. If the sample is uniform, the dependence on P' drops out and it is no longer necessary to take a limit with respect to A'. Furthermore, if the sample is uniform with respect to rotation about an axis normal to the boundary as well,  $G_x(\lambda) \vec{U}' \vec{P}' / h$  can be written  $G_x(\lambda) \Gamma / h$  where  $\Gamma$ , as before, is the angle between the incident direction and the normal to the boundary. It is the latter, simpler version of  $G_x(\lambda)$  which is most commonly called the spectral directional/hemispherical reflectance.

### 4.3 Defining Relative Measurements ( $F_{xc}$ )

The measurement of G's (with possible exception of regular transmittance) is not easily done in practice. The reasons can be seen upon examination of expressions such as (18) or (19). The radiance measurement indicated in the numerator is of radiance leaving the sample space, whereas the measurement indicated in the denominator is of radiance entering the sample space. This requires two distinct measurements to be made under what are usually quite different conditions. For example in the case of the directional/hemispherical reflectance just discussed, the input flux is collimated and directed at a small spot, whereas the emergent flux which is to be compared to it is spread over a whole hemisphere. In addition, either because of the geometrical arrangement of the measurement or the nature of the sample, the emergent flux may be much smaller than the incident flux, thereby calling for comparisons over a large dynamic range. Any dissimilarity between the two fluxes being measured can lead to errors in the calculated G's unless great care is taken in measuring the fluxes.

One way to make accurate measurements more simply is to measure relative to a chosen sample, i.e., to take the ratio of two G's. If the radiance input is stable, it will be the same for both samples and hence will cancel out of the ratio, leaving

$$F_{xc} = \frac{\int^5 L S_x R \vec{U} \cdot d\vec{A} \, d\Omega \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda}{\int^5 L S_c R \vec{U} \cdot d\vec{A} \, d\Omega \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda} \quad (22)$$

where  $S_x$  is the scattering function with the sample being measured and  $S_c$  is the scattering function of the chosen comparison sample. It is apparent from the form of the expression that as the properties of the measured and comparison samples become more and more alike, the value of  $F_{xc}$  becomes independent of the form of L and R, until, in the limit when the



uniform hemispherical irradiance and directional responsivity. Since factors ( $F_x$ ) are merely a special case of relative measurements, it follows that reciprocity can apply to the definition and measurement of factors in the same way. G's, however, do not possess symmetry with respect to L and R (see expression (18)), and therefore reciprocity usually does not apply to these quantities.

#### 4.6 Fluorescence and Phosphorescence

Since measurements of fluorescence and phosphorescence are more complicated and since there is not such universal agreement on how they should be defined, we will reserve detailed treatment of these measurements for writings dealing specifically with them. In general, the incident and emergent wavelengths are well separated, so that reduction in wavelength cannot be applied. From the point of view of macroscopic measurements, the principal difference between fluorescence and phosphorescence is that in the case of fluorescence the time constants associated with the decay of the excited states is short enough that reduction in time is still a valid approximation. Because the time constants involved in either case are generally much longer than for elastic scattering, there is a correspondingly greater chance for non-linearity in the scattering function S due to the depletion of the ground state population. Since significant emission of fluorescent and phosphorescent radiation from the excited states requires a population of these states far above that which exists without the incoming radiation, reciprocity does not apply. In spite of these complications, however, the present scheme for writing descriptions and definitions of spectrophotometric measurements is sufficiently general for use with fluorescence and phosphorescence.

#### 5. Real Measurements and Errors

In the preceding section, we have dealt principally with defined measurements in which idealized radiance inputs L and relative responsivities R were used. In practice, L and R are not identical to the defining L and R, so that a possibility for error is introduced. The specific treatment used in analyzing a particular measurement for possible errors must be determined by a detailed study of that measurement. A portion of one such analysis is given as an example in Appendix B of this Technical Note, but beyond this, treatment of the error analysis for a specific measurement will be reserved for publications dealing with that measurement. There are, however, certain problems, approaches, and general conclusions involved with real measurements which can be discussed in a general way using the descriptors. Some of these will be presented in the following sections, not as new ideas, but rather as an illustration of how the descriptor approach to spectrophotometric measurements can be used to present and analyze such measurements.

##### 5.1 Optimization of a G Measurement

In defining a measurement, L and R are specified, and G can then be exactly specified for a sample in terms of its scattering function S. Under the assumptions of linearity (3.2.2) which have been made, the exact magnitude of L is not important to the measurements. This is indicated by the fact that an arbitrary constant multiplier of L will cancel out in the definition of G in expression (18). However, in a real measurement, it is usually impossible to realize the spectral and geometrical form of L exactly, and a compromise must be accepted. The choice of such a compromise is involved in the problem of "normalization" which is discussed in the literature [9]. In the following paragraphs, the problem is illustrated by giving one approach to the compromise which might be used by a standardizing laboratory which has considerable instrumentation for auxiliary measurements at its disposal.

##### 5.1.1 Choosing a Characteristic Scattering Function $S_k$

For purposes of this discussion, we will represent the radiance input used in the definition by L and the actual radiance input in the instrument by  $L_r$ . Similarly the relative responsivity of definition will be represented by R and the actual relative responsivity will be represented by  $R_r$ . If  $L_r$  cannot be made proportional to L, or if  $R_r$  cannot be made equal to R for every value of the variables involved, a measurement error

which depends upon the scattering function of the sample may exist. When measurements are to be made on a particular class of samples, there may be an advantage to choosing a characteristic scattering function, which we will call  $S_k$ , which represents the class of samples to be measured. For example, if diffuse reflectors are to be measured, a reasonable characteristic scattering function would be the ideal Lambertian reflector, in which case  $S_k$  would be  $\delta(\vec{p}-\vec{p})/\pi$ . The choice of a compromise  $L_r$  and  $R_r$  would then be based on optimizing measurements for the scattering function  $S_k$ .

### 5.1.2 Optimizing $L_r$

In the instruments used in standardizing laboratories (or, for that matter, in designing an instrument), there is a certain flexibility of choice of  $L_r$ , such as choice of sources or irradiation, aperture sizes, etc. As a first condition on the choice of  $L_r$ , it is reasonable to require that it be possible to measure a sample with the characteristic scattering function exactly, if the response were as defined, i.e.

$$\int L_r S_k R = \int L S_k R^* \quad . \quad (27)$$

This requirement determines the value of the scaling of  $L_r^\dagger$ . An equivalent way of expressing this condition is:

$$\int \delta L S_k R = 0 \quad (28)$$

where

$$\delta L = L_r - L \quad . \quad (29)$$

This condition can generally be realized for a wide range of forms of  $L_r$ , including ones for which  $L_r$  and  $L$  may differ greatly. Since it is desirable that samples with scattering functions differing slightly from  $S_k$  also be measured accurately,  $L_r$  should not differ too greatly from  $L$  for any choice of the variables. One way of approaching this is to choose from the available  $L_r$ , one for which an integral of the form  $\int |\delta L S_k R|^n$ ;  $n > 0$  is minimum. The choice of the exponent  $n$  is arbitrary and should be made with the application in mind. Choosing too low a value of  $n$  may favor an  $L_r$  which departs too strongly from  $L$  over a limited range of one or more of the variables. On the other hand, minimizing the integral for too large a value of  $n$  may favor an  $L_r$  which departs from  $L$  over a very extended range of one or more of the variables. For purposes of practical calculation, it has become customary to choose  $n$  as its smallest even integer value, 2, and to minimize  $\int (\delta L S_k R)^2$ .

### 5.1.3 Optimizing $R_r$

The preceding discussion for  $L_r$  applies in an analogous way to  $R_r$ . One can normalize  $R_r$  so that

$$\int L S_k \delta R = 0 \quad (30)$$

---

\*To reduce the complexity of the notation in the interest of making the course of our discussion more apparent, we will not explicitly express the differentials involved with our notation for integrals. These would be filled in as appropriate when the expressions are used with a specific measurement.

†In this context, we will use the word "scaling" to mean "multiplying by a constant".

where

$$\delta R = R_r - R \quad (31)$$

and choose from the available  $R_r$ , the one for which the integral  $\int |(LS_k \delta R)|^n$  is minimum. In certain cases in which a reduction with respect to an input variable can be made, it is useful to optimize  $L_r$  and  $R_r$  together by scaling the combination so that

$$\int \delta(LR) S_k = 0 \quad (32)$$

where

$$\delta(LR) = L_r R_r - LR \quad (33)$$

#### 5.1.4 Corrections When the Form of $S_x$ is Known

When a sample is measured, the measured value of  $G$ ,  $G_{xm}$ , is that given by

$$G_{xm} = \frac{\int L_r S_x R_r}{\int L_r} \quad (34)$$

where  $L_r$  and  $R_r$  have already been optimized as discussed in the preceding section. If, in addition, the form of  $S_x$ ,  $S_{xf}$  is known, a correction for the measured value can be calculated. One can first determine  $S'_{xf}$ , which is scaled from  $S_{xf}$  so that  $S'_{xf}$  satisfies (34) above for the known optimized  $L_r$  and  $R_r$  and the measured  $G_{xm}$ . Then a corrected value  $G'_{xm}$  for the measured  $G$  can be determined from

$$G'_{xm} = \frac{\int L S'_{xf} R}{\int L} \quad (35)$$

Notice that this correction need not be made with respect to all variables, but can be made just for the variables for which a more detailed investigation of  $S_x$  is possible.

## 5.2 The Advantage of Relative Measurements

The discussion in section 5.1 was from the point of view of the standardization laboratory or possibly the instrument designer, where a detailed analysis of  $L_r$  and  $R_r$  might be undertaken, and where details of the scattering function could be taken into account. In the case of the user in industry or an analytical laboratory, such detailed measurements are not practical and generally not possible. Therefore, such a user accepts the  $L_r$  and  $R_r$  associated with his instrument and simply makes a measurement. The fractional error in a direct measurement  $G_x$  due to departure from the defining  $L$  and  $R$  would be

$$\frac{\delta G_x}{G_x} = \frac{\int L_r S_x R_r}{\int L_r} \frac{\int L}{\int L S_x R} - 1 \quad (36)$$

where  $\delta G_x = G_{xm} - G_x$  where  $G_x$  is defined by expression (18) and  $G_{xm}$  is defined by expression (34). Because of the presence of  $L$  and  $L_r$  both in the numerator and in the denominator, these quantities may be scaled arbitrarily without changing the value of  $\delta G_x / G_x$ . In order to simplify the appearance of the expression, we can choose the scaling so that

$$\int L = \int L_r \quad (37)$$

and let  $\delta L$  denote the difference between  $L_r$  and  $L$  as in expression (29). Generally, the measurement of the incoming flux  $\int L_r$  and the measurement of the outgoing response weighted flux  $\int L_r S_x R_r$  require separate calibrations, so that calibration errors will not cancel out when the measured  $G$  is calculated. Since the expressions for the two fluxes appear as a ratio in expression (36), we will associate the resultant calibration error with the real detector response  $R_r$  and write

$$R_r = R + \delta R \quad (38)$$

where we include in  $\delta R$  the effects of the calibration errors (which appear so as to scale  $R_r$ ) as well as the difference in form between  $R$  and  $R_r$ . With the aid of expressions (29) (37), and (38), the expression (36) can be written as

$$\frac{\delta G_x}{G_x} = \frac{\int \delta L S_x R}{\int L S_x R} + \frac{\int L S_x \delta R}{\int L S_x R} + \frac{\int \delta L S_x \delta R}{\int L S_x R} \quad (39)$$

The fractional error in a relative measurement  $F_{xc}$  on the same instrument is given by

$$\frac{\delta F_{xc}}{F_{xc}} = \frac{\int L_r S_x R_r}{\int L_r S_c R_r} \frac{\int L S_c R}{\int L S_x R} - 1 \quad (40)$$

In order to place this expression in a form in which it is readily comparable to expression (39), we can first take advantage of the appearance of both  $R$  and  $R_r$  in the numerator and in the denominator of the first term on the right in expression (40) to scale the relative values of  $R$  and  $R_r$  so that

$$\int R_r = \int R \quad (41)$$

Notice that no calibration is needed in a relative measurement since the same detector is involved in the same way in measuring both samples, so it is not necessary to account for calibration errors in  $R_r$  as in the case of measuring  $G$  (see the discussion surrounding expression (38)), and we are free to choose  $R_r$  so that (41) is satisfied. We will further rewrite  $S_x$  and  $S_c$  in terms of an intermediate scattering function  $S$  as

$$S_x = k(S + \delta S/2) \quad (42)$$

$$S_c = (1/k)(S - \delta S/2) \quad (43)$$

where

$$S = ((1/k)S_x + kS_c)/2 \quad (44)$$

$$\delta S = (1/k)S_x - kS_c \quad (45)$$

and

$$k \equiv \sqrt{\int L S_x R / \int L S_c R} \equiv \sqrt{F_{xc}} \quad (46)$$

Note that in this form of expression,

$$\int L \delta S R = 0 \quad (47)$$

Making use of expressions (29), (38), (42), and (43), expression (40) can be rewritten in terms of L,  $\delta L$ , S,  $\delta S$ , R, and  $\delta R$

$$\frac{\delta F_{xc}}{F_{xc}} = \frac{\int L \delta S \delta r}{\int LSR} + \frac{\int \delta L \delta SR}{\int LSR} + \dots \quad (48)$$

where the remaining terms are of higher order than two in the quantities  $\delta L$ ,  $\delta R$ , or  $\delta S$ . If  $S_x$  and  $S_c$  are alike in form,  $\delta S$  will be very small compared to S, which in turn guarantees that the fractional error in  $F_{xc}$  is small. (Note that if the instrument response is linear,  $S_x$  and  $S_c$  can differ considerably in magnitude, i.e., k can be much different from 1, without affecting the measurement, but they must be similar in functional form if the measurement error is to be small.) No such assurance occurs in the case of the  $G_x$  measurements, as can be seen from expression (39). Thus, the chance of having a large error introduced by imperfect instrumentation can be greatly reduced by measuring against suitable, accurately measured comparison samples.

## 6. Summary

What has been presented on the preceding pages is a method for describing spectrophotometric measurements. This method has been chosen in such a way that a complete analysis of a measurement should be possible from a description written using the method. It also provides a means of writing a definition of a measurement in a way that allows one to readily analyze attempts to perform the measurement. In this method, all space is divided into instrument space or sample space, with no space unaccounted for. The measurement is defined at the boundary between the instrument and sample space, and real measurements which are made in attempts to produce the defined measurements are also described on the boundary. Such definitions and descriptions consist of a radiance input L, a function to describe the incoming radiation; a scattering function S which describes the way in which the radiation reacts in sample space to produce a distribution of outgoing radiation; and a relative responsivity R, a weighting function which describes the relative contribution of various portions of the outgoing radiation to the instrument output. A final function, the scaling function K, is introduced to account for the performance of electronics, mechanical meter movements, etc. The method has been presented in a very general way in order that it could be used to cover most conceivable measurements. In order to illustrate how the method can be used, it has been applied to a specific measurement problem in Appendix B.

One very general conclusion which is confirmed by analysis using the general method is that it is possible to make spectrophotometric measurements relative to a comparison sample with much less error than it would be possible to make the corresponding measurement directly with the same equipment. The implications of this conclusion for the standards laboratories are apparent. First, it is important that a central laboratory such as NBS be able to accurately measure the comparison samples to be used as standards in order to provide a meaningful and consistent scale of measurement. Second, since relative measurements of similar samples can be very accurately made with good instrumentation, it is possible for secondary standards laboratories to provide standards which are "traceable" to the central laboratory within acceptable limits of error. Finally, since there is generally a considerable difference between the standards and the materials being measured in practice, it is important that instruments in the field conform as well as possible in

their characteristics to the ideal characteristics used to define the measurements. The central laboratory can support improved instrument performance through close cooperation with instrument manufacturers by helping them to make their product adhere as close as practical to the ideal.

Very high accuracy can be achieved in spectrophotometric measurements, and efforts are being made to make use of this high accuracy in many applications in industry and science. The approach to describing spectrophotometric measurements provided in this Technical Note is designed as a tool to aid in seeing that high accuracy in spectrophotometry is realized.

## 7. Appendices

### A. Radiance (Spectral)

One of the most useful concepts in dealing with quantitative evaluation of radiation is the concept of radiance. Therefore, we would like to provide an introduction to this concept as an appendix to this Technical Note.

#### A.1 Formal Definition

Spectral radiance is a vector function used to describe spectral radiative flux density. For each point and direction in space, each time, and each wavelength, there is one and only one value of the spectral radiance. This value tells the amount of energy (or number of photons) per unit of time, per unit of wavelength, per unit of area normal to the direction of interest and per unit of solid angle in the direction of interest which passes the point at which the radiance is being specified. To calculate the amount of energy (number of photons) passing through a given area with a given solid angle and in a given time and over a given wavelength interval, one integrates the radiance over the time interval, over the wavelength, over the directions within the solid angle, and over the projection of the area onto a plane normal to each of these directions in turn. This is just the integration (except for not integrating over time) which is indicated in expression (3). It is important to remember in taking such an integration that the radiance is not a vector field, which would have only one direction at a given point, but it is a vector function, with a value in each direction at each point. Therefore, the area must be appropriately projected for each direction as the integration over the solid angle is taken.

#### A.2 A Second Approach

A second way to approach the definition of radiance is quite helpful in understanding the geometry involved and also can be used to show a property of radiance which is very useful for purposes of calculation. We will use the drawing in Fig. 8 to illustrate this definition. Suppose we wish to define the radiance at point P in a given direction. We can first select a second and different point Q such that the directed line segment PQ from P to Q lies in the direction for which we wish to evaluate the radiance. We next construct a circle of area  $\Delta A$  centered at P and in a plane normal to  $\overrightarrow{PQ}$  and a circle of area  $\Delta B$  centered at Q and also in a plane normal to  $\overrightarrow{PQ}$ . We will designate by  $\Delta W$  the amount of energy (number of photons) which passes through the area  $\Delta A$  in the direction  $\overrightarrow{PQ}$  during the time  $\Delta T$  and within the wavelength range  $\Delta \lambda$  which also passes through the area  $\Delta B$ . We will now set up the ratio  $\bar{L}$  as follows:

$$\bar{L} = \frac{\Delta W(PQ)^2}{\Delta \lambda \Delta T \Delta A \Delta B} \quad (A1)$$

where (PQ) is used to indicate the distance from P to Q. We now proceed to take the classical limits as  $\Delta \lambda$ ,  $\Delta T$ ,  $\Delta A$ , and  $\Delta B$  become vanishingly small. (NOTE: The magnitude of  $\Delta W$  depends upon each of the foregoing  $\Delta$  quantities.) As  $\Delta \lambda$  approaches zero, we get a

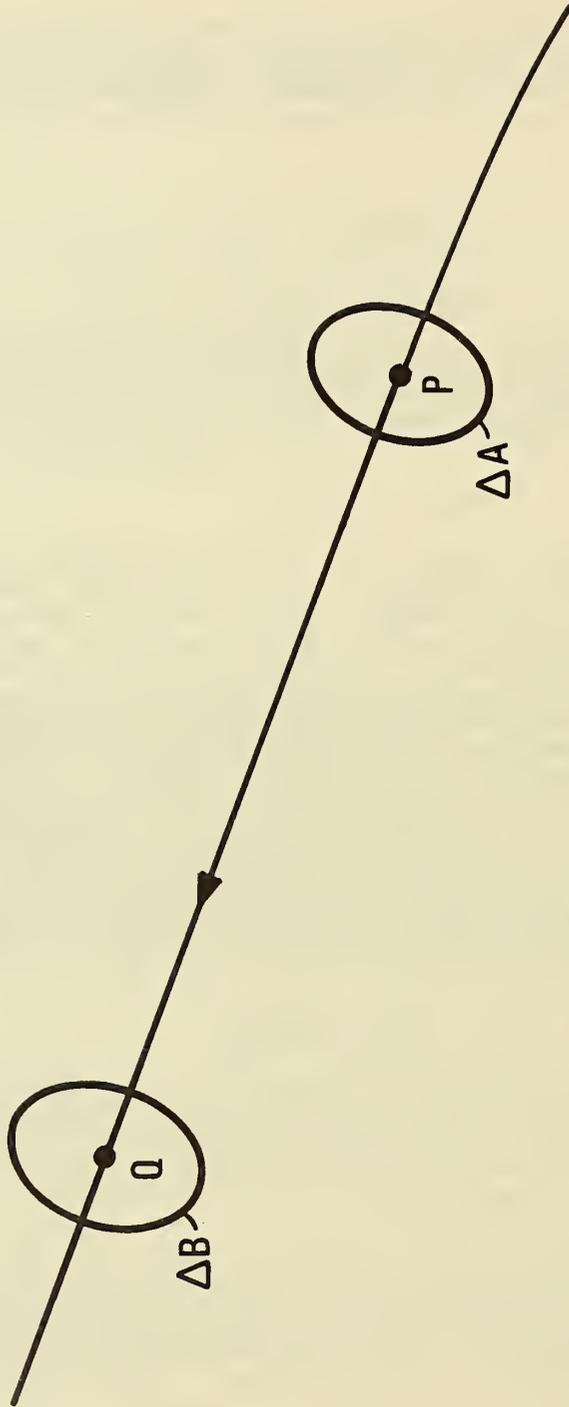


Fig. 8 Figure used to define radiance

spectral density of particles going through area  $\Delta A$  during  $\Delta T$  and then passing through area  $\Delta B$ . As we also let  $\Delta T$  approach zero, we obtain the spectral rate of energy (photons) at P which passes through both  $\Delta A$  and  $\Delta B$ . As  $\Delta A$  approaches zero as well, we obtain at P the spectral rate of energy (photons) per unit area normal to PQ which passes through  $\Delta B$ . The area  $\Delta B$  subtends a solid angle at P which is approximately  $\Delta B / (PQ)^2$ , and as  $\Delta B$  approaches zero, that approximation becomes better and better. With this final limit we obtain the spectral rate of energy (photons) per unit area per unit solid angle, i.e., the spectral radiance. Thus, in this case

$$L = \lim_{\substack{\Delta \lambda \rightarrow 0, \\ \Delta T \rightarrow 0, \Delta A \rightarrow 0, \\ \text{and } \Delta B \rightarrow 0}} \frac{\Delta W(PQ)^2}{\Delta \lambda \Delta T \Delta A \Delta B} \quad (A2)$$

This approach to the definition can be made in a manner which appears to be much more general by allowing more general shaped areas than the circles to be used, using projections of these areas on a plane normal to the line PQ, etc. Although such a general approach is not necessary, it is instructive in that it gives a feeling for what must be done to make use of the concept of radiance.

### A.3 A Useful Property

If one examines the foregoing definition, it is quite apparent that the mathematics of deriving the radiance at Q in the direction PQ would be identical. The directed line PQ is what is referred to in classical ray optics as a ray. Thus, at least in the case in which the medium is uniform and the ray is a straight line, the radiance associated with a ray is constant. We can extend the concept to a ray passing through any optical system by replacing the straight line by a ray in a more general sense. Such an extension, if done rigorously, involves application of Fermat's principal and Malus' theorem and is beyond the scope of this work. However, the result can be quite simply stated for the practical purposes of radiometry and spectrophotometry: Except for losses or gains along the way due to absorption, emission, scattering or reflections, the quantity  $L(\lambda)/n^3$  associated with a given ray remains constant, where n is the index of refraction of the medium at the point where  $L(\lambda)$  is evaluated.

The foregoing property is very useful in estimating such things as the radiance input in spectrophotometric measurements. As an example, consider the instrument depicted in Fig. 11 and discussed in Appendix B. If one makes the fairly reasonable assumption that, within the range of angles for rays which pass from the filament through the input mask, the radiance from the lamp filament is uniform, it follows that the radiance in any given direction will be uniform over the projection of the input mask onto the sample mask in that direction. (Here, one has also made the assumption that the transmittance of the lens does not depend upon the direction in which the rays are traveling.) If one wishes a better evaluation of the radiance input, one can trace through ray by ray, taking differences of emission and reflection with angles into account. Notice, that the flux through any surface separating the filament from the sample plane is constant (again ignoring the loss by reflection), but at the filament the radiance is non-zero over a small area and a large solid angle, while at the sample mask, the radiance is non-zero over a large area and over a small solid angle at each point on the area.

### B. Analysis of a Specific Measurement Made According to Fed. Test Method Std. No. 141a, Method 6121

The main body of this Technical Note discusses a method for describing spectrophotometric measurements. This method is expressed in a very general type of mathematical notation. In order to illustrate an application of this approach to describing measurements, we will use in illustration an actual case of measurement error which was brought to our attention. The problem arose between a paint manufacturer, which we will call Seller, and a large purchasing department, which we will call Buyer. Seller was to supply white paint with a specified minimum reflectance relative to fresh smoked MgO in the region

of 85%, and measured the paint before delivery to be sure the reflectance was above the minimum value. Buyer tested the paint upon receipt and found it to measure about 1% lower than the minimum value. An agreement was worked out between Buyer and Seller for that particular shipment, but an expression of concern both from Seller and the manufacturer of Buyer's instrument brought the matter to the attention of the Optical Radiation Section of NBS, where the matter is being resolved. The physical basis for the discrepancy has been discovered, and an analysis of this measurement problem is presented here in terms of descriptions based on the method presented in this Technical Note in order to provide specific examples of how the method can be used.

### B.1 Definition

The basis for defining the measurement is found in Federal Test Method Standard Number 141a, Method 6121 dated September 1, 1965, which is presented in its entirety in Fig. 9. We will very briefly abstract a description of the measurement in terms of the method given in this Technical Note.

**INSTRUMENT SPACE, SAMPLE SPACE, AND BOUNDARY.** According to paragraph 4.1.1 of Method 6121, the sample is to be a layer of paint on a plane surface. Therefore, it is sensible to take the boundary between the instrument space and the sample space to be a plane parallel to the average painted surface and tangent to it at its farthest point from the plane surface on which the paint is applied. The instrument space will be on the side of the boundary away from the painted surface and the sample space will be toward the painted surface, as illustrated in cross section in Fig. 10. Note that it is the paint which is to be measured, so that, in a strict interpretation, the surface on which the paint is applied should be included as part of the instrument. However, since 4.1.1 places the condition that the paint be so thick that the reflectance will not change with additional coats, the optical character of the surface onto which the paint is applied can be ignored.

**RADIANCE INPUT AND RESPONSIVITY.** Paragraph 2.2 of the specification provides that the spectral characteristics of the source-filter-photoreceiver combination shall provide an equivalent of source C illumination and luminous evaluation. Since the spectral requirements are placed on the source and receiver in combination, one must assume that reduction in wavelength (see section 3.2.3 of this Technical Note) is assumed, and therefore that the specification does not apply when significant photoluminescence is involved. Since the spectral distribution known as source C is presumed to represent that of daylight, and since luminous evaluation represents the spectral response of the eye, it is natural to represent the spectral portion of the radiance input  $L$  with the source C relative weighting  $C_\lambda$  and the spectral portion of the responsivity  $R$  with the luminous response  $V_\lambda$  as shown in Table I. No mention is made of the distribution of  $L$  and  $R$  with respect to location on the boundary plane, hence it will be assumed that  $L$  is non-zero over a finite range and that  $R$  is uniform over the entire boundary. (Failure to specify the area to be measured indicates that a uniform sample is expected.) The geometric characteristics of  $L$  and  $R$  are indicated by the name "45-degree, 0-degree directional reflectance". The angular limitations described in paragraph 2.3 of the method require that  $L=0$  outside the range  $35^\circ < \Gamma < 55^\circ$  and that  $R=0$  outside the range  $0 \leq \gamma < 15^\circ$ . No mention is made of azimuth, hence azimuthal isotropy is assumed, and the expression "and centered on" in each of the requirements suggests an ideal instrument for which

$$L = C_\lambda \quad \text{for } (45-\Delta\Gamma) < \Gamma < (45+\Delta\Gamma) \quad \text{over a finite area} \quad (B1)$$

and zero elsewhere and

$$R = V_\lambda \quad \text{over the entire boundary for } 0 \leq \gamma < 15^\circ \quad (B2)$$

and is zero at other angles.

## 45-DEGREE, 0-DEGREE DIRECTIONAL REFLECTANCE

### 1. SCOPE

1.1 This method is used for determining daylight 45°, 0° luminous directional reflectance of opaque, nonfluorescent, white or near-white specimens. For reflectance of chromatic specimens use method 4252.

#### 1.2 Definition.

1.2.1 Daylight 45°, 0° luminous directional reflectance is the ratio of the luminous flux reflected from a specimen to the luminous flux reflected from a standard magnesium oxide layer, for 45° CIE source C illumination and perpendicular view.

#### 1.3 Standards.

1.3.1 *Primary standard.* The primary standard is a layer of magnesium oxide freshly prepared in accordance with ASTM D-986. A value of 100 is assigned to this standard.

1.3.2 *Secondary standards.*<sup>1</sup> Plaques of porcelain enamel or other material known to be reasonably permanent and uniform in their reflective properties may be calibrated and used as secondary standards.

### 2. APPARATUS

2.1 *Instrumental components.* The apparatus shall be a reflectometer having source filter and receptor characteristics that will measure reflectance to within 1.0 percent of full-scale reading.

2.2 *Special characteristics.* The spectral response of the source-filter photoreceiver com-

<sup>1</sup> Suitable working standards for directional reflectance measurements are available from the Gardner Laboratory, Inc., Bethesda 14, Md., the Hunter Associates Laboratory, Inc., 9529 Lee Highway, Fairfax, Va., and the Photovolt Corporation, 1115 Broadway, New York 10, N.Y.

bination shall provide the equivalent of CIE source C illumination and luminous evaluation.

2.3 *Geometric characteristics.* Illumination shall be within 10° of, and centered on a direction 45° from the perpendicular to the test specimen surface; viewing shall be within 15° of, and centered on the perpendicular. The illuminating and viewing conditions may be interchanged without altering the results.

### 3. REAGENTS

3.1 None required.

### 4. PROCEDURE

#### 4.1. Preparation of specimen.

4.1.1 Unless otherwise specified, use a doctor blade to apply the coating material under test to a suitable plane surface. Apply a sufficient number of coats, each at right angles to the preceding coat, until an additional coat produces no measurable change in the reflectance. Allow each coat to dry for 48 hours in a dust-free and fume-free location.

#### 4.2 Obtaining reflectance.

4.2.1 Obtain the reflectance of each specimen relative to a standard having a reflectance close to the specimen.

#### 4.3 Reporting of results.

4.3.1 Report values of reflectance in percent relative to magnesium oxide.

4.3.2 Report instrument and standards used.

### 5. NOTES

5.1. None.

### 6. PRECISION

6.1 Results obtained on the same specimens on the same instrument should be repeatable to within  $\pm 0.2$  percent. Results obtained on the same specimens measured on different instruments employing calibrated standards of nearly the same reflectance should be reproducible to within  $\pm 0.5$  percent.

FED. TEST METHOD STD. NO. 141a

Fig. 9 Federal Test Method 6121: 45-degree, 0-degree directional reflectance

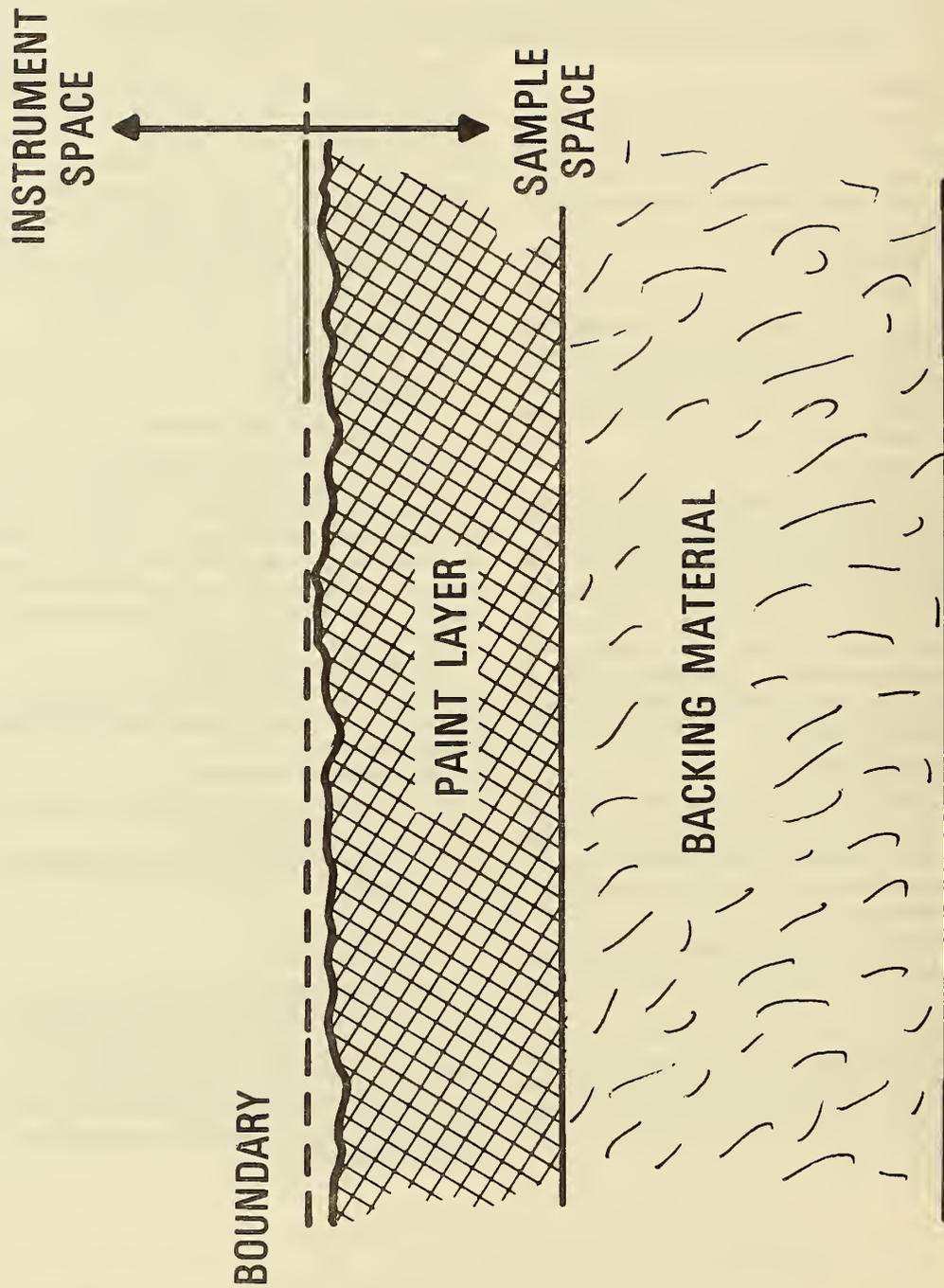


Fig. 10 Representation of a painted surface

TABLE I.

## Peak Normalized Luminous Response and CIE Source C Weighting Functions

$\lambda$	$V_\lambda$	$C_\lambda$	$\lambda$	$V_\lambda$	$C_\lambda$
380	0.0000	0.266	580	0.8689	0.788
390	0.0003	0.382	590	0.7774	0.751
400	0.0020	0.510	600	0.6583	0.723
410	0.0088	0.650	610	0.5280	0.712
420	0.0214	0.791	620	0.3981	0.710
430	0.0387	0.906	630	0.2835	0.709
440	0.0621	0.979	640	0.1798	0.708
450	0.0895	0.999	650	0.1076	0.712
460	0.1282	0.992	660	0.0603	0.708
470	0.1852	0.998	670	0.0318	0.695
480	0.2536	0.998	680	0.0159	0.677
490	0.3391	0.973	690	0.0077	0.646
500	0.4608	0.903	700	0.0037	0.615
510	0.6067	0.824	710	0.0018	0.583
520	0.7618	0.781	720	0.0008	0.550
530	0.8752	0.790	730	0.0004	0.519
540	0.9620	0.823	740	0.0002	0.496
550	0.9918	0.848	750	0.0001	0.477
560	0.9973	0.849	760	0.0000	0.468
570	0.9555	0.824	770	0.0000	0.469
580	0.8689	0.788	780	0.0000	0.476

RELATIVE MEASUREMENT. The reflectance of the paint would depend strongly on  $\Delta\gamma$  and would also depend to some extent upon  $\Delta\Gamma$ . However, the method calls for reflectance relative to a magnesium oxide standard. Since the non-specular reflectance from the paint and the reflectance from magnesium oxide are similar in their angular distribution, the specific choices of  $\Delta\gamma$  and  $\Delta\Gamma$  are not critical, provided they are within the limits indicated in paragraph 2.3 of the method, i.e.,  $\Delta\gamma < 15^\circ$  and  $\Delta\Gamma < 10^\circ$ . An obvious unique choice of angular range for purposes of definition is that both  $\Delta\gamma$  and  $\Delta\Gamma$  approach zero, with the reflectance defined in the limit as they go to zero, i.e.,

$$F_{pm} = \lim_{\Delta\gamma \text{ and } \Delta\Gamma \rightarrow 0} \frac{100 \int^5 LS_p R \vec{U} \cdot d\vec{A} \, d\Omega \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda}{\int^5 LS_m R \vec{U} \cdot d\vec{A} \, d\Omega \vec{u} \cdot d\vec{a} \, d\omega \, d\lambda} \quad (B3)$$

where the subscript p is used to indicate the paint sample and the subscript m is used to indicate the MgO sample. In the limit as  $\Delta\Gamma$  approaches zero, the integral with respect to  $\Omega$  becomes equal to the integrand evaluated at  $45^\circ$  and multiplied by the differential evaluated at  $\Gamma=45^\circ$ . The dot product  $\vec{U} \cdot d\vec{A}$  can also be evaluated at  $45^\circ$  so that

$$\begin{aligned} (\vec{U} \cdot d\vec{A}) \, d\Omega \Big|_{45^\circ} &= (\cos\Gamma dA) \, 2\pi \sin\Gamma \, 2\Delta\Gamma \Big|_{45^\circ} \\ &= \cos 45^\circ dA \, 2\pi \sin 45^\circ \, 2\Delta\Gamma \\ &= 2\pi dA \, \Delta\Gamma \end{aligned} \quad (B4)$$

Similarly, in the limit as  $\Delta\gamma$  approaches zero, the integral with respect to  $\omega$  becomes equal to the integrand evaluated at  $\gamma=0^\circ$  multiplied by the differential evaluated at  $0^\circ$ . The dot product  $\vec{u} \cdot d\vec{a}$  can also be evaluated so that

$$\begin{aligned} (\vec{u} \cdot d\vec{a}) \, d\omega \Big|_{0^\circ} &= (\cos\gamma da) \, \pi(\Delta\gamma)^2 \Big|_{0^\circ} \\ &= \cos 0^\circ da \, \pi(\Delta\gamma)^2 \\ &= \pi da \, (\Delta\gamma)^2 \end{aligned} \quad (B5)$$

Upon substituting these results into expression (B3), we obtain

$$F_{pm} = \frac{100 \int^3 C_\lambda S_p (45^\circ, \vec{P}; 0^\circ, \vec{p}, \lambda) \, v_\lambda \, dA \, da \, d\lambda}{\int^3 C_\lambda S_m (45^\circ, \vec{P}; 0^\circ, \vec{p}, \lambda) \, v_\lambda \, dA \, da \, d\lambda} \quad (B6)$$

where the integral with respect to A is taken over the area where L is non-zero, the integral with respect to a is taken over the entire boundary, and the integral with respect to  $\lambda$  is taken over all wavelengths. If we represent the integral in the numerator by  $\hat{S}_p$  and that in the denominator by  $\hat{S}_m$  we can represent expression (B6) as

$$F_{pm} = \frac{100 \hat{S}_p}{\hat{S}_m} \quad (B7)$$

If, as suggested in paragraph 1.3.2 of the test method, one chooses to use a secondary standard (which we will designate by the letter s), its reflectance relative to magnesium oxide can be defined in the same manner as for the paint sample, i.e.,

$$F_{sm} = \frac{100 \hat{S}_s}{\hat{S}_m} \quad (B8)$$

and the relative reflectance of the paint sample can be defined in terms of a measurement relative to the secondary standard as

$$F_{pm} = F_{sm} \frac{\hat{S}_p}{\hat{S}_s} \quad (B9)$$

Finally, then, if the paint sample, the MgO sample, and (if used) the secondary standard are all uniform and homogeneous, the defined value of the 45-degree, 0-degree Directional Reflectance are uniquely defined. Actually, the test method does not require that the solid angles go to zero, so that the reflectance defined in the test method is not unique. However, since the scattering function in the region of 45° incidence and 0° emergence for typical MgO and paint samples are slowly varying functions of angle, one would not expect the ratio of the integrals over the finite angles to differ greatly from the limiting ratio of expression (B3).

## B.2 Evidence of the Problem

Upon request of NBS, both Buyer and Seller agreed to an interlaboratory intercomparison. Three plaques were used in the intercomparison:

- 1) A paint sample, vinyl latex flat white paint (interior). Prepared as specified in the test method to obtain a uniform opaque surface 10 x 10 cm.
- 2) A sample of Vitrolite white glass 10 x 10 cm and 1 cm thick.
- 3) A sample of thermometer white glass, one side ground and one side polished, 10 x 10 cm. This sample was to be measured on both sides.

All three plaques were measured by NBS, by Buyer, by Seller, and again by NBS, each using his own standards to make the measurement. The results of these measurements are summarized in Table II. Both Buyer and Seller have instruments which are considered to be quite adequate for these measurements, and both were making measurements relative to secondary standards with assigned value relatable to NBS measurements. Since the angular distribution of reflected light from the paint and standards would be similar, there appeared to be little likelihood that angular distribution could be a major factor in errors in relative measurements. This brought our attention to the spatial aspect of the measurement, since the instruments differed with regard to the areas illuminated and viewed and the secondary standards were quite different in the spatial portions of their scattering functions. However, before describing the investigation and its outcome, we will indicate how a real instrument of the type involved can be described both to illustrate the use of the method for description and to provide a background for discussing the solution of this particular measurement problem.

## B.3 A Typical Instrument

The arrangement of an instrument typical of those used for this kind of measurement is shown in Fig. 11. Light from a lamp filament centered at point p passes through a collimating lens and the input mask. The central ray, emitted from point p on the center of the filament and passing through the center of the lens at P<sub>L</sub>, through the center of the input

TABLE II.

Raw Reflectance Values From the Laboratory Intercomparison

	NBS Initial	Buyer	Seller	NBS Final
Paint	83. <u>04</u>	83. <u>04</u>	84. <u>49</u>	83. <u>30</u>
Vitrolite	91. <u>66</u>	90. <u>41</u>	90. <u>51</u>	91. <u>95</u>
Thermometer Glass (ground)	95. <u>06</u>	94. <u>7</u>	95. <u>7</u>	95. <u>14</u>
Thermometer Glass (polished)	94. <u>39</u>	93. <u>5</u>	93. <u>2</u>	94. <u>36</u>

TABLE III.

Reflectance Values From the Laboratory Intercomparison, Scaled  
to Make the Reflectance of the Paint 83.17

	NBS Initial	Buyer		Seller		NBS Final	
		value	diff.	value	diff.	value	diff.
Paint	83.17	83.17	0.00	83.17	0.00	83.17	0.00
Vitrolite	91.80	90.55	1.25	89.10	2.71	91.81	0.01
Thermometer Glass (ground)	95.21	94.85	0.36	94.20	1.00	94.99	0.22
Thermometer Glass (polished)	94.54	93.65	0.89	91.74	2.79	94.21	0.33

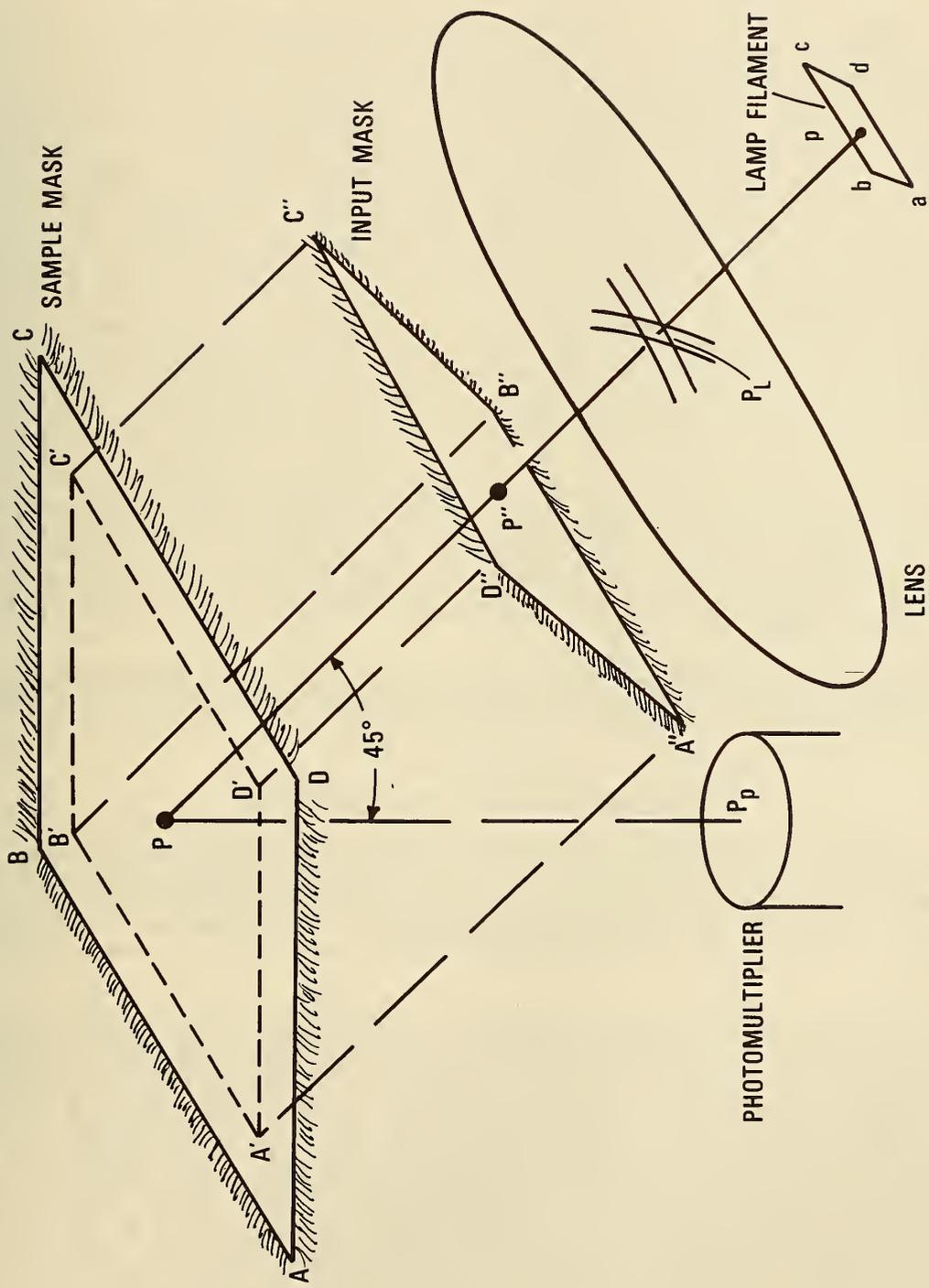


Fig. 11 Sketch representing a 45°/0° reflectometer

mask P", and through the center of the sample mask P; travels upward at an angle of  $45^\circ$  from the vertical. The center  $P_p$  of the photomultiplier detector lies on a line vertically downward from the center of the sample mask. The plane of the sample mask defines the boundary between instrument space and sample space, with sample space lying above the plane and instrument space lying below it. The sample is placed faced down on the sample mask when a measurement is made.

The details of the analytical geometry will not be worked out here, but the nature of L and R can be described in terms of the drawing. The radiation originating at the center of the lamp filament will emerge from the lens in a direction parallel to the central ray. The input mask is appropriately shaped so that for these rays its projection onto the plane of the sample mask is the rectangle A'B'C'D'. Light originating from any other point on the filament will emerge from the lens in a direction parallel to a line connecting that point and  $P_L$  and will project the input mask onto the sample mask in a rectangle slightly distorted and somewhat displaced from the central rectangle. Thus, for perfect optics, the radiance input associated with each particular direction will be constant over the associated rectangular area and zero elsewhere. The slight aberrations connected with good quality real optics will not distort this radiance input significantly. The responsivity is also easily deduced. If one assumes that the active portion of the photomultiplier cathode is uniform, then the responsivity at any point within the sample mask rectangle ABCD will be unity within the solid angle subtended by the photocathode at that point and zero elsewhere. Also, importantly, the responsivity will be zero outside the rectangle ABCD. If the distances are properly chosen with respect to the filament and photocathode sizes, it is possible to construct an instrument which meets the requirements of the test method in this manner. The fact that the photocathode may not be uniformly sensitive or the lamp filament may not be emitting uniformly may violate the "centered" requirements of paragraph 2.3 of the method, but this will probably not degrade the relative measurements of diffuse reflectance much. In cases where the details of the radiance input and relative responsivity might be important, one could either map the emission of the filament and the sensitivity of the photocathode and derive detailed expressions for the radiance input and responsivity, or else one could determine these quantities by direct measurements made at the plane of the sample mask.

In summary, with the present availability of high quality and inexpensive detectors and electronics, it should be possible for even a modestly priced instrument of this type to produce relative measurements within the specifications.

#### B.4 The Translucent Blurring Effect

When the ideal instrument described in B.1 and the real instrument described in B.3 are compared, one obvious difference is that the relative responsivity of the real instrument is zero outside the rectangle ABCD of the mask in Fig. 11, whereas the ideal relative responsivity is uniform over the entire boundary plane. This discrepancy could lead to measurement errors, and, therefore it was more closely investigated in terms of the samples to be measured.

The reflection from a sample such as paint or white glass can be divided into two parts. As the radiation strikes the sample, it moves from air into a medium of higher index of refraction (varnish in the case of the paint, and glass in the case of the white glass). At the point where the radiation passes from one medium to another, a fraction is reflected (Fresnel reflection). This fraction is on the order of five percent of the incoming flux. In the case of the smooth glass, the interface between the media is essentially parallel to the sample-instrument boundary, so that the surface reflected radiation is excluded from the measurement. In either case, however, this surface reflected radiation leaves the surface very near to its point of incidence, so that if we represent the scattering function as the sum of a scattering function to represent the surface reflection and a second scattering function to represent the remaining reflection, the surface reflection portion of the scattering function can be reduced in space (see the discussion to expression (7) in 3.2.3). Therefore, the response of the instrument to surface reflection will not be affected by the finite area of non-zero responsivity.

In both samples, more than ninety percent of the incident flux passes through the surface and into the sample. A large fraction of this radiation escapes after being randomly reflected from grains of pigment within the material. The main part of the radiation which contributes to the response travels this route. One can gain an intuitive feeling for this process if one thinks of the radiation in terms of point photons. As is indicated in Fig. 12, the photon enters at point P, moves from one scattering point to another until at last it emerges at another point, p. The probability that the photon will emerge at a particular point decreases with the distance of that point from the point of entry, but there is a finite possibility that the photon might emerge at a relatively large distance from P. A clue as to how far the light might travel is given by the opacity of the material. Since a very thin layer of paint will "hide" the underlying surface, one assumes that the probability for a photon to travel down through the paint and back up through it is very small. It follows that the probability for the photon to travel the same distance sideways and emerge is equally small. In real instruments, the clearance between the edge of the region where L is non-zero and the edge of the sample mask is orders of magnitude larger than the thickness of the paint film, and therefore the finite size of the sample mask should not affect the measurement of the paint. In the case of the porcelain enamel standard which was used by Buyer, the opaque layer was thicker but still much less than the distance from the edge of the illuminated area to the edge of the sample mask. The standard used by Seller, however, was a glass standard supplied by the manufacturer of his instrument, and most white glass is quite translucent. Therefore, it is quite possible that a significant portion of the radiation which emerges from such a standard emerges beyond the edge of the sample mask and does not contribute to the response. We will call the tendency for a point irradiation to produce reflected radiation over a considerably larger area the "translucent blurring effect".

To test the measurements under question for this effect, we assumed that the paint sample was uniform and had a reflectance of 83.17, the average of the two NBS values. Each set of measurements was scaled by a multiplying factor so that the paint reflectance values were all 83.17. The values so scaled appear in Table III. The figures in the columns labeled diff. give the difference between a given reading and the corresponding initial NBS value. It was assumed that there might be a constant difference between the NBS initial and final value because they were measured against separate freshly prepared samples of MgO, but if the readings for any sample were brought into agreement by scaling, it should follow that all would agree according to the same scaling. This was true for the vitrolite, as can be seen in Table III, but there was a residual difference in the thermometer white glass measurements. Further investigation of this sample revealed non-uniformity in reflectance over its surface, so further quantitative measurements were not made on this sample. The functional dependence of S on the distance between point of entry and point of emergence on the sample (see discussion leading to expression (10) in section 3.2.4) was found by illuminating a small spot on the vitrolite and using a series of different diameter circular sample masks concentric with the spot. A similar instrument to that of Seller was borrowed and both L and S were mapped for this instrument. From this data, it was calculated that the losses amounted to 2.2% of the reflected radiation for that instrument.

It is presumed from the foregoing that Seller's glass standard, while its assigned value may be accurate, is too translucent for his instrument to measure accurately. At the time of this writing, we are awaiting the arrival of Seller's standard so that confirmation of this hypothesis may be made. Contacts are also being made with the manufacturer of Seller's instrument to assist him in providing more appropriate standards for the instrument. Since the instrument has been on the market for some time and many are in use, it would not make sense to try to have the instruments modified to include a larger region of non-zero responsivity. Although some improvement could be obtained by assigning a new value to the standards to represent some average blurring effect loss for that design, this would still allow considerable variation from instrument to instrument and even with the same instrument from adjustment to adjustment. The most satisfactory solution to the measurement problem would be to supply new, more opaque standards for the instruments and to caution the users concerning the difficulties involved in using it to measure translucent materials such as opal glass or plastics.

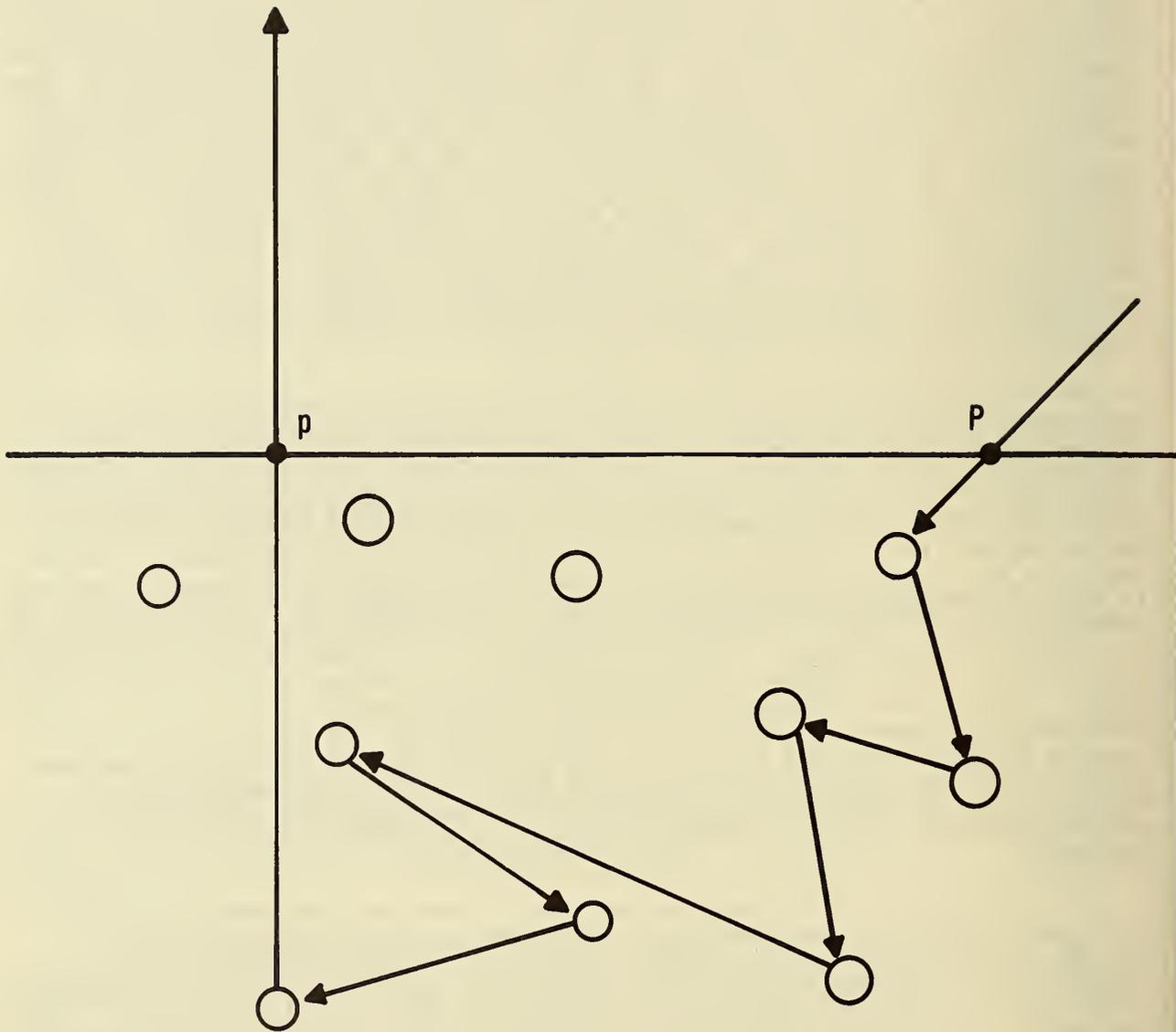


Fig. 12 Path of a photon in a diffuse reflector

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