Toward AN IMPROVED TERMINOLOGY *for* FLUORESCENCE SPECTROPHOTOMETRY

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Overview

- ❖ Introduction

I. Purpose & Definition of Terms
II. Refinements to ILV Terminology by ASTM E12
III. Further Refinements: Geometric Generalization

- ❖ Conclusion

INTRODUCTION

One piece of the puzzle

- Goal: A Unified Terminology, spanning:
  - Colorimetry
  - Analytical Chemistry
  - Materials Science

- The scope of this presentation is limited to considering a few terms defined in the ILV.

Provisional Terms, Unispectral

(Each quantity comprises both a luminescent and a non-luminescent component.)

	EXTERNAL		**INTERNAL**	
	Quantum	**Radiant**	**Quantum**	**Radiant**
Yield	$\gamma_p(\mu)$ external spectral quantum yield	$\gamma_e(\mu)$ external spectral radiant yield	$\varphi_p(\mu)$ internal spectral quantum yield	$\varphi_e(\mu)$ internal spectral radiant yield
Yield Factor	$G_p(\mu)$ spectral quantum yield factor*	$G_e(\mu)$ spectral radiant yield factor		

Provisional Terms, Unispectral

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	Quantum	**Radiant**	**Quantum**	**Radiant**
Yield	$\gamma_p(\mu)$ external spectral quantum yield	$\gamma_e(\mu)$ external spectral radiant yield	$\varphi_p(\mu)$ internal spectral quantum yield	$\varphi_e(\mu)$ internal spectral radiant yield
Yield Factor	$G(\mu)$ spectral yield factor			

Provisional Terms, Bispectral

(Each quantity comprises both a luminescent and a non-luminescent component.)

	EXTERNAL		**INTERNAL**	
	Quantum	**Radiant**	**Quantum**	**Radiant**
Yield	$\gamma_{p,\lambda}(\mu,\lambda)$ external bispectral quantum yield	$\gamma_{e,\lambda}(\mu,\lambda)$ external bispectral radiant yield	$\varphi_{p,\lambda}(\mu,\lambda)$ internal bispectral quantum yield	$\varphi_{e,\lambda}(\mu,\lambda)$ internal bispectral radiant yield
Yield Factor	$G_{p,\lambda}(\mu,\lambda)$ bispectral quantum yield factor**	$G_{e,\lambda}(\mu,\lambda)$ bispectral radiant yield factor**		

Provisional Terms, Bispectral

(Each quantity comprises both a luminescent and a non-luminescent component.)

	EXTERNAL		INTERNAL	
	Quantum	**Radiant**	**Quantum**	**Radiant**
Yield	$\gamma_{p,\lambda}(\mu,\lambda)$ external bispectral quantum yield	$\gamma_{e,\lambda}(\mu,\lambda)$ external bispectral radiant yield	$\varphi_{p,\lambda}(\mu,\lambda)$ internal bispectral quantum yield	$\varphi_{e,\lambda}(\mu,\lambda)$ internal bispectral radiant yield
Yield Factor	$G_{\lambda}(\mu,\lambda)$ bispectral yield factor			

I.

PURPOSE
& DEFINITIONS

Purpose

1) To present a critique of the following terms as defined in the ILV:

$\beta_{L,\lambda}(\mu)$ - bispectral luminescent radiance factor

$\beta(\lambda)$ - spectral radiance factor

$\eta_{\mu}(\mu)$ - spectral quantum efficiency of the fluorescent process

2) To propose more appropriate alternatives:

$G_{\lambda}(\mu,\lambda)$ - bispectral yield factor

$P(\lambda)$ - spectral power factor

$G(\mu)$ - spectral yield factor

Proposed Alternative Terms

ILV Term	Proposed Alternative
$\beta_{L,\lambda}(\mu)$	$G_{\lambda}(\mu, \lambda)$
$\beta(\lambda)$	$P(\lambda)$
$\eta_{\mu}(\mu)$	$G(\mu)$

DEF (ILV): $\beta_{L,\lambda}(\mu)$

bispectral luminescent radiance factor ($\beta_{L,\lambda}(\mu)$) - The ratio of the radiance per unit emission bandpass, at wavelength λ, due to photoluminescence from the specimen when irradiated at wavelength μ, to the radiance of the perfect reflecting diffuser, identically irradiated and viewed. [unit: nm^{-1}]

New DEF: $G_\lambda(\mu,\lambda)$

bispectral yield factor ($G_\lambda(\mu,\lambda)$) - ratio of the flux per unit emission bandpass, at wavelength λ, from the specimen when irradiated at wavelength μ, to the flux emitted by the perfect reflecting diffuser, identically irradiated and viewed. [unit: nm^{-1}]

NOTE For photoluminescent media, the bispectral yield factor contains 2 components, the bispectral reflectant yield factor, $G_{R\lambda}(\mu,\lambda)$, and the bispectral luminescent yield factor, $G_{L\lambda}(\mu,\lambda)$. The sum of the reflectant and luminescent components is the total bispectral yield factor, $G_{T\lambda}(\mu,\lambda)$: $G_{T\lambda}(\mu,\lambda) = G_{R\lambda}(\mu,\lambda) + G_{L\lambda}(\mu,\lambda)$.

DEF (ILV): $\boldsymbol{\beta}$

radiance factor (*at a surface element of a non self-radiating medium, in a given direction, under specified conditions of irradiation*) [$\boldsymbol{\beta}$] - ratio of the radiance of the surface element in the given direction to that of the perfect reflecting or transmitting diffuser identically irradiated and viewed. [Unit: 1]

NOTE For photoluminescent media, the radiance factor contains 2 components, the reflected radiance factor, β_R, and the luminescent radiance factor, β_L. The sum of the reflected and luminescent radiance factors is the total radiance factor, β_T: $\beta_T = \beta_R + \beta_L$….

Implicit DEF: $\beta(\lambda)$

spectral radiance factor (*at a surface element of a non self-radiating medium, in a given direction, under specified conditions of irradiation*) [$\beta(\lambda)$] - ratio of the spectral radiance of the surface element in the given direction to that of the perfect reflecting or transmitting diffuser identically irradiated and viewed. [Unit: 1]

NOTE For photoluminescent media, the spectral radiance factor contains 2 components, the reflected spectral radiance factor, $\beta_R(\lambda)$, and the luminescent spectral radiance factor, $\beta_L(\lambda)$. The sum of the reflected and luminescent components is the total spectral radiance factor, $\beta_T(\lambda)$: $\beta_T(\lambda) = \beta_R(\lambda) + \beta_L(\lambda)$.

New DEF: $\boldsymbol{P(\lambda)}$

spectral power factor (*at a surface element of a non self-radiating medium, under specified conditions of irradiation and view*) [$\boldsymbol{P(\lambda)}$] - ratio of the spectral flux emitted by the sample over the specified viewing aperture to that emitted by the perfect reflecting diffuser, identically irradiated and viewed. [Unit: 1]

NOTE For photoluminescent media, the spectral power factor contains 2 components, the reflected spectral power factor, $P_R(\lambda)$, and the luminescent spectral power factor, $P_L(\lambda)$. The sum of the reflected and luminescent components is the total spectral power factor, $P_T(\lambda)$: $P_T(\lambda) = P_R(\lambda) + P_L(\lambda)$.

DEF (ILV): $\eta_\mu(\mu)$

spectral quantum efficiency of the fluorescent process ($\eta_\mu(\mu)$) - the ratio of the total number of photons of all wavelengths emitted from the specimen by the fluorescent process for an excitation at wavelength μ to the number of photons of wavelength μ reflected from the perfectly reflecting diffuser identically irradiated and viewed. [unit: 1]

New DEF: $\boldsymbol{G(\mu)}$

spectral yield factor [$\boldsymbol{G(\mu)}$] (*at a surface element, for given geometric conditions of irradiation and view, and for monochromatic incident radiation of given wavelength* (μ), *and polarisation*) - ratio of the flux emitted by the sample over the specified viewing aperture to that emitted by the perfect reflecting diffuser, identically irradiated and viewed. [Unit: 1]

NOTE For photoluminescent media, the spectral yield factor contains 2 components, the reflected spectral yield factor, $G_R(\lambda)$, and the luminescent spectral yield factor, $G_L(\lambda)$. The sum of the reflected and luminescent components is the total spectral yield factor, $G_T(\lambda)$: $G_T(\lambda) = G_R(\lambda) + G_L(\lambda)$.

II.

REFINEMENTS TO ILV TERMS ADOPTED BY ASTM E12

Refinements by ASTM E12

1) "$\boldsymbol{\beta_{L,\lambda}(\mu)}$" is *misleading*:
$\therefore$ "$\boldsymbol{\beta_{L,\lambda}(\mu)}$" → "$\mathbf{b}_{F,\lambda}(\mu)$"

2) $\mathbf{b}_{F,\lambda}(\mu)$ is *unnecessarily limited*:
$\therefore$ ***LET*** $\mathbf{b}_{\lambda}(\mu) \equiv \mathbf{b}_{F,\lambda}(\mu) + \mathbf{b}_{R,\lambda}(\mu)$

3) "$\boldsymbol{\eta_{\mu}(\mu)}$" is *grossly misleading*….
$\therefore$ "$\boldsymbol{\eta_{\mu}(\mu)}$" → "$\mathbf{b}_{F}(\mu)$"

1) "$\boldsymbol{\beta_{L,\lambda}(\mu)}$" is *misleading*

- Consider the notation convention described in DEF (ILV): *Spectral:*

…

DEF (ILV): *Spectral*

spectral - adjective that, when applied to a quantity X pertaining to electromagnetic radiation, indicates:

either that X is a function of the wavelength λ, symbol:

$$X(\lambda)$$

or that the quantity referred to is the spectral concentration of X, symbol:

$$X_\lambda = \frac{dX}{d\lambda}$$

NOTE 1 In the latter case, in French, "spectrique" is preferred to "spectral".

NOTE 2 X_λ is also a function of λ and in order to stress this, may be written $X_\lambda(\lambda)$ without any change of meaning.

NOTE 3 The quantity X can also be expressed as a function of frequency ν, wave number σ, etc.; the corresponding symbols are $X(\nu)$, $X(\sigma)$, etc. and X_ν, X_σ, etc.

"$\boldsymbol{\beta_{L,\lambda}(\mu)}$" is misleading

$$"\beta_{L,\lambda}(\mu)" \rightarrow \exists \beta_L(\mu) : \beta_{L,\lambda}(\mu) = \frac{d}{d\lambda}\beta_L(\mu)$$

$$\nexists \beta_L(\mu)$$

"$\boldsymbol{b_{F,\lambda}(\mu)}$" is *enlightening*

$$"b_{F,\lambda}(\mu)" \rightarrow \exists b_F(\mu) : b_{F,\lambda}(\mu) = \frac{d}{d\lambda} b_F(\mu)$$

$$\exists b_F(\mu)$$

$\boldsymbol{b_{F,\lambda}(\mu)}$ is the *spectral concentration*, with respect to emission wavelength, of $\boldsymbol{b_F(\mu)}$

DEF: $b_F(\mu)$

spectral fluorescence efficiency factor [$b_F(\mu)$] (*at a surface element, for given geometric conditions of irradiation and view, and for monochromatic incident radiation of given wavelength* (μ)*, and polarisation*) - ratio of the flux due to fluorescence emitted by the sample over the specified viewing aperture to that emitted by the perfect reflecting diffuser, identically irradiated and viewed. [Unit: 1]

2) Bispectral description needn't be limited to luminescence:

DEF: $\boldsymbol{b}_{\sout{F},\lambda}(\mu)$

bispectral ~~luminescent~~ radiance factor ($\boldsymbol{b}_{\sout{F},\lambda}(\mu)$) - The ratio of the *radiance* per unit emission bandpass, at wavelength λ, ~~due to photoluminescence~~ from the specimen when irradiated at wavelength μ, to the *radiance* of the perfect reflecting diffuser, identically irradiated and viewed. [unit: nm^{-1}]

NOTE For photoluminescent media, the bispectral radiance factor contains 2 components, the bispectral reflectant radiance factor, $b_{R\lambda}(\lambda)$, and the bispectral fluorescent radiance factor, $b_{F\lambda}(\lambda)$. The sum of the reflectant and luminescent components is the total bispectral radiance factor, $b_{T\lambda}(\lambda)$: $b_{T\lambda}(\lambda) = b_{R\lambda}(\lambda) + b_{L\lambda}(\lambda)$.

2) Bispectral description needn't be limited to luminescence:

DEF: $\boldsymbol{b_\lambda(\mu)}$

bispectral radiance factor ($b_\lambda(\mu)$) - The ratio of the *radiance* per unit emission bandpass at wavelength λ from the specimen when irradiated at wavelength μ, to the *radiance* of the perfect reflecting diffuser, identically irradiated and viewed. [unit: nm^{-1}]

NOTE For photoluminescent media, the bispectral radiance factor contains 2 components, the bispectral reflectant radiance factor, $b_{R\lambda}(\lambda)$, and the bispectral fluorescent radiance factor, $b_{F\lambda}(\lambda)$. The sum of the reflectant and luminescent components is the total bispectral radiance factor, $b_{T\lambda}(\lambda)$: $b_{T\lambda}(\lambda) = b_{R\lambda}(\lambda) + b_{L\lambda}(\lambda)$.

$b_\lambda(\mu)$ as a Unified Descriptor

- $b_\lambda(\mu)$ provides a unified, bispectral description
  - Including <u>*both*</u>:
    - A luminescent component: $b_{F,\lambda}(\mu)$
    - A non-luminescent component, e.g.: $b_{R,\lambda}(\mu)$

$$b_\lambda(\mu) = b_{R,\lambda}(\mu) + b_{F,\lambda}(\mu)$$

- *NOTE:* $b_{R\lambda}(\mu)$ is a rather unusual function*

*Bispectral Representation of Reflection

- $\boldsymbol{b_{R\lambda}(\mu)}$ is a rather unusual function:
  - discontinuous
  - zero everywhere except at (λ=μ), where it's very large;
  - integrates to the value of $R(\lambda)$.
- Nevertheless, $\boldsymbol{b_{R\lambda}(\mu)}$ is a perfectly valid concept:

- $\boldsymbol{b_{R\lambda}(\mu)}$ is closely related to the more familiar $\boldsymbol{R(\lambda)}$.
  - in terms of the Dirac delta-function, $\delta(\lambda-\mu)$:

$$b_{R,\lambda}(\mu) = R(\lambda)\delta(\lambda - \mu)$$

Bispectral Measurement: Theory *vs*. Practice

- While the concept of $\boldsymbol{b_{R\lambda}(\mu)}$, and therefore $\boldsymbol{b_{\lambda}(\mu)}$, seems complicated in theory,…
- The measurement of $\boldsymbol{b_{\lambda}(\mu)}$ is relatively straightforward in practice:
  - Bispectral data is naturally presented as a two-dimensional array of values - a *matrix*, with dimensions corresponding to μ and λ.
  - Though $\boldsymbol{b_{\lambda}(\mu)}$ is a function of continuous spectral variables, matrix values are a function of *discrete spectral variables* (μ_j, λ_i).

3) "$\boldsymbol{\eta_\mu(\mu)}$" is *grossly misleading*

$$"\eta_\mu(\mu)" \rightarrow \exists\, \eta(\mu) : \eta_\mu(\mu) = \frac{d}{d\mu}\eta_\mu(\mu)$$

i.e., it implies that $\boldsymbol{\eta_\mu(\mu)}$ [unit:1]

is some sort of spectral concentration [unit: nm^{-1}];

It is not.

$\therefore$ "$\boldsymbol{\eta_\mu(\mu)}$" → "$\boldsymbol{b_F\,(\mu)}$"

Proposed Refinement (ASTM E12)

4) "$\boldsymbol{b_{\lambda}(\mu)}$" is *unclear re: dimensions*.

- Though the ILV indicates that e.g. "$\boldsymbol{b_{\lambda}(\mu)}$" indicates a function of <u>both</u> μ and λ, many correspondents have found this to be unclear.
- The consensus seems to be that "$\boldsymbol{b_{\lambda}(\mu,\lambda)}$" would be a preferable notation.
- Such notation is already allowed by the ILV.

∴ "$\boldsymbol{b_{\lambda}(\mu)}$" → "$\boldsymbol{b_{\lambda}(\mu,\lambda)}$"

DEF (ILV): *Spectral*

spectral - adjective that, when applied to a quantity X pertaining to electromagnetic radiation, indicates:

either that X is a function of the wavelength λ, symbol:

$$X(\lambda)$$

or that the quantity referred to is the spectral concentration of X, symbol:

$$X_\lambda = \frac{dX}{d\lambda}$$

NOTE 1 In the latter case, in French, "spectrique" is preferred to "spectral".

NOTE 2 X_λ is also a function of λ and in order to stress this, may be written $X_\lambda(\lambda)$ without any change of meaning.

NOTE 3 The quantity X can also be expressed as a function of frequency ν, wave number σ, etc.; the corresponding symbols are $X(\nu)$, $X(\sigma)$, etc. and X_ν, X_σ, etc.

III.
FURTHER REFINEMENTS: GEOMETRIC GENERALIZATION

Further Refinements
for Geometric Generalization

1) DEF: $\boldsymbol{\beta(\lambda)}$ is geometrically limited.

$\therefore \boldsymbol{\beta(\lambda)} \rightarrow \boldsymbol{P(\lambda)}$

Likewise, DEFs: $\boldsymbol{b(\mu)}$, $\boldsymbol{b_\lambda(\mu,\lambda)}$ are limited;

2) $\therefore \boldsymbol{b(\mu)} \rightarrow \boldsymbol{G(\mu)}$

3) $\therefore \boldsymbol{b_\lambda(\mu,\lambda)} \rightarrow \boldsymbol{G_\lambda(\mu,\lambda)}$

1) DEF: $\beta(\lambda)$ is limited

- Like radiance, β is defined in the ILV only “in a given direction”
  - i.e., in the limit, as the solid angle of collection $(\Omega)\rightarrow 0$.
- Nevertheless, for small Ω it’s reasonable to speak of measuring the average β about a given direction.
  - But β is not defined when Ω is finite, and significant,
- For large Ω, e.g. for d/h geometries ($\Omega = 2\pi$), it’s not reasonable to speak of measuring an average β.
  - The definition of such an average would be problematic.

DEF: $\boldsymbol{P(\lambda)}$ is not so limited

- $\boldsymbol{P(\lambda)}$ is a ratio of spectral flux emitted by the sample to spectral flux emitted by the perfect reflecting diffuser (PRD).

- $\boldsymbol{P(\lambda)}$ is defined for any given collection solid angle (Ω).

We don’t measure $\beta(\lambda)$; rather $\boldsymbol{P(\lambda)}$

- When we consider spectrophotometric practice, we recognize that we are actually measuring $\boldsymbol{P(\lambda)}$.
  - For directional collection geometries, this difference is not of practical importance, since:

    $$\boldsymbol{P(\lambda) \rightarrow \beta(\lambda)} \qquad \text{as} \qquad \boldsymbol{\Omega \rightarrow 0}$$

  - For hemispherical collection geometries, however, this difference is important, since $\beta(\lambda)$ is not defined.

Acknowledging Historical Usage

- *Spectral radiance factor* ($\beta(\lambda)$) is equivalent to $\boldsymbol{P(\lambda)}$ for directional geometries,
  - but <u>undefined</u> for hemispherical geometries.
- Nevertheless, $\beta(\lambda)$ has been widely used in the literature without regard to this distinction
- In such cases, $\beta(\lambda)$ may be understood loosely as a synonym for $\boldsymbol{P(\lambda)}$.

2) DEF: $\boldsymbol{b(\mu)}$ is limited, as DEF: $\boldsymbol{G(\mu)}$ is not.

- $\boldsymbol{G(\mu)}$ is a ratio of flux emitted by the sample to flux emitted by the PRD.
- $\boldsymbol{G(\mu)}$ is defined for any given collection solid angle ($\boldsymbol{\Omega}$).
- $\boldsymbol{b(\mu)}$ is a radiance ration of radiance;
- Radiance is properly defined <u>only</u> in a given direction ($\boldsymbol{\Omega \rightarrow 0}$).
  - For small $\boldsymbol{\Omega}$, it's reasonable to speak of measuring an average about a given direction, but for large solid angle of collection, e.g. $\boldsymbol{\Omega = 2\pi}$, it is not.

We measure ***G(μ)***, not ***b(μ)***

- ***G(μ)*** is essentially ratio of the flux emitted by the sample to flux emitted by the PRD.

- ***b(μ)*** is a ratio of the sample's radiance to the radiance of the PRD.

- What we actually measure with a spectrophotometer (using monochromatic illumination) is ***G(μ)*** .

3) DEF: $\boldsymbol{b_\lambda(\mu,\lambda)}$ is limited, as DEF: $\boldsymbol{G_\lambda(\mu,\lambda)}$ is not.

- $\boldsymbol{G_\lambda(\mu,\lambda)}$ is essentially a ratio of the spectral flux emitted by the sample to flux emitted by the PRD.
- $\boldsymbol{G_\lambda(\mu,\lambda)}$ is defined $\forall$ collection solid angles ($\boldsymbol{\Omega}$).

- $\boldsymbol{b_\lambda(\mu,\lambda)}$ is essentially a ratio of the sample radiance to the radiance of the PRD.
- $\boldsymbol{b_\lambda(\mu,\lambda)}$ is properly defined <u>only</u> in a given direction ($\boldsymbol{\Omega} \rightarrow \mathbf{0}$).

We measure $\boldsymbol{G_\lambda(\mu, \lambda)}$, not $\boldsymbol{b_\lambda(\mu,\lambda)}$

- $\boldsymbol{G_\lambda(\mu,\lambda)}$ is essentially ratio of the spectral flux emitted by the sample to flux emitted by the PRD.

- $\boldsymbol{b_\lambda(\mu,\lambda)}$ is a ratio of the sample's spectral radiance to the radiance of the PRD.

- What we actually measure with a bispectrometer is $\boldsymbol{G_\lambda(\mu,\lambda)}$.

CONCLUSION

Provisional Recommendations

ILV Term	Preferred Term
$\beta_{L,\lambda}(\mu)$	$G_{L,\lambda}(\mu,\lambda)$
$\beta(\lambda)$	$P(\lambda)$
$\eta_{\mu}(\mu)$	$G_{L}(\mu)$

ILV Term	Generalization
$\beta_{L,\lambda}(\mu)$	$G_{\lambda}(\mu,\lambda)$
$\beta(\lambda)$	$P(\lambda)$
$\eta_{\mu}(\mu)$	$G(\mu)$

QUESTIONS?

Copia LLC

Consultants in Optical Science