Designation: E 520 – 98

Standard Practice for
Describing Photomultiplier Detectors in Emission and Absorption Spectrometry[1]

This standard is issued under the fixed designation E 520; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 Radiation in the frequency range common to analytical emission and absorption spectrometry is detected by photomultipliers presently to the exclusion of most other transducers. Detection limits, analytical sensitivity, and accuracy depend on the characteristics of these current-amplifying detectors as well as other factors in the system.

1.2 This practice surveys photomultiplier properties that are essential to their judicious selection and use of photomultipliers in emission and absorption spectrometry. Descriptions of these properties can be found in the following sections:

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[2]

3. Terminology

3.1 *Definitions*—For terminology relating to detectors refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *solar blind*, *n*—photocathode of photomultiplier tube does not respond to wavelengths on the high side.

3.2.1.1 *Discussion*—In general, solar blind photomultiplier tubes used in optical emission spectroscopy transmit radiation below about 300 nm and do not transmit wavelengths above 300 nm.

4. Structural Features

4.1 *General*—The external structure and dimensions, as well as the internal structure and electrical properties, can be significant in the selection of a photomultiplier.

4.2 *External Structure*—The external structure consists of envelope configurations, window materials, electrical contacts through the glass-wall envelopes, and exterior housing.

4.2.1 *Envelope Configurations*—Glass envelope shapes and dimensions are available in an abundant variety. At present, two envelope configurations are common, the end-on (or head-on), side-on types (see Fig. 1).

4.2.2 *Window Materials*—Various window materials, such as glass, quartz and quartz-like materials, sapphire, magnesium fluoride, and cleaved lithium fluoride, cover the ranges of spectral transmission essential to efficient detection in spectrometric applications. Window cross sections for the end-on type photomultipliers include plano-plano, plano-concave, convexo-concave forms, and a hemispherical form for collection of 2-π radians of light flux.

4.2.3 *Electrical Connections*—Standard pin bases, flying-leads, or potted pin bases are available to facilitate the location of a photomultiplier, or for the use of a photomultiplier at low temperatures. TFE-fluorocarbon receptacles for pin-base types are recommended to minimize the current leakage between pins.

4.2.4 *Housing*—The housing for a photomultiplier should be "light tight." Light leaks into a housing or monochromator from fluorescent lamps are particularly bad noise sources which can be readily detected with an oscilloscope adjusted for twice the power line frequency. A mu-metal housing or shield is recommended to diminish stray magnetic field interferences with the internal focus on electron trajectories between tube elements.

4.3 *Internal Structure*—The internal structure consists of arrangements of cathode, dynodes, and anodes.

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[1] This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.20 on Fundamental Practices.

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[2] *Annual Book of ASTM Standards*, Vol 03.05.

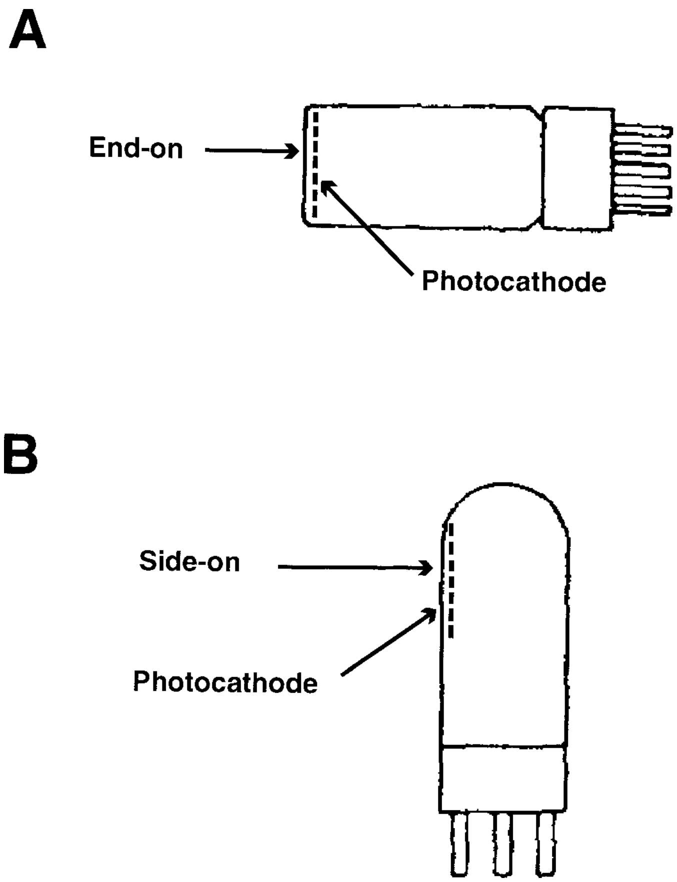


FIG. 1 Envelope Configurations

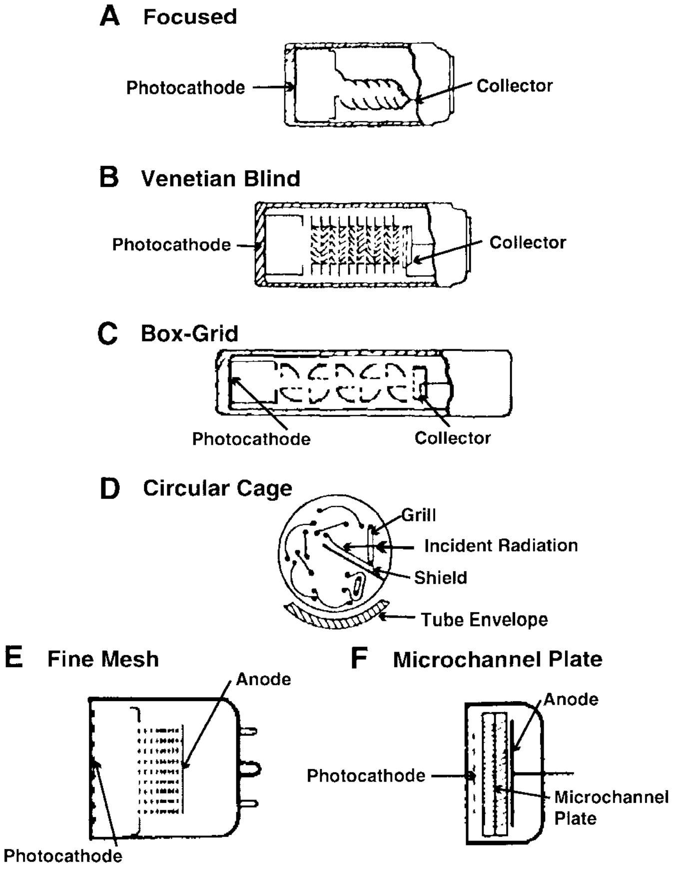


FIG. 2 Electrostatic Dynode Structures

4.3.1 *Photocathode*—A typical photomultiplier of the end-on configuration possesses a semitransparent to opaque layer of photoemissive material that is deposited on the inner surface of the window segment in an evacuated glass envelope. In the side-on window types, the cathode layer is on a reflective substrate within the evacuated tube or on the inner surface of the window.

4.3.2 *Dynodes and Anode*—Secondary-electron multiplication systems are designed so that the electrons strike a dynode at a region where the electric field is directed away from the surface and toward the next dynode. Six of these configurations are shown in Fig. 2. Ordinarily a photomultiplier uses from 4 to 16 dynodes. There are several different configurations of anodes including multianodes and cross wire anodes for position sensitivity.

4.3.3 *Rigidness of Structural Components*— The standard structural components generally will not endure exceptional mechanical shocks. However, specifically constructed photomultipliers (ruggedized) that are resistant to damage by mechanical shock and stress are available for special applications, such as geophysical uses or in mobile laboratories.

5. Electrical Properties

5.1 *General*—The electrical properties of a photomultiplier are a complex function of the cathode, dynodes, and the voltage divider bridge used for gain control.

5.2 *Optical-Electronic Characteristics of the Photocathode*—Electrons are ejected into a vacuum from the conduction bands of semiconducting or conducting materials if the surface of the material is exposed to electromagnetic radiation having a photon energy higher than that required by the photoelectric work-function threshold. The number of electrons emitted per incident photon, that is, the quantum efficiency, is likely to be less than unity and typically less than 0.3.

5.2.1 *Spectral Response*—The spectral response of a photocathode is the relative rate of photoelectron production as a function of wavelength of the incident radiation of constant flux density and solid angle. Spectral response is measured at the cathode with a simple anode or at the anode of a secondary-electron photomultiplier. Usually, this wavelength-dependent response is expressed in amperes per watt at anode.

5.2.1.1 Spectral response curves for several common standard cathode-types are shown in Fig. 3. The S-number is a standard industrial reference number for a given cathode type and spectral response. Some of the common cathode surface compositions are listed below. Semiconductive photocathodes, for example, GaAs(Cs) and InGaAs(Cs), as well as red-enhanced multialkali photocathodes (S-25) are also available. A “solar blind” response cathode of CsI, not shown in Fig. 3, provides a low-noise signal in the 160 to 300-nm region of the spectrum. Intensity measurements at wavelengths below 100 nm can be made with a windowless, gold-cathode photomultiplier.

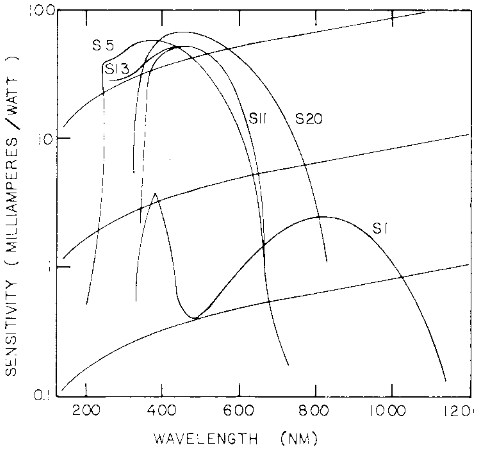


FIG. 3 Spectral Response Curves for Several Cathode Types

Response Type Designation	Examples of Cathode Surfaces Window	Cathode Surface
S-1	Lime Glass	Ag-O-Cs (Reflection)
S-5	Ultraviolet Transmitting Glass	Sb-Cs (Reflection)
S-11	Lime Glass	Sb-Cs (Semitransparent)
S-13	Fused Silica	Sb-Cs (Semitransparent)
S-20	Lime Glass	Sb-Na-K-Cs (Semitransparent)

5.3 *Current Amplification*—The feeble photoelectron current generated at the cathode is increased to a conveniently measurable level by a secondary electron multiplication system. The mechanism for electron multiplication simply depends on the principle that the collision of an energetic electron with a low work-function surface (dynode) will cause the ejection of several secondary electrons. Thus, a primary photoelectron that is directed by an electrostatic field and through an accelerating voltage to the first tube dynode will effectively be amplified by a factor equal to the number of secondary electrons ejected from the single collision.

5.3.1 *Gain per Stage*—The amplification factor or gain produced at a dynode stage depends both on the primary electron energy and the work function of the material used for the dynode surface. Most often dynode surfaces are Cs-Sb or Be-O composites on Cu/Be or Ni substrates. The gain per dynode stage generally is purposely limited.

5.3.2 *Overall Gain*—A series of dynodes, arranged so that a stepwise amplification of electrons from a photocathode occurs, constitutes a total secondary electron multiplication system. Ordinarily, the number of dynodes employed in a photomultiplier ranges from 4 to 16. The overall gain for a system, G, is related to the mean gain per stage, g, and the number of dynode stages, n, by the equation $G = g^n$. Overall gains in the order of 10^6 can be achieved easily.

5.3.3 *Gain Control (Voltage-Divider Bridge)*—Since, for a given photomultiplier the cathode and dynode surface materials and arrangement are fixed, the only practical means to change the overall gain is to control the voltages applied to the individual tube elements. This control is accomplished by adjusting the voltage that is furnished by a high-voltage supply and that is imposed across a voltage-divider bridge (see Fig. 4). Selection of proper resistance values and the configuration for the voltage-divider bridge ultimately determine whether a given photomultiplier will function with stability and linearity in a certain application. Operational stability is determined by the stability of the high voltage supplied to the divider-bridge by the relative anode and divider-bridge currents and by the stability of each dynode voltage as determined by the divider-bridge.

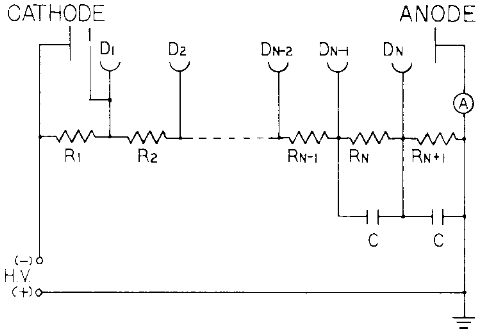


FIG. 4 Voltage-Divider Bridge

5.3.3.1 To a first approximation, the error in the gain varies proportionately to the error in the applied high voltage multiplied by the number of stages. Therefore, for a ten-stage tube, a gain stability of ± 1 % is attained with a power-supply voltage stability of ± 0.1 %.

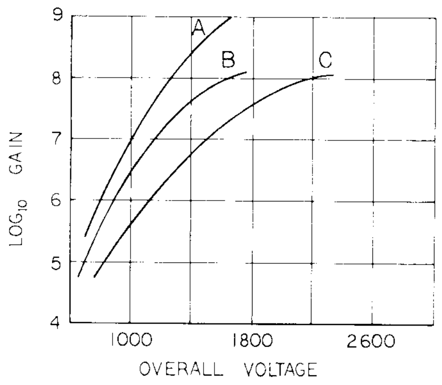
5.3.3.2 For a tube stability of 1 %, the current drawn from the heaviest loaded stage must be less than 1 % of the total current through the voltage divider bridge. For most spectroscopic applications, a bridge current of about 0.5 to 1 mA is sufficient.

5.3.3.3 The value of R_1 (see Fig. 4) is set to give a voltage between the cathode and the first dynode as recommended by the manufacturer. Resistors R_2, $R_3 \cdots R_{n-2}$, R_{n-1}, R_n, and R_{n+1} may be graded to give interstage voltages which are appropriate to the required peak current. With higher interstage voltages at the output end of the tube, higher peak currents can be drawn, but average currents above 1 mA are not normally recommended. The value selected for decoupling-capacitors, C, which serve to prevent sudden significant interstage voltage changes between the last few dynodes, is dependent on the signal frequency. Typically, $C = 2$ nF. In Fig. 4, A, can be a load resistor (1 to 10 MΩ) or the input impedance to a current-measuring device.

5.3.3.4 The overall gain of a photomultiplier varies in a nonlinear fashion with the overall voltage applied to the divider bridge as shown in Fig. 5.

5.3.4 *Linearity of Response*—A photomultiplier is capable of providing a linear response to the radiant input signal over several orders of magnitude. Usually, the dynamic range at the photomultiplier exceeds the range capability of the common linear voltage amplifiers used in measuring circuits.

5.3.5 *Anode Saturation*—As the light intensity impinging on a photocathode is increased, an intensity level is reached, above which the anode current will no longer increase. A current-density saturation at the anode, or anode saturation, is responsible for this effect. A photomultiplier should never be operated at anode saturation conditions nor in the nonlinear



A. Venetian Blind-15 Dynodes
B. Box and Grid-11 Dynodes
C. Venetian Blind-11 Dynodes

FIG. 5 Overall Gain Dependence on Applied Voltage (SbCs Cathode)

response region approaching saturation because of possible damage to the tube.

5.4 *Signal Nature*—The current through a photomultiplier is composed of discrete charge carriers. Each effective photoelectron is randomly emitted from the cathode and travels a distance to the first dynode where a small packet of electrons is generated. This packet of electrons then travels to the next dynode where yet a larger bunch of electrons is produced, and this process continues repetitively until a final large packet of electrons reaches the anode to produce a measurable electrical impulse. Therefore, the true signal output of a multiplier is a train of pulses that occur during an interval of photocathode illumination. These pulse amplitudes are randomly distributed and follow Poisson statistics. This is a characteristic of so-called "shot-effect" noise.

5.5 *Dark Current*—Thermal emission of electrons from the cathode and dynodes, ion feed-back, and field emission, along with internal leakage currents, furnish an anode current that exists even when the cathode is not illuminated. This total current is referred to as dark current.

5.5.1 *Spectral Response and Dark Current*— In general, those cathode surfaces which provide extended red response have both low photoelectric-work functions and low thermionic-work functions. Therefore, higher dark currents can be expected for tubes with red-sensitive cathodes. However, the S-20 surface, which has much better red response and higher quantum efficiency than the S-11 surface, has a thermionic emission level that is equal to or lower than that of the S-11.

5.5.2 *Cathode Size*—The dark current from thermionic electrons is directly proportional to the area of photocathode viewed by the first dynode.

5.5.3 *Internal Apertures*—Some photomultipliers are provided with a defining aperture plane (or plate) between the photocathode and the first dynode. The target plate defines an aperture that limits the area of the cathode viewed by the first dynode and effectively reduces dark current.

5.5.4 *Refrigeration of Photocathodes*— Dark current from S-1-type photomultipliers can be reduced considerably by cooling the photocathode. The S-1 dark current is reduced by an approximate factor of ten for each 20 K temperature decrease.

5.6 *Noise Nature*—Since noise power is an additive circuit property, a consideration of the major sources of noise in a photomultiplier is important. The four principal noise sources of concern are shot noise, thermionic emission noise, field emission noise, and leakage-current noise. Johnson noise is a property of the anode load resistor in a measuring circuit and will not be treated here.

(*a*) The shot-noise equation describes the maximum shot-effect noise as follows:

$$i_{rms} = (2qI\Delta f)^{1/2} \tag{1}$$

where:

i_{rms} = root-mean-square (quadratic) noise current,
q = charge on each carrier, C,
I = total current through tube, A, and
Δf = band pass, Hz.

The shot-noise component is inversely proportional to the cathode radiant sensitivity.

(*b*) The Nyquist equation describes the thermal noise as follows:

$$i_{rms} = [(4kT\Delta f/R)]^{1/2} \tag{2}$$

where:

R = resistance of a conducting element, Ω,
k = Boltzmann constant (1.38×10^{-23} J/K), and
T = absolute temperature, K.

Noise that results from thermionic emission of electrons at the cathode can be reduced by use of internal apertures or by refrigeration. For an S-1 response cathode, current noise has been noted to diminish about an order of magnitude for every 20 K temperature decrease. Leakage current noise is a function of design and construction of individual photomultipliers and is classified as sporadic noise, that is, non-fundamental.

5.6.1 *Additivity of Noise Power*—The quadratic content of the resultant noise at the anode is the sum of the individual quadratic components of noise introduced by fundamental and sporadic noise sources in the photomultiplier.

5.6.2 *Signal-to-Noise Ratio*—The figure of merit customarily chosen to describe the purity of a signal waveform is the signal-to-noise ratio (*S/N*). Usually, this value is given as power ratio in decibels as follows:

$$S/N\ (\text{dB voltage}) = 20 \log\ (\text{signal voltage/noise voltage}) \tag{3}$$

5.6.2.1 More properly for a photomultiplier, a similar quantity, the signal-to-dark noise ratio (*S/DN*), is measured as the ratio of the *rms* value of the fundamental component of a chopped square wave signal current to the *rms* value of the noise current in the dark at 1 Hz. A general definition of the (*S/DN*) at the anode of any photomultiplier is given in the following equation:

$$S/DN = \epsilon(0.45SF_i)^2/2ekA_kJ_k \tag{4}$$

where:

ϵ = current collection efficiency of the first dynode for electrons emitted from the photocathode,
S = photocathode sensitivity,

F_i = dc value of input flux before chopping to convert to a square-wave form,
e = basic electron charge, C,
k = multiplying noise factor ($K = g/(g - 1)$, where g = gain/stage),
A_k = effective cathode area, and
J_k = dark emission current density.

5.6.3 *Equivalent Noise Input*—A signal detection threshold has been defined for photomultipliers in terms of an equivalent noise input (ENI). The lowest level signal that can be detected at the photocathode is that radiant power incident on the cathode which produces a peak signal current equal to the *rms* noise current from all sources at the photocathode. Therefore:

$$ENI = (2ekA_k J_k \epsilon)^{1/2}/0.45S \tag{5}$$

The roles of the various physical parameters for threshold definitions are quite clear. Cathode sensitivity, *S*, and collection efficiency, ϵ, should be made as high as possible, whereas the noise factor, *k*, cathode area, A_k, and dark emission current density, J_k, should be made as low as possible.

5.7 *Photomultiplier as a Component in an Electrical Circuit*—The photomultiplier has certain intrinsic electrical properties important to measurement considerations that can be treated without a discussion of measuring circuits, for example, output impedance and response time.

5.7.1 *Output Impedance*—The anode output of the photomultiplier provides an extremely high impedance that is easily matched to any external circuit. Therefore, the anode of a photomultiplier can be conveniently coupled to a load resistor or electrometer-input.

5.7.2 *Response Time*—The response time of a typical photomultiplier is usually a few nanoseconds. However, the time-spread in output for a pulsed input is a complex function of the geometrical structure, spacing of the tube elements, and inter-element capacitances. The time dispersion of electrons in their passage through the dynode-multiplication system is roughly an-order-of-magnitude lower for the linearly-focused type than for the other types shown in Fig. 2. The time spread phenomenon sets an upper limit for the frequency response of a photomultiplier.

5.7.3 *Signal Gating and Integration Possibilities*—For special signal-recovery techniques, capabilities to gate or integrate signals exists. A type of photomultiplier that has a gating-grid between the cathode and first dynode is commercially available. Also, orthicons, vidicons, and image-dissector tubes may be applicable to signal-integration techniques.

6. Precautions and Problems

6.1 *General*—Numerous problems in the useage of photomultipliers occur. Foremost are fatigue and hystersis effects on gain, cathode illumination, and the noise and effective lifetime attributable to gas leakage.

6.2 *Fatigue and Hysteresis Effects*— Changes in gain with time are of both a short-term (hysteresis) and long-term (fatigue) nature.

6.2.1 The hysteresis effect most recently has been ascribed to variations in electron transfer through a photomultiplier that are produced by electrostatic charge accumulations on insulator-supports for tube elements. This effect can be minimized by illumination of only the central region of the photocathode. However, superior tubes have insulator supports that, for most of their area, have been coated (either evaporated or deposited) with conductive material to reduce isolated areas along electron trajectory on the insulator-supports.

6.2.2 Fatigue arises from changes in the secondary emission ratio that results from volatilization of cesium from the dynode surfaces. Unlike hysteresis, the fatigue process is cumulative. However, fatigue rate can be kept low if the inter-dynode currents are kept low. If the current in the last stage of the photomultiplier is kept below 10 nA, most photomultipliers will give a gain shift of less than 1 %.

6.2.3 For optimum performance a photomultiplier that has noticeable hysteresis and fatigue effects should be stabilized by prior exposure of the photocathode to radiation of a frequency and flux density similar to the radiation intensity to be measured.

6.3 *Illumination of Photocathode*—Only the central portion of a photocathode should be illuminated, because photoelectrons emanating from this area are collected more efficiently than those from the electrostatic-focus fringe region for the cathode. Also, central illumination reduces the hysteresis-gain effect.

6.4 *Gas Leakage*—The useful lifetime of a photomultiplier is generally determined by the leak-rate of atmospheric gases into the tube envelope. The leak-rate depends on the envelope material. Helium, with the worse leak-rate, can easily leak through quartz or fused silica glass. However, this is not a serious problem under ambient or atmospheric conditions. The noise level of a tube photomultiplier increases considerably with gas leakage. Ionized gases in a tube gradually destroy the photocathode by a sputtering process. Therefore, even storage periods are important "deterioration" intervals.

7. Recommendations on Important Selection Criteria

7.1 The criteria most important in the selection of a photomultiplier for emission and absorption spectrometry are spectral response and equivalent-noise-input.

7.2 The photomultiplier with the greatest cathode response in a spectral region of interest is invariably the best choice. Naturally, the spectral response of a photomultiplier can be altered with a simple light filter.

7.3 The equivalent-noise-input, ENI, is a characteristic of a photomultiplier essential to a complete description. The ENI rating enables direct comparisons of photomultipliers of the same spectral response type. A photomultiplier with the lowest ENI rating from a group of photomultipliers invariably will have the highest cathode sensitivity and collection efficiency, and the lowest multiplier noise factor, cathode area, and dark emission intensity.

8. Keywords

8.1 absorption; detectors; emission; photomultiplier; spectrometry

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