Photomultiplier Tubes

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PHOTOMULTIPLIER TUBES

Construction and Operating Characteristics

INTRODUCTION

Among the photosensitive devices in use today, the photomultiplier tube (or PMT) is a versatile device that provides extremely high sensitivity and ultra-fast response. A typical photomultiplier tube consists of a photoemissive cathode (photocathode) followed by focusing electrodes, an electron multiplier and an electron collector (anode) in a vacuum tube, as shown in Figure 1.

When light enters the photocathode, the photocathode emits photoelectrons into the vacuum. These photoelectrons are then directed by the focusing electrode voltages towards the electron multiplier where electrons are multiplied by the process of secondary emission. The multiplied electrons are collected by the anode as an output signal.

Because of secondary-emission multiplication, photomultiplier tubes provide extremely high sensitivity and exceptionally low noise among the photosensitive devices currently used to detect radiant energy in the ultraviolet, visible, and near infrared regions. The photomultiplier tube also features fast time response, low noise and a choice of large photosensitive areas.

This section describes the prime features of photomultiplier tube construction and basic operating characteristics.

CONSTRUCTION

The photomultiplier tube generally has a photocathode in either a side-on or a head-on configuration. The side-on type receives incident light through the side of the glass bulb, while in the head-on type, it is received through the end of the glass bulb. In general, the side-on type photomultiplier tube is relatively low priced and widely used for spectrophotometers and general photometric systems. Most of the side-on types employ an opaque photocathode (reflection-mode photocathode) and a circular-cage structure electron multiplier which has good sensitivity and high amplification at a relatively low supply voltage.

The head-on type (or the end-on type) has a semitransparent photocathode (transmission-mode photocathode) deposited upon the inner surface of the entrance window. The head-on type provides better spatial uniformity (see page 7) than the side-on type having a reflection-mode photocathode. Other features of head-on types include a choice of photosensitive areas from tens of square millimeters to hundreds of square centimeters.

Figure 1: Cross-Section of Head-On Type PMT

Figure 2: External Appearance

a) Side-On Type

b) Head-On Type

Figure 3: Types of Photocathode

a) Reflection Mode

b) Transmission Mode

ELECTRON MULTIPLIER

The superior sensitivity (high current amplification and high S/N ratio) of photomultiplier tubes is due to the use of a low-noise electron multiplier which amplifies electrons by a cascade secondary electron emission process. The electron multiplier consists of from 8, up to 19 stages of electrodes called dynodes. There are several principal types in use today.

1) Circular-cage type

The circular-cage is generally used for the side-on type of photomultiplier tube. The prime features of the circular-cage are compactness and fast time response.
2) Box-and-grid type
This type consists of a train of quarter cylindrical dynodes and is widely used in head-on type photomultiplier tubes because of its relatively simple dynode design and improved uniformity, although time response may be too slow in some applications.

3) Linear-focused type
The linear-focused type features extremely fast response time and is widely used in head-on type photomultiplier tubes where time resolution and pulse linearity are important.

4) Venetian blind type
The venetian blind type has a large dynode area and is primarily used for tubes with large photocathode areas. It offers better uniformity and a larger pulse output current. This structure is usually used when time response is not a prime consideration.

5) Mesh type
The mesh type has a structure of fine mesh electrodes stacked in close proximity. This type provides high immunity to magnetic fields, as well as good uniformity and high pulse linearity. In addition, it has position-sensitive capability when used with cross-wire anodes or multiple anodes.

6) Microchannel plate (MCP)
The MCP is a thin disk consisting of millions of micro glass tubes (channels) fused in parallel with each other. Each channel acts as an independent electron multiplier. The MCP offers much faster time response than the other discrete dynodes. It also features good immunity from magnetic fields and two-dimensional detection ability when multiple anodes are used.

7) Metal channel type
The Metal channel dynode has a compact dynode construction manufactured by our unique fine machining technique.

In addition, hybrid dynodes combining two of the above dynodes are available. These hybrid dynodes are designed to provide the merits of each dynode.

SPECTRAL RESPONSE
The photocathode of a photomultiplier tube converts energy of incident light into photoelectrons. The conversion efficiency (photocathode sensitivity) varies with the wavelength of the incident light. This relationship between photocathode sensitivity and wavelength is called the spectral response characteristic. Figure 4 shows the typical spectral response of a bialkali photomultiplier tube. The spectral response characteristics are determined on the long wavelength side by the photocathode material and on the short wavelength side by the window material. Typical spectral response characteristics for various types of photomultiplier tubes are shown on pages 88 and 89. In this catalog, the longwavelength cut-off of spectral response characteristics is defined as the wavelength at which the cathode radiant sensitivity becomes 1% of the maximum sensitivity for bialkali and Ag-O-Cs photocathodes, and 0.1% of the maximum sensitivity for multialkali photocathodes.

Spectral response characteristics are typical curves for representative tube types. Actual data may be different from type to type.
PHOTOCATHODE MATERIALS

The photocathode is a photoemissive surface usually consisting of alkali metals with very low work functions. The photocathode materials most commonly used in photomultiplier tubes are as follows:

1) Ag-O-Cs

The transmission-mode photocathode using this material is designated S-1 and sensitive from the visible to infrared range (300 to 1200nm). Since Ag-O-Cs has comparatively high thermionic dark emission (refer to “ANODE DARK CURRENT” on page 8), tubes of this photocathode are mainly used for detection in the near infrared region with the photocathode cooled.

2) GaAs(Cs)

GaAs activated in cesium is also used as a photocathode. The spectral response of this photocathode usually covers a wider spectral response range than multialkali, from ultraviolet to 930nm, which is comparatively flat over 300 to 850nm.

3) InGaAs(Cs)

This photocathode has greater extended sensitivity in the infrared range than GaAs. Moreover, in the range between 900 and 1000nm, InGaAs has much higher S/N ratio than Ag-O-Cs.

4) Sb-Cs

This is a widely used photocathode and has a spectral response in the ultraviolet to visible range. This is not suited for transmission-mode photocathodes and mainly used for reflection-mode photocathodes.

5) Bialkali (Sb-Rb-Cs, Sb-K-Cs)

These have a spectral response range similar to the Sb-Cs photocathode, but have higher sensitivity and lower noise than Sb-Cs. The transmission mode bialkali photocathodes also have a favorable blue sensitivity for scintillator flashes from NaI (TI) scintillators, thus are frequently used for radiation measurement using scintillation counting.

6) High temperature bialkali or low noise bialkali (Na-K-Sb)

This is particularly useful at higher operating temperatures since it can withstand up to 175°C. A major application is in the oil well logging industry. At room temperatures, this photocathode operates with very low dark current, making it ideal for use in photon counting applications.

7) Multialkali (Na-K-Sb-Cs)

The multialkali photocathode has a high, wide spectral response from the ultraviolet to near infrared region. It is widely used for broad-band spectrophotometers. The long wavelength response can be extended out to 930nm by special photocathode processing.

8) Cs-Te, Cs-I

These materials are sensitive to vacuum UV and UV rays but not to visible light and are therefore called solar blind. Cs-Te is quite insensitive to wavelengths longer than 320nm, and Cs-I to those longer than 200nm.

WINDOW MATERIALS

The window materials commonly used in photomultiplier tubes are as follows:

1) Borosilicate glass

This is frequently used glass material. It transmits radiation from the near infrared to approximately 300nm. It is not suitable for detection in the ultraviolet region. For some applications, the combination of a bialkali photocathode and a low-noise borosilicate glass (so called K-free glass) is used. The K-free glass contains very low potassium (K2O) which can cause background counts by 40K. In particular, tubes designed for scintillation counting often employ K-free glass not only for the faceplate but also for the side bulb to minimize noise pulses.

2) UV-transmitting glass (UV glass)

This glass transmits ultraviolet radiation well, as the name implies, and is widely used as a borosilicate glass. For spectroscopy applications, UV glass is commonly used. The UV cut-off is approximately 185nm.

3) Synthetic silica

The synthetic silica transmits ultraviolet radiation down to 160nm and offers lower absorption in the ultraviolet range compared to fused silica. Since thermal expansion coefficient of the synthetic silica is different from Kovar which is used for the tube leads, it is not suitable for the stem material of the tube (see Figure 1 on page 1). Borosilicate glass is used for the stem, then a graded seal using glasses with gradually different thermal expansion coefficients are connected to the synthetic silica window. Because of this structure, the graded seal is vulnerable to mechanical shock so that sufficient care should be taken in handling the tube.

4) MgF2 (magnesium fluoride)

The crystals of alkali halide are superior in transmitting ultraviolet radiation, but have the disadvantage of deliquesce. Among these, MgF2 is known as a practical window material because it offers low deliquesce and transmits ultraviolet radiation down to 115nm.
blue sensitivity and red/white ratio

For simple comparison of spectral response of photomultiplier tubes, cathode blue sensitivity and red/white ratio are often used.

The cathode blue sensitivity is the photoelectric current from the photocathode produced by a light flux of a tungsten lamp at 2856K passing through a blue filter (Corning CS No. 5-58 polished to half stock thickness). Since the light flux, once transmitted through the blue filter cannot be expressed in lumens, blue sensitivity is conveniently expressed in A/Im-b (amperes per lumen-blue). The blue sensitivity is an important parameter in scintillation counting using an NaI (Tl) scintillator since the NaI (Tl) scintillator produces emissions in the blue region of the spectrum, and may be the decisive factor in energy resolution.

The red/white ratio is used for photomultiplier tubes with a spectral response extending to the near infrared region. This parameter is defined as the quotient of the cathode sensitivity measured with a light flux of a tungsten lamp at 2856K passing through a red filter (Toshiba IR-D80A for the S-1 photocathode or R-68 for others) divided by the cathode luminous sensitivity with the filter removed.

LUMINOUS SENSITIVITY

Since the measurement of the spectral response characteristic of a photomultiplier tube requires a sophisticated system and much time, it is not practical to provide customers with spectral response characteristics for each tube ordered. Instead cathode or anode luminous sensitivity is commonly used.

The cathode luminous sensitivity is the photoelectric current from the photocathode per incident light flux (10^-5 to 10^-2 lumens) from a tungsten filament lamp operated at a distribution temperature of 2856K. The anode luminous sensitivity is the anode output current (amplified by the secondary emission process) per incident light flux (10^-10 to 10^-5 lumens) on the photocathode. Although the same tungsten lamp is used, the light flux and the applied voltage are adjusted to an appropriate level. These parameters are particularly useful when comparing tubes having the same or similar spectral response range. Hamamatsu final test sheets accompanying the tubes usually indicate these parameters except for tubes with Cs-I or Cs-Te photocathodes, which are not sensitive to tungsten lamp light. (Radiant sensitivity at a specific wavelength is listed for those tubes instead.)

Both the cathode and anode luminous sensitivities are expressed in units of A/Im (amperes per lumen). Note that the lumen is a unit used for luminous flux in the visible region and therefore these values may be meaningless for tubes which are sensitive beyond the visible region. (For those tubes, the blue sensitivity or red/white ratio is often used.)
Photoelectrons emitted from a photocathode are accelerated by an electric field so as to strike the first dynode and produce secondary electron emissions. These secondary electrons then impinge upon the next dynode to produce additional secondary electron emissions. Repeating this process over successive dynode stages, a high current amplification is achieved. A very small photoelectric current from the photocathode can be observed as a large output current from the anode of the photomultiplier tube.

Current amplification is simply the ratio of the anode output current to the photoelectric current from the photocathode. Ideally, the current amplification of a photomultiplier tube having \( n \) dynode stage and an average secondary emission ratio \( \delta \) per stage is \( \delta^n \). While the secondary electron emission ratio \( \delta \) is given by:

\[
\delta = A \cdot E^n
\]

where \( A \) is constant, \( E \) is an interstage voltage, and \( \alpha \) is a coefficient determined by the dynode material and geometric structure. It usually has a value of 0.7 to 0.8.

When a voltage \( V \) is applied between the cathode and the anode of a photomultiplier tube having \( n \) dynode stages, current amplification, \( \mu \), becomes:

\[
\mu = \delta^n = (A \cdot E^n)^n = \left\{ A \cdot \left( \frac{V}{n+1} \right) \right\}^n
\]

Since photomultiplier tubes generally have 9 to 12 dynode stages, the anode output varies directly with the 6th to 10th power of the change in applied voltage. The output signal of the photomultiplier tube is extremely susceptible to fluctuations in the power supply voltage, thus the power supply must be very stable and provide minimum ripple, drift and temperature coefficient. Various types of regulated high-voltage power supplies designed with this consideration are available from Hamamatsu.

**ANODE DARK CURRENT**

A small amount of current flows in a photomultiplier tube even when the tube is operated in a completely dark state. This output current, called the anode dark current, and the resulting noise are critical factors in determining the detectivity of a photomultiplier tube. As Figure 9 shows, dark current is greatly dependent on the supply voltage.

**Major sources of dark current may be categorized as follows:**

1) **Thermionic emission of electrons**

Since the materials of the photocathode and dynodes have very low work functions, they emit thermionic electrons even at room temperature. Most of dark currents originate from the thermionic emissions, especially those from the photocathode as they are multiplied by the dynodes. Cooling the photocathode is most effective in reducing thermionic emission and, this is particularly useful in applications where
low dark counts are essential such as in photon counting.

Figure 10 shows the relationship between dark current and temperature for various photocathodes. Photocathodes which have high sensitivity in the red to infrared region, especially S-1, show higher dark current at room temperature. Hamamatsu provides thermoelectric coolers (C659 and C4877) designed for various sizes of photomultiplier tubes.

Figure 10: Temperature Characteristics of Dark Current

2) Ionization of residual gases (ion feedback)
Residual gases inside a photomultiplier tube can be ionized by collision with electrons. When these ions strike the photocathode or earlier stages of dynodes, secondary electrons may be emitted, thus resulting in relatively large output noise pulses. These noise pulses are usually observed as afterpulses following the primary signal pulses and may be a problem in detecting light pulses. Present photomultiplier tubes are designed to minimize afterpulses.

3) Glass scintillation
When electrons deviating from their normal trajectories strike the glass envelope, scintillations may occur and dark pulses may result. To minimize this type of dark pulse, photomultiplier tubes may be operated with the anode at high voltage and the cathode at ground potential. But this is inconvenient to handle the tube. To obtain the same effect without difficulty, Hamamatsu provides “HA coating” in which the glass bulb is coated with a conductive paint connected to the cathode. (See “GROUND POLARITY AND HA COATING” on page 10.)

4) Leakage current (ohmic leakage)
Leakage current resulting from the glass stem base and socket may be another source of dark current. This is predominant when the photomultiplier tube is operated at a low voltage or low temperature. The flatter slopes in Figures 9 and 10 are mainly due to leakage current. Contamination from dirt and moisture on the surface of the tube may increase the leakage current, and therefore should be avoided.

5) Field emission
When a photomultiplier tube is operated at a voltage near the maximum rated value, electrons may be emitted from electrodes by the strong electric field and may cause noise pulses. It is therefore recommended that the tube be operated at a voltage 20 to 30% lower than the maximum rating. The anode dark current decreases with time after the tube is placed in a dark state. In this catalog, anode dark currents are measured after 30-minute storage in a dark state.

**ENI (EQUIVALENT NOISE INPUT)**
ENI is an indication of the photon-limited signal-to-noise ratio. It refers to the amount of light usually in watts or lumens necessary to produce a signal-to-noise ratio of unity in the output of a photomultiplier tube. ENI is expressed in units of lumens or watts. For example the value of ENI (in watts) is given by

\[
ENI = \frac{\sqrt{2q \cdot l_{db} \cdot \mu \cdot \Delta f}}{S}
\]

where
- \( q \) = electronic charge (1.60 \times 10^{-19} \ \text{coul.})
- \( l_{db} \) = anode dark current in amperes after 30-minute storage in darkness
- \( \mu \) = current amplification
- \( \Delta f \) = bandwidth of the system in hertz (usually 1 hertz)
- \( S \) = anode radiant sensitivity in amperes per watt at the wavelength of interest or anode luminous sensitivity in amperes per lumen

For the tubes listed in this catalog, the value of ENI may be calculated by the above equation. Usually it has a value between 10^{-15} and 10^{-16} watts or lumens.

**MAGNETIC FIELD EFFECTS**
Most photomultiplier tubes are affected by the presence of magnetic fields. Magnetic fields may deflect electrons from their normal trajectories and cause a loss of gain. The extent of the loss of gain depends on the type of photomultiplier tube and its orientation in the magnetic field. Figure 11 shows typical effects of magnetic fields on some types of photomultiplier tubes. In general, tubes having a long path from the photocathode to the first dynode are very vulnerable to magnetic fields. Therefore head-on types, especially large diameter tubes, tend to be more adversely influenced by magnetic fields.
Hamamatsu provides photomultiplier tubes using fine mesh dynodes. These tube types exhibit much higher immunity to external magnetic fields than the photomultiplier tubes using other dynodes. In addition, when the light level to be measured is rather high, triode or tetrode type photomultiplier tubes can be used in highly magnetic fields.

**SPATIAL UNIFORMITY**

Spatial uniformity is the variation of sensitivity with position of incident light on a photocathode.

Although the focusing electrodes of a photomultiplier tube are designed so that electrons emitted from the photocathode or dynodes are collected efficiently by the first or following dynodes, some electrons may deviate from their desired trajectories in the focusing and multiplication processes, resulting in a loss of collection efficiency. This loss of collection efficiency varies with the position on the photocathode from which the photoelectrons are emitted and influences the spatial uniformity of a photomultiplier tube. The spatial uniformity is also determined by the photocathode surface uniformity itself.

In general, head-on type photomultiplier tubes provide better spatial uniformity than side-on types because of the photocathode to first dynode geometry. Tubes especially designed for gamma camera applications have excellent spatial uniformity, because uniformity is the decisive factor in the overall performance of a gamma camera.

**Figure 11: Typical Effects by Magnetic Fields Perpendicular to Tube Axis**

When a tube has to be operated in magnetic fields, it may be necessary to shield the tube with a magnetic shield case. Hamamatsu provides a variety of magnetic shield cases. To express the effect of a magnetic shield case, the magnetic shielding factor is used. This is the ratio of the strength of the magnetic field outside the shield case, $H_{out}$, to that inside the shield case, $H_{in}$. It is determined by the permeability $\mu$, the thickness $t$ (mm) and inner diameter $D$ (mm) of the shield case, as follows:

$$\frac{H_{out}}{H_{in}} = \frac{3\mu t}{4D}$$

It should be noted that the magnetic shielding effect decreases towards the edge of the shield case as shown in Figure 12. It is recommended that the tube be covered by a shield case longer than the tube length by at least half the tube diameter.

**Figure 12: Edge Effect of Magnetic Shield Case**

Spatial uniformity is the variation of sensitivity with position of incident light on a photocathode.
TEMPERATURE CHARACTERISTICS
By decreasing the temperature of a photomultiplier tube, dark current originating from thermionic emission can be reduced. Sensitivity of the photomultiplier tube also varies with the temperature. In the ultraviolet to visible region, the temperature coefficient of sensitivity usually has a negative value, while near the long wavelength cut-off it has a positive value. Figure 14 shows temperature coefficients vs. wavelength of typical photomultiplier tubes. Since the temperature coefficient change is large near the long wavelength cutoff, temperature control may be required in some applications.

DRIFT AND LIFE CHARACTERISTIC
While operating a photomultiplier tube continuously over a long period, anode output current of the photomultiplier tube may vary slightly with time, although operating conditions have not changed. This change is referred to as drift or in the case where the operating time is 10^3 to 10^4 hrs it is called life characteristics. Figure 16 shows typical life characteristics.

Drift is primarily caused by damage to the last dynode by heavy electron bombardment. Therefore the use of lower anode current is desirable. When stability is of prime importance, the use of average anode current of 1μA or less is recommended.

HYSTERESIS
A photomultiplier tube may exhibit an unstable output for several seconds to several tens of seconds after voltage and light are applied, i.e., output may slightly overshoot or undershoot before reaching a stable level (Figure 15). This instability is called hysteresis and may be a problem in spectrophotometry and other applications.

Hysteresis is mainly caused by electrons being deviated from their planned trajectories and electrostatically charging the dynode support ceramics and glass bulb. When the applied voltage is changed as the light input changes, marked hysteresis can occur. As a countermeasure, many Hamamatsu side-on photomultiplier tubes employ "anti-hysteresis design" which virtually eliminate hysteresis.

TIME RESPONSE
In the measurement of pulsed light, the anode output signal should reproduce a waveform faithful to the incident pulse waveform. This reproducibility is greatly affected by the electron transit time, anode pulse rise time, and electron transit time spread (TTS).

As illustrated in Figure 17, the electron transit time is the time interval between the arrival of a delta function light pulse (pulse width less than 50ns) at the photocathode and the instant when the anode output pulse reaches its peak amplitude. The anode pulse rise time is defined as the time required to rise from 10% to 90% of the peak amplitude when the whole photocathode is illuminated by a delta function light pulse (pulse width less than 50 ps). The electron transit time has a fluctuation between individual light pulses. This fluctuation is called transit time spread (TTS) and defined as the FWHM of the frequency distribution of electron transit times (Figure 18) at single photoelectron event. The TTS is an important factor in time-resolved measurement.

The time response characteristics depend on the dynode structure and applied voltage. In general, tubes of the linear-focused or circular-cage structure exhibit better time response than tubes of the box-and-grid or venetian blind structure. MCP-PMTs, which employ an MCP in place of conventional dynodes, offer better time response than tubes using other dynodes. For example, the TTS can be significantly improved compared to normal photomultiplier tubes because a nearly parallel electric field is applied between the photocathode, MCP and the anode. Figure 19 shows typical time response characteristics vs. applied voltage for types R2059 (51mm dia. head-on, 12-stage, linear-focused type).

Figure 14: Typical Temperature Coefficients of Anode Sensitivity

Figure 15: Hysteresis Measurement

Figure 16: Examples of Life

Figure 17: Typical Temperature Coefficients of Anode Sensitivity

Figure 18: Hysteresis Measurement

Figure 19: Time Response Characteristics
VOLTAGE-DIVIDER CONSIDERATION

Interstage voltages for the dynodes of a photomultiplier tube are usually supplied by a voltage-divider circuit consisting of series-connected resistors. Schematic diagrams of typical voltage-divider circuits are illustrated in Figure 20. Circuit (a) is a basic arrangement (DC output) and (b) is for pulse operations. Figure 21 shows the relationship between the incident light level and the average anode output current of a photomultiplier tube using the voltage-divider circuit (a). Deviation from the ideal linearity occurs at a certain incident level (region B). This is caused by an increase in dynode voltage due to the redistribution of the voltage loss between the last few stages, resulting in an apparent increase in sensitivity. As the input light level is increased, the anode output current begins to saturate near the value of the current flowing through the voltage divider (region C). Therefore, it is recommended that the voltage-divider current be maintained at least at 20 times the average anode output current required from the photomultiplier tube.

Figure 20: Schematic Diagrams of Voltage-Divider Circuits
(a) Basic arrangement for DC operation
(b) For pulse operation

Figure 21: Output Characteristics of a PMT Using Voltage-Divider Circuit (a)
Generally high output current is required in pulsed light applications. In order to maintain dynode potentials at a constant value during pulse durations and obtain high peak currents, large capacitors are used as shown in Figure 20 (b). The capacitor values depend on the output charge. If linearity of better than 1% is needed, the capacitor value should be at least 100 times the output charge per pulse, as follows:

$$C > 100 \frac{I}{V}$$ (farads)

where $I$ is the peak output current in amperes, $V$ is the pulse width in seconds, and $V$ is the voltage across the capacitor in volts.

In high energy physics applications where a high pulse output is required, as the incident light is increased while the interstage voltage is kept fixed, output saturation will occur at a certain level. This is caused by an increase in the electron density between the electrodes, causing space charge effects which disturb the electron current. As a corrective action to overcome space charge effects, the voltage applied to the last few stages, where the electron density becomes high, should be set at a higher value than the standard voltage distribution so that the voltage gradient between those electrodes is enhanced. For this purpose, a so-called tapered bleeder circuit (Figure 22) is often employed. Use of this tapered bleeder circuit improves pulse linearity 5 to 10 times better than that obtained with normal bleeder circuits (equally divided circuits).

Hamamatsu provides a variety of socket assemblies incorporating voltage-divider circuits. They are compact, rugged, lightweight and ensure the maximum performance for a photomultiplier tube by simple wiring.

**Figure 22: Tapered Bleeder Circuit**

**GROUND POLARITY AND HA COATING**

The general technique used for voltage-divider circuits is to ground the anode with a high negative voltage applied to the cathode, as shown in Figure 20. This scheme facilitates the connection of such circuits as ammeters or current-to-voltage conversion operational amplifiers to the photomultiplier tube. However, when a grounded anode configuration is used, bringing a grounded metallic holder or magnetic shield case near the bulb of the tube can cause electrons to strike the inner bulb wall, resulting in the generation of noise. Also, for head-on type photomultiplier tubes, if the faceplate or bulb near the photocathode is grounded, the slight conductivity of the glass material causes a current to flow between the photocathode (which has a high negative potential) and ground. This may cause significant deterioration of the photocathode. For this reason, when designing the housing for a photomultiplier tube and when using an electrostatic or magnetic shield case, extreme care is required.

In addition, when using foam rubber or similar material to mount the tube in its housing, it is essential that material having sufficiently good insulation properties be used. This problem can be solved by applying a black conductive layer around the bulb and connecting to the cathode potential (called HA Coating), as shown in Figure 23.

As mentioned above, the HA coating can be effectively used to eliminate the effects of external potential on the side of the bulb. However, if a grounded object is located on the photocathode faceplate, there are no effective countermeasures. Glass scintillation, if it occurs in the faceplate, has a larger influence on the noise. It also causes deterioration of the photocathode sensitivity and, once deteriorated, the sensitivity will never recover to the original level. To solve these problems, it is recommended that the photomultiplier tube be operated in the cathode ground scheme, as shown in Figure 24, with the anode at a positive high voltage. For example, in scintillation counting, since the grounded scintillator is directly coupled to the photomultiplier tube, it is recommended that the cathode be grounded, with a high positive voltage applied to the anode. Using this scheme, a coupling capacitor $C_c$ is used to separate the high positive voltage applied to the anode from the signal, making it impossible to obtain a DC signal output.

**Figure 23: HA Coating**

**Figure 24: Cathode Ground Scheme**
SINGLE PHOTON COUNTING

Photon counting is one effective way to use a photomultiplier tube for measuring very low light levels. It is widely used in astronomical photometry and chemiluminescence or bioluminescence measurement. In the usual application, a number of photons enter the photomultiplier tube and create an output pulse train like (a) in Figure 25. The actual output obtained by the measurement circuit is a DC current with a fluctuation as shown at (b).

Figure 25: Overlapping Output Pulses
(a)
(b)

When the light intensity becomes so low that the incident photons are separated as shown in Figure 26. This condition is called a single photon (or photoelectron) event. The number of output pulses is in direct proportion to the amount of incident light and this pulse counting method has advantages in S/N ratio and stability over the DC method averaging all the pulses. This pulse counting technique is known as the photon counting method.

Figure 26: Discrete Output Pulses (Single Photon Event)

Since the photomultiplier tube output contains a variety of noise pulses in addition to the signal pulses representing photoelectrons as shown in Figure 27, simply counting the pulses without some form of noise elimination will not result in an accurate measurement. The most effective approach to noise elimination is to investigate the height of the output pulses.

Figure 27: Output Pulse and Discrimination Level

A typical pulse height distribution (PHD) for the output of photomultiplier tubes is shown in Figure 28. In this PHD, the lower level discrimination (LLD) is set at the valley trough and the upper level discrimination (ULD) at the foot where the output pulses are very few. Most pulses smaller than the LLD are noise and pulses larger than the ULD result from cosmic rays, etc. Therefore, by counting pulses between the LLD and ULD, accurate light measurements becomes possible. In the PHD, Hm is the mean height of the pulses. It is recommended that the LLD be set at 1/3 of Hm and the ULD at triple Hm. In most cases, however, the ULD setting can be omitted.

Considering the above, a clear definition of the peak and valley in the PHD is a very significant characteristic for photomultiplier tubes for use in photon counting.

SCINTILLATION COUNTING

Scintillation counting is one of the most sensitive and effective methods for detecting radiation. It uses a photomultiplier tube coupled to a transparent crystal called scintillator which produces light by incidence of radiation.

Figure 29: Diagram of Scintillation Detector

In radiation measurements, there are two parameters that should be measured. One is the energy of individual particles and the other is the amount of particles. Radiation measurements should determine these two parameters.

When radiation enters the scintillator, it produce light flashes in response to each particle. The amount of flash is proportional to the energy of the incident radiation. The photomultiplier tube detects individual light flashes and provides the output pulses
which contain information on both the energy and amount of pulses, as shown in Figure 30. By analyzing these output pulses using a multichannel analyzer (MCA), a pulse height distribution (PHD) or energy spectrum is obtained, and the amount of incident particles at various energy levels can be measured accurately. Figure 31 shows typical PHDs or energy spectra when gamma rays ($^{55}$Fe, $^{137}$Cs, $^{60}$Co) are detected by the combination of a NaI(Tl) scintillator and a photomultiplier tube. For the PHD, it is very important to have distinct peaks at each energy level. This is evaluated as pulse height resolution (energy resolution) and is the most significant characteristic in radiation particle measurements. Figure 32 shows the definition of energy resolution taken with a $^{137}$Cs source.

Figure 30: Incident Particles and PMT Output

Figure 31: Typical Pulse Height Distributions (Energy Spectra)

a) $^{55}$Fe+NaI (Tl)

b) $^{137}$Cs+NaI (Tl)

c) $^{60}$Co+NaI (Tl)

Figure 32: Definition of Energy Resolution

Figure 33: Spectral Response of PMT and Spectral Emission of Scintillators

Pulse height resolution is mainly determined by the quantum efficiency of the photomultiplier tube in response to the scintillator emission. It is necessary to choose a tube whose spectral response matches with the scintillator emission. In the case of thallium-activated sodium iodide, or NaI(Tl), which is the most popular scintillator, head-on type photomultiplier tube with a bialkali photocathode is widely used.
Connections to External Circuits

LOAD RESISTANCE

Since the output of a photomultiplier tube is a current signal and the type of external circuit to which photomultiplier tubes are usually connected has voltage inputs, a load resistance is used to perform a current-voltage transformation. This section describes considerations to be made when selecting this load resistance. Since for low output current levels, the photomultiplier tube may be assumed to act as virtually an ideal constant-current source, the load resistance can be made arbitrarily large, thus converting a low-level current output to a high-level voltage output. In practice, however, using very large values of load resistance creates the problems of deterioration of frequency response and output linearity described below.

Figure 34: PMT Output Circuit

If, in the circuit of Figure 34, we let the load resistance be $R_L$ and the total of the capacitance of the photomultiplier tube anode to all other electrodes, including such stray capacitance as wiring capacitances be $C_s$, the cutoff frequency $f_c$ is expressed by the following relationship.

$$f_c = \frac{1}{2\pi R_L C_s}$$

From this relationship, it can be seen that, even if the photomultiplier tube and amplifier have very fast response, response will be limited to the cutoff frequency $f_c$ of the output circuit. If the load resistance is made large, at high current levels the voltage drop across $R_L$ becomes large, affecting a potential difference between the last dynode stage and the anode. As a result, a loss of output linearity (output current linearity with respect to incident light level) may occur.

Figure 35: Amplifier Internal Resistance

In Figure 35, let us consider the effect of the internal resistance of the amplifier. If the load resistance is $R_L$ and the input impedance of the amplifier is $R_i$, the combined parallel output resistance of the photomultiplier tube, $R_0$, is given by the following equation.

$$R_0 = \frac{R_L + R_i}{R_L + R_i}$$

This value of $R_0$, which is less than the value of $R_L$, is then the effective load resistance of the photomultiplier tube. If, for example, $R_L = R_i$, the effective load resistance is $1/2$ that of $R_L$ alone. From this we see that the upper limit of the load resistance is actually the input resistance of the amplifier and that making the load resistance much greater than this value does not have significant effect. While the above description assumed the load and input impedances to be purely resistive, in practice, stray capacitances, input capacitance and stray inductances influence phase relationships. Therefore, as frequency is increased, these circuit elements must be considered as compound impedances rather than pure resistances.

From the above, three guides can be derived for use in selection of the load resistance:

1) In cases in which frequency response is important, the load resistance should be made as small as possible.
2) In cases in which output linearity is important, the load resistance should be chosen such that the output voltage is below several volts.
3) The load resistance should be less than the approximate input impedance of the external amplifier.

HIGH-SPEED OUTPUT CIRCUIT

For the detection of high-speed and pulsed light signals, a coaxial cable is used to make the connection between the photomultiplier tube and the electronic circuit, as shown in Figure 36. Since commonly used cables have characteristic impedances of 50 Ω or 75 Ω, this cable must be terminated in a pure resistance equivalent to the characteristic impedance to provide impedance matching and ensure distortion-free transmission for the signal waveform. If a matched transmission line is used, the impedance of the cable as seen by the photomultiplier tube output will be the characteristic impedance of the cable, regardless of the cable length, and no distortion will occur in signal waveforms. If proper matching at the signal receiving end is not achieved, the impedance seen at the photomultiplier tube output will be a function of both frequency and cable length, resulting in significant waveform distortion. Such mismatched conditions can be caused by the connectors used as well, so that the connector to be used should be chosen with regard given to the frequency range to be used, to provide a match to the coaxial cable.

When a mismatch at the signal receiving end occurs, all of the pulse energy from the photomultiplier tube is not dissipated at the receiving end, but is partially reflected back to the photomultiplier tube via the cable. While this reflected energy will be fully dissipated at the photomultiplier tube when an impedance match has been achieved at the tube, if this is not the case, because the photomultiplier tube itself acts as an open circuit, the energy will be reflected and, thus returned to the signal-receiving end. Since part of the pulse makes a round trip in the coaxial cable and is again input to the receiving end, this reflected signal is delayed with respect to the main pulse and results in waveform distortion (so called ringing phenomenon). To prevent this phenomenon, in addition to providing impedance matching at the receiving end, it is necessary to provide a resistance matched to the cable impedance at the photomultiplier tube end as well. If this is done, it is possible to virtually eliminate the ringing caused by an impedance mismatch, although the output pulse height of the photomultiplier tube is reduced to one-half of the normal level by use of this impedance matching resistor.
This relationship is derived for the following reason. If the input impedance of the operational amplifier is extremely large, and the output current of the photomultiplier tube is allowed to flow into the input terminal of the amplifier, most of the current will flow through $R_t$ and subsequently to the operational amplifier output circuit. Therefore, the output voltage $V_o$ is given by the expression $-R_f \times I_p$. When using such an operational amplifier, it is of course, not possible to increase the output voltage without limit, the actual maximum output being approximately equal to the operational amplifier power supply voltage. At the other end of the scale, for extremely small currents, limitations are placed by the operational amplifier offset current ($I_{os}$), the quality of $R_t$, and other factors such as the insulation materials used.

- **OPERATIONAL AMPLIFIERS**

In cases in which a high-sensitivity ammeter is not available, the use of an operational amplifier will enable measurements to be made using an inexpensive voltmeter. This technique relies on converting the output current of the photomultiplier tube to a voltage signal. The basic circuit is as shown in Figure 38, for which the output voltage, $V_o$, is given by the following relationship.

$$V_o = -R_f \times I_p$$

It is relatively simple to implement a high-speed amplifier using a wide-band video amplifier or operational amplifier. However, in exchange of design convenience, use of these ICs tends to create problems related to performance (such as noise). It is therefore necessary to know their performance limit and take corrective action.

As the pulse repetition frequency increases, baseline shift creates one reason for concern. This occurs because the DC signal component has been eliminated from the signal circuit by coupling with a capacitor which does not pass DC components. If this occurs, the reference zero level observed at the last dynode stage is not the actual zero level. Instead, the apparent zero level is the time-average of the positive and negative fluctuations of the signal waveform. This will vary as a function of the pulse density, and is known as baseline shift. Since the height of the pulses above this baseline level is influenced by the repetition frequency, this phenomenon is of concern when observing waveforms or discriminating pulse levels.

Next, let us consider waveform observation of high-speed pulses using an oscilloscope (Figure 37). This type of operation requires a low load resistance. Since, however, there is a limit to the oscilloscope sensitivity, an amplifier may be required. For cables to which a matching resistor has been connected, there is an advantage that the cable length does not affect the characteristics of the cable. However, since the matching resistance is very low compared to the usual load resistance, the output voltage becomes too small. While this situation can be remedied with an amplifier of high gain, the inherent noise of such an amplifier can itself be detrimental to measurement performance. In such cases, the photomultiplier tube can be brought as close as possible to the amplifier and a load resistance as large as possible should be used (consistent with preservation of frequency response), to achieve the desired input voltage.
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Solid State Emitters
CdS Photoconductive Cells
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Quality, technology, and service are part of every product.
APPENDIX

1) Photon Counting

Photon counting is one effective way to use a photomultiplier tube for measuring very low light. It is widely used in astronomical photometry and fluorescence spectroscopy. In the usual application, a number of photons enters the photomultiplier tube and creates an output pulse train like (a) in Figure 31. The actual output obtained by the measurement circuit is a DC with fluctuation as shown at (b).

Figure 31: Overlapping Output Pulses

(a) ![Output Pulses](image)

(b) ![Output Pulses](image)

When the light intensity becomes so low that the incident photons are separated as shown in Figure 32. This condition is called single photon event. The number of output pulses is in direct proportion to the amount of incident light and this pulse counting method has advantages in S/N ratio and stability over the DC method averaging all the pulses. This pulse counting technique is the photon counting method.

Figure 32: Single Photon Event

![Single Photon Event](image)

Since the photomultiplier tube output contains a variety of noise pulses in addition to the signal pulses representing photoelectrons as shown in Figure 33, simply counting the pulses without some form of noise elimination will not result in an accurate measurement. The most effective approach to noise elimination is to investigate the height of the output pulses.

Figure 33: Output Pulse and Discrimination Level

![Output Pulse and Discrimination Level](image)

A typical pulse height distribution (PHD) of output of photomultiplier tubes is shown in Figure 34. In this PHD, the lower level discrimination (LLD) is set at the valley and the upper level discrimination (ULD) at the foot. Most pulses smaller than the LLD are noise and pulses larger than the ULD result from cosmic rays, etc. Therefore, by counting pulses between the LLD and ULD, accurate light measurements are made possible. In the PHD, Hm is the mean height of pulses. It is recommended that the LLD be set at 1/3 of Hm and the ULD at triple Hm.

Considering the above, clear definition of the peak and valley in the PHD is a very significant characteristic for photomultiplier tubes for use in photon counting. All of Hamamatsu photomultiplier tubes selected for photon counting are supplied with such PHD data.

Figure 34: Typical Pulse Height Distribution

![Typical Pulse Height Distribution](image)

2) Scintillation Counting

Scintillation counting is one of the most common and effective methods in detecting radiation particles. It uses a photomultiplier tube coupled to a scintillator which produces light by incidence of radiation particles.

Figure 35: Diagram of Scintillation Detector

![Diagram of Scintillation Detector](image)

In radiation particle measurements, there are two parameters that should be measured: one is the energy of individual particles and the other is the amount of particles. When radiation particles enter the scintillator, it produces light flashes in response to each particle. The amount of flash is proportional to the energy of the incident particle and individual light flashes are detected by the photomultiplier tube. Consequently, the output pulses obtained from the photomultiplier tube contain information on both the energy and amount of pulses, as shown in Figure 36.
By analyzing these output pulses using a multi-channel analyzer (MCA), a pulse height distribution (PHD) or energy spectrum as shown in Figure 37 is obtained. From the PHD, the amount of incident particles at various energy levels can be measured. For the PHD, it is very important to have distinct peaks at each energy level. This is evaluated as pulse height resolution and is the most significant characteristic in radiation particle measurements. Figure 38 shows the definition of pulse height resolution for a $^{133}$Cs source.

![Figure 36: Incident Particles and PMT Output](image)

![Figure 37: Pulse Height Distribution (Energy Spectrum)](image)

![Figure 38: Definition of Pulse Height Resolution](image)

Pulse height resolution is mainly determined by the quantum efficiency of the photomultiplier tube in response to the scintillator emission. It is necessary to choose the tube whose spectral response matches the scintillator emission. For thallium-activated sodium iodide, NaI(Tl) which is the most popular scintillator, head-on type photomultiplier tubes with a bialkali photocathode are widely used. Hamamatsu has a 30-page catalog "Photomultiplier Tubes for Scintillation Counting and High Energy Physics" available from our sales office.

**BASIC DIAGRAM SYMBOLS**

All basic diagrams show terminals viewed from the base end of the tube.

- SY: Anode
- GF: Grid (Focusing Electrode)
- AG: Grid (Accelerating Electrode)
- R: Photocathode
- P: Anode
- SH: Shield
- IC: Internal Connection (Do not use)
- NC: No Connection (Do not use)
## Side-On Type Photomultiplier Tubes

<table>
<thead>
<tr>
<th>Type No.</th>
<th>Remarks</th>
<th>Spectral Response</th>
<th>Dynode Structure</th>
<th>Anode Voltage (Vac)</th>
<th>Average Anode Current (mA)</th>
<th>Luminous Intensity (µA/ln)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R906</td>
<td>Fit true channel flying spot exposures</td>
<td>350K 300-650 400 Sb-Cs K</td>
<td>CC9</td>
<td>EB78-12C</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>1-1/8 Inch (28 mm) Dia. Type with Glass Base</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 1-1/8 Inch (28 mm) Dia. Types with UV to Visible Sensitivity

<table>
<thead>
<tr>
<th>Type No.</th>
<th>Remarks</th>
<th>Spectral Response</th>
<th>Dynode Structure</th>
<th>Anode Voltage (Vac)</th>
<th>Average Anode Current (mA)</th>
<th>Luminous Intensity (µA/ln)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R31A</td>
<td>5A-response, general purpose</td>
<td>350K 300-650 400 Sb-Cs K</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>R31E</td>
<td>Same as R31A but with Bialkali photocathode, high visibility</td>
<td>350K 300-650 400 Bi K</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>1P21</td>
<td>Medium gain and very low dark current variant of R31A, high gain variant of 1P21 with relaxed dark spec.</td>
<td>350K 300-650 400 Sb-Cs K</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>R106</td>
<td>Same as R106 but with synthetic silica window</td>
<td>350K 300-650 400 Sb-Cs Q</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>R106U</td>
<td>Same as R106 but with synthetic silica window</td>
<td>350K 300-650 400 Sb-Cs Q</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>1P28A</td>
<td>Extended red S-A response</td>
<td>351U 185-750 350 Bi-Cs S</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>R32U</td>
<td>Red-extended bialkali photocathode</td>
<td>351U 185-750 350 Bi-Cs S</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
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<tr>
<td>R905</td>
<td>Same as R905 but with UV glass <em>Window material</em></td>
<td>351U 185-750 350 Bi-Cs S</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>R151U</td>
<td>Tantalum or steel holder replacement for R151U</td>
<td>351U 185-750 350 Bi-Cs S</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
<tr>
<td>R179U</td>
<td>Same, high pulse linearity, fast rise time response</td>
<td>351U 185-750 350 Bi-Cs S</td>
<td>CC9</td>
<td>EB78-11A</td>
<td>1250</td>
<td>0.1</td>
</tr>
</tbody>
</table>

- **K**: Borosilicate glass
- **U**: UV glass
- **Q**: Synthetic silica

### Diagrams

- Side view of the photomultiplier tube.
- Bottom view of the photomultiplier tube.
<table>
<thead>
<tr>
<th>Cathode Sensitivity</th>
<th>Anode Characteristics</th>
<th>(at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anode Sensitivity</td>
<td>Current Amplification Typ.</td>
</tr>
<tr>
<td>Blue Typ.</td>
<td>Red/White Ratio Typ.</td>
<td>Luminous Radiant Typ. (mA/W)</td>
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<tr>
<td>(A/μm²)</td>
<td>(milling)</td>
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<tr>
<td>7.5</td>
<td>72</td>
<td>1000</td>
</tr>
<tr>
<td>5.0</td>
<td>48</td>
<td>1000</td>
</tr>
<tr>
<td>7.1</td>
<td>60</td>
<td>1000</td>
</tr>
<tr>
<td>5.0</td>
<td>48</td>
<td>1000</td>
</tr>
<tr>
<td>5.0</td>
<td>48</td>
<td>1000</td>
</tr>
<tr>
<td>5.5</td>
<td>60</td>
<td>1000</td>
</tr>
<tr>
<td>5.0</td>
<td>48</td>
<td>1000</td>
</tr>
<tr>
<td>5.0</td>
<td>48</td>
<td>1000</td>
</tr>
<tr>
<td>5.5</td>
<td>60</td>
<td>1000</td>
</tr>
<tr>
<td>8.4</td>
<td>0.005</td>
<td>87</td>
</tr>
<tr>
<td>7.0</td>
<td>60</td>
<td>1000</td>
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<td>65</td>
<td>1000</td>
</tr>
<tr>
<td>5.0</td>
<td>48</td>
<td>800</td>
</tr>
</tbody>
</table>

- Sockets may be available from electronic supply houses or our sales offices.
- The maximum ambient temperature range is -50 to +50°C. When using a tube with glass base at -50°C or below, see precautions on page 76.
- Averaged over any interval of 30 seconds maximum.
- At the wavelength of peak response.
- Voltage distribution ratios used to measure characteristics are shown on page 62.
- Anode characteristics are measured with the supply voltage and the voltage distribution ratio specified by note (9).
- 2.2: At 2000 Vdc

Units: mm
9. 1 Spectrophotometry

9. 1. 1 Overview

Spectrophotometry is a study of the transmission and reflection properties of material samples as a function of wavelength, but the term commonly means chemical analysis of various substances utilizing photometry. Photometric instruments used in this field are broadly divided into two methods: one utilizes light absorption, reflection or polarization at specific wavelengths and the other uses external energy to excite a sample and measures the subsequent light emission. Photomultiplier tubes have been most widely used in this field for years. Major principles used in spectrophotometry are classified as illustrated in Figure 9-1 below.

![Figure 9-1: Major principles of spectrophotometry](TPMOC0017EB)

Specific photometric instruments currently used are:

1) Visible to UV spectrophotometers (absorption, reflection)
2) Infrared spectrophotometers (absorption, reflection)
3) Far UV spectrophotometers (absorption, reflection)
4) Emission spectrophotometers
5) Fluorescence spectrophotometers
6) Atomic absorption spectrophotometers
7) Azimuthal, circular dichroism meters
8) Raman spectrophotometers
9) Densitometers, colorimeters and color analyzers etc.
9.1.2 Specific applications

The following paragraphs explain major, specific applications of spectrophotometers, divided into two methods utilizing absorption or emission.

(1) Utilizing Absorption

A. UV, visible and infrared spectrophotometers

When light passes through a substance, the light energy causes changes in the electronic state of the substance (electron transition) or induces characteristic vibration of the molecules, resulting in a loss of partial energy. This is referred to as absorption, and quantitative analysis can be performed by measuring the extent of absorption.

The principle and simplified block diagram of an absorption spectrophotometer are shown in Figure 9-2.

![Figure 9-2: Principle and block diagram of a absorption spectrophotometer](TPMOC0018EB)

There are various optical systems in use today for spectrophotometers. Figure 9-3 illustrates the optical system of a spectrophotometer using sequential plasma emission as the light source for covering from the ultraviolet to visible and infrared range.

![Figure 9-3: Optical system of a UV to visible spectrophotometer](TPMOC0019EA)
B. Atomic absorption spectrophotometers

The atomic absorption spectrophotometer employs special light sources (hollow cathode lamps) constructed for the respective elements to be analyzed. A sample is dissolved in solvent and burned for atomization, and light from the specific hollow cathode lamp is passed through the flame. The amount of light that is absorbed is proportional to the concentration of the sample material. Therefore, by comparing the extent of absorption between the sample to be analyzed and a standard sample measured in advance, it is possible to know the concentration of the specific element contained in the sample. A typical optical system used for atomic absorption spectrophotometers is shown in Figure 9-4.

![Figure 9-4: Optical system used for atomic absorption spectrophotometers](TPMOC0021EA)

(2) Utilizing Emission

A. Photoelectric emission spectrophotometers (direct readers)

When external energy is applied to a sample, light emission occurs from the sample. Dispersing this emission using a monochromator, into characteristic spectral lines of elements and measuring their presence and intensity simultaneously, enables rapid qualitative and quantitative analysis of the elements contained in the sample. Figure 9-5 illustrates the block diagram of a photoelectric emission spectrophotometer in which multiple photomultiplier tubes are used.

![Figure 9-5: Block diagram illustrating a photoelectric emission spectrophotometer](TPMOC0022EA)
B. Fluorospectrophotometers

The fluorospectrophotometer is mainly used for chemical analysis in biochemistry, especially in molecular biology. When a substance is illuminated and excited by visible or ultraviolet light, it may emit light with a wavelength longer than that of the excitation light. This light emission is known as fluorescence and its emission process is shown in Figure 9-6. Measuring the fluorescent intensity and spectra allows quantitative and qualitative analysis of the elements contained in the substance.

![Figure 9-6: Fluorescent molecular energy levels](image1)

Figure 9-6: Fluorescent molecular energy levels

Figure 9-7 shows the structure of a fluorospectrophotometer using photomultiplier tubes as the detectors. This instrument roughly consists of a light source, excitation monochromator, fluorescence monochromator and fluorescence detector. A xenon lamp is commonly used as the light source because it provides a continuous spectrum output over a wide spectral range. The excitation and fluorescence monochromators use the same diffraction grating or prism, as are used in general-purpose monochromators.

![Figure 9-7: Fluorospectrophotometer structure](image2)

Figure 9-7: Fluorospectrophotometer structure
9. 1. 3 Characteristics required of photomultiplier tubes

The following photomultiplier tube characteristics are required in this application.

a) High stability

b) Low dark current

c) High signal-to-noise ratio

d) Wide spectral response (ultraviolet to infrared)

e) Low hysteresis

f) Excellent polarization properties

Side-on and head-on photomultiplier tubes having a multialkali photocathode and silica window are most frequently used in these applications.
9.4 **In-vitro Assay**

The analysis and inspection of blood or urine samples collected out of a living body is referred to as in-vitro assay. It is used for physical checkups, diagnosis, and evaluation of drug potency. The in-vitro assay can be classified as shown in Table 9-3. Of these, the concentrations of most tumor markers, hormones, drugs and viruses which are classified under immunological assay are exceedingly low. This requires extremely high-sensitivity inspection equipment for frequently requiring use of photomultiplier tubes.

<table>
<thead>
<tr>
<th>Sample Inspection</th>
<th>Biochemistry</th>
<th>Enzyme, protein, sugar, lipid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immunology</td>
<td>Tumor marker, serum protein, hormone, reagent, virus</td>
</tr>
<tr>
<td></td>
<td>Hematology</td>
<td>(Leukocyte, red corpuscle, hemoglobin, platelet) computation, classification, coagulation</td>
</tr>
<tr>
<td></td>
<td>Microbiology</td>
<td>Bacteria identification, susceptibility</td>
</tr>
</tbody>
</table>

**Table 9-3: Classification of in-vitro inspection**

Immunoassay, a measurement technique making use of specificity of the antigen-antibody reaction, is widely used. The principles of immunoassay\(^9\) are illustrated in Figure 9-19 below, and the procedures of each method are explained in the subsequent paragraphs.
Figure 9-19: Principles of immunoassay

Figure 9-19 (a) is a technique known as the sandwich method. Step (1): Samples are introduced into a vessel in which antibodies responding to object antigens (hormones, tumor markers, etc.) are fixed (solid-phase antibody). Step (2): Antigen-antibody reaction occurs, and each object antigen combines with a solid-phase antibody. This reaction has an extremely high singularity and hardly ever occurs with a different antigen. After antigen-antibody reaction, the liquid layer is removed leaving the combined antigen and antibody. Step (3): Labeled antibodies are added, which combine with object antigens. Step (4): Antigen-antibody reaction occurs again so that the object antigen is sandwiched between the antibodies. Then the liquid layer is removed. Step (5): The quantity of labels is optically measured using a photomultiplier tube.
Figure 9-19 (b) is another technique called the competitive method. Step (1): Antibodies responding to object antigens are fixed on the bottom of a vessel. Step (2): Samples are added along with the labeled object antigens. Step (3): Competitive reaction in which object antigens and labeled antigens combine with labeled antibodies in proportional to their concentration, reaching a state of equilibrium. After the antigen-antibody reaction, the unnecessary upper layer is removed. Step (4): The quantity of labels is measured using a photomultiplier tube. In the sandwich method, the higher the concentration of object antigens, the larger the signal. Conversely, in the competitive method, the higher the concentration of the object antigens, the lower the signal.

Immunooassay can be further categorized according to the material used for labeling as follows

(1) Using radioactive isotopes for labeling
   (Radioimmunoassay)

(2) Using enzymes for labeling
   (Enzymeimmunoassay)

9.4.1 RIA (Radioimmunoassay) method

(1) Overview

Radioactive isotope (RI) is used for the labeling as was explained above, and radiation (gamma or beta rays) emitting from the RI labels is detected by the combination of a scintillator and a photomultiplier tube, so that the object antigen can be quantitatively measured. Radioactive isotopes most frequently used for labeling are $^3$H, $^{14}$C, $^{57}$Co, $^{75}$Se, $^{125}$I and $^{131}$I. (See Table 9-4.) Of these, $^{125}$I offers useful characteristics for labeling and is very widely used. Because radioactive isotopes other than $^3$H and $^{14}$C emit gamma rays, sodium iodide crystals are used as a scintillator, providing a high conversion efficiency.

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Half-life</th>
<th>Energy</th>
<th>Detection Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>12.26 years</td>
<td>$\beta$</td>
<td>Liquid scintillation</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>5730 years</td>
<td>$\beta$</td>
<td>Liquid scintillation</td>
</tr>
<tr>
<td>$^{57}$Co</td>
<td>270 days</td>
<td>$\gamma$</td>
<td>Scintillation crystal</td>
</tr>
<tr>
<td>$^{75}$Se</td>
<td>120.4 days</td>
<td>$\gamma$</td>
<td>Scintillation crystal</td>
</tr>
<tr>
<td>$^{125}$I</td>
<td>60 days</td>
<td>$\gamma$</td>
<td>Scintillation crystal</td>
</tr>
<tr>
<td>$^{131}$I</td>
<td>8 days</td>
<td>$\beta, \gamma$</td>
<td>Scintillation crystal</td>
</tr>
</tbody>
</table>

Table 9-4: Radioactive isotopes used for labeling in radioimmunoassay

Recently, for in-vitro assays, the quantity of samples and the number of items to be measured are rapidly increasing. To meet this trend, the equipment for radioimmunoassay has been automated. A typical piece of automated equipment in use today is the well scintillation counter that makes use of sodium iodide scintillators having a well-like hole to enhance the conversion efficiency of the radiation into light. Measurements are made by automatically inserting test tubes, which contain a mixture of antigens and antibodies including labels, into each hole in the scintillator. (See Figure 9-20.) Each detector section including a scintillator is covered by lead shield to block extraneous radiation.

Isotopes $^3$H and $^{14}$C can be used for labeling; however, because they emit extremely low-energy beta rays, a liquid scintillation counter explained in Section 9.5, is used to make measurements with these two isotopes.
Figure 9-20: Schematic block diagram illustrating a well scintillation counter

(2) Major characteristics required of photomultiplier tubes

Photomultiplier tubes used in RIA must have the following characteristics.

a) High energy resolution or pulse height resolution (PHR)

b) High level of stability

c) Low noise

To obtain high energy resolution, the photomultiplier tube should have high quantum efficiency at the peak emission wavelength (410 nanometers) of the sodium iodide (NaI(Tl)) scintillator. (See Figure 9-16.) In addition, because this application field deals with quite a few samples that emit extremely small amounts of radiation, it is also very important that the photomultiplier tube exhibits sufficiently low noise.

9. 4. 2 EIA (Enzymeimmunoassay) method

(1) Overview

An enzyme is used as a label utilizing the antigen-antibody reaction. As Figure 9-21 (2) shows, RIA offers exceptionally high sensitivity among various immunoassay techniques. However, because it uses radioactive isotopes, various restrictions are imposed on its use. On the other hand, though its sensitivity is inferior to RIA, EIA is more popular because of its easy use. EIA sensitivity is gradually increasing due to improvements in reagents and detection method.
Figure 9-21: Comparison of various immunoassay techniques and measurable concentration range
(Use this comparison data just for a general guide.)

In the EIA procedure, an enzyme used as a label in the antigen-antibody mixture in the last step in Figure 9-19 is activated to create a product. Then, color or fluorescence emitted from the product is detected by a photomultiplier tube. (See Figure 9-22.) The extent of color or fluorescent intensity is proportional to the quantity of enzyme (enzyme concentration).

Figure 9-22: Label enzyme reaction

(2) Major characteristics required of photomultiplier tubes

a) High sensitivity at the wavelength of color or fluorescence emitted from the product of the enzyme reaction

b) Low dark current

c) High signal-to-noise ratio

d) Compact size
9. 4. 3 Other immunoassay methods

(1) Overview

Besides EIA, several non radioactive immunoassay techniques not using radioisotopes are under research and development.

One of these is fluoroimmunoassay in which a fluorescent substance is used for labeling. The final remaining mixture of antigens and antibodies is irradiated by an excitation light and the resulting fluorescence is measured with regard to the intensity, wavelength shift and polarization. This technique offers slightly higher sensitivity than that of EIA. Figure 9-23 shows the schematic of a fluorescence-polarization photometer, which is used for fluoroimmunoassay.

![Figure 9-23: Schematic presentation of a fluorescence-polarization photometer](TPMHC0027EB)

To achieve high sensitivity equal to RIA by using non-radioactive immunoassay, intensive research and development of emission-immunoassay has been carried out. This immunoassay uses a chemiluminous substance or bioluminous substance for labeling and allows the final remaining mixture of antigens and antibodies to emit light, which is detected by a photomultiplier tube. There are three types of emission-immunoassay methods, as follows:

1) Use of a chemiluminous substance such as luminol and acridinium for labeling
2) Use of chemiluminescence or bioluminescence for activation of the label enzyme used in EIA
3) Use of a catalyst for the bioluminescence reaction

Methods 2) and 3) can be thought of as kinds of EIA techniques. As shown in Figure 9-21 previously, emission-immunoassay is a high sensitivity equivalent to RIA.
(2) Major characteristics required of photomultiplier tubes

Fluoroimmunoassay
a) High sensitivity at fluorescent wavelengths
b) High level of stability
c) Low dark current
d) High signal-to-noise ratio
e) Compact size

Emission-immunoassay
a) High sensitivity at emission wavelengths
b) Excellent single-photoelectron pulse height distribution
c) Low dark current pulse
d) High gain
e) Compact size
9.6 Biotechnology

In life science applications, photomultiplier tubes are mainly used for detection of fluorescence and scattered light. Major equipment used for life science includes cell sorters, fluorometers and DNA sequencers.

9.6.1 Overview

(1) Cell sorters

When light is irradiated onto a rapidly flowing solution which contains cells or chromosomes, a scattered light or fluorescence is released from the cells or chromosomes. By analyzing this scattered light or fluorescence, it is possible to elucidate cell properties and structures and separate the cells based on these properties. This field is known as flow cytometry. A cell sorter like the one illustrated in Figure 9-26 is most frequently used. The cell sorter is an instrument that selects and collects only specific cells labeled by a fluorescent substance from a mixture of cells in a solution.

Figure 9-26: Major components for a cell sorter

In a cell sorter, a fluorescent probe is first attached to the cells. The cells pass through a thin tube at a fixed velocity. When each cell passes through a small area onto which an intense laser beam is focused, the fluorescence is emitted from the cell and is detected by a photomultiplier tube. The photomultiplier tube outputs an electrical signal in proportion to the number of fluorescent molecules attached to each cell. At the same time, the laser beam light is scattered forward by the cell, and detecting this scattered light gives information on the cell volume. After processing these two signals, the cell sorter creates an electrical pulse that deflects a drop of liquid, containing the desired cell into one of the collection tubes.
(2) **Fluorometers**

While the ultimate purpose of the cell sorter explained above is to separate cells, the fluorometer\(^{(16)}\) is used to analyze cells and chemical substances by measuring the fluorescence or scattered light from a cell or chromosome with regard to such factors as the fluorescence spectrum, fluorescence quantum efficiency, fluorescence anisotropy (polarization) and fluorescence lifetime. (See Figure 9-27.)

![Figure 9-27: Automatic fluorescence-depolarization photometer](TPMOC0026EA)

The basic configuration of the fluorometer is nearly identical with that of the fluorospectrophotometer and thus a description is omitted here. There are a variety of models of fluorometers which are roughly categorized into: filtering fluorescence photometers, spectrofluorescence photometers, compensated-spectrofluorescence photometers, fluoroanisotropy analyzers, and phase fluorescence lifetime measurement systems. Of these, the fluoroanisotropy analyzer is an instrument specially dedicated to measurement of fluorescence-depolarization.

When performing research on biological samples such as proteins, nucleic acid and lipid membranes, rotational relaxation of a fluorescent molecule takes place only slowly and the fluorescence is polarized in most cases. It is still necessary to compensate for the effect of fluorescence depolarization when measuring quantum efficiency and spectrum. For this purpose, the automatic fluorescence-depolarization photometer uses a pair of photomultiplier tubes which detect the two polarized components at the same time.
(3) DNA sequencers

This is an instrument used to decode the base arrangement of DNA extracted from a cell. The principle of a DNA sequencer is shown in Figure 9-28. An extracted DNA segment is injected onto gel electrophoresis plate along with a fluorescent label which combines with the DNA. When an electric potential is applied across the gel, the DNA begins to migrate and separate based on size and charge. When the DNA segment reaches the position of the scanning line, it is excited by a laser, causing only the portion with the labeling pigment to give off fluorescence. This fluorescent light is passed through monochromatic filters and detected by photomultiplier tubes. Computer-processing of the position at which the fluorescence has occurred gives information on where the specific bases are located. The DNA sequencer is used for the genetic study of living organisms, research into the cause and treatment of genetic diseases and decoding of human genes.

9. 6. 2 Major characteristics required of photomultiplier tubes

Because the photomultiplier tube detects very-low fluorescence emitted from a cell or DNA, the following characteristics are required as in the case of spectrophotometry.

a) High stability
b) Low dark current
c) High signal-to-noise ratio
d) Wide spectral response
e) Low hysteresis
f) Excellent polarization properties
9. 9 Mass Spectrometry/Solid Surface Analysis

Mass spectrometry is a technique used to identify and analyze the mass, makeup and minute quantity of a sample through the measurement of the difference in mass and movement of ions by exerting electric or magnetic energy on the sample which is ionized.

Solid state surface analysis is used to examine the surface state of a sample through the measurement of photoelectrons, secondary electrons, reflected electrons, transmitting electrons, Auger electrons or X-rays which are generated as a result of interactions of incident electrons with atoms composing the sample, which take place when an electron beam or X-ray irradiates the sample.

9. 9. 1 Mass spectrometers

(1) Overview\(^{(23)}\)\(^{(24)}\)

Mass spectrometers are broadly classified into two groups: one using magnetic force (magnet) and one not using magnetic force. Currently used mass spectrometers fall under one of the following four types.

- Time of flight (TOF) type
- Quadrupole (Q-Pole) or ion trap type
- Magnetic field type
- Ion cyclotron (FTICR) type

Among these, the quadrupole (Q-Pole) type mass spectrometer is most widely used and its block diagram is shown in Figure 9-39.

![Figure 9-39: Block diagram of a quadrupole (Q-Pole) type mass spectrometer](TEMC0019EA)

When a sample is guided into the ionizer, it is ionized through the electronic ionization (EI method), chemical ionization (CI method), fast atomic bombardment (FAB method), electro-spray ionization (ESI method) or atmospheric pressure chemical ionization (APCI method). The ionized sample is sent to the analyzer section (quadrupolar electrodes) in which the sample is separated depending on the mass per charge count \((m/z)\) by the DC voltage and high-frequency voltage applied to the quadrupolar electrodes. After passing through the analyzer section, the ions then reach the detector section where they are detected by an electron multiplier tube.
Mass spectrometers are often combined with a gas chromatograph or liquid chromatograph to build a gas chromatograph mass spectrometer (GC-MS) or liquid chromatograph mass spectrometer (LC-MS). Mass spectrometers are used to identify, measure and analyze the composition of various samples such as petrochemicals, fragrance materials, medicines, biogenic components and substances causing environmental pollution. Figure 9-40 shows the schematic drawing of a gas chromatograph mass spectrometer.

![Schematic drawing of a gas chromatograph mass spectrometer.](TEMC0200EA)

Figure 9-40: Schematic drawing of a gas chromatograph mass spectrometer.

(2) Major characteristics required of electron multiplier tubes

Since the mass spectrometer measures and analyzes the sample in minute amounts, electron multiplier tubes should have the following characteristics.

a) High gain
b) Low noise
c) Long operating life

9.9.2 Solid surface analyzers

(1) Overview

Solid surface analyzers are broadly divided into two groups: one using electron beams to irradiate a sample and the other using X-rays. Major solid surface analyzers presently used are as follows.

• Scanning electron microscope (SEM)
• Transmission electron microscope (TEM)
• Auger electron spectrometer (AES)
• Electron spectrometer for chemical analysis (ESCA)

When a sample is irradiated by electron beams, interactions of the incident electrons with atoms which compose the sample occur and generate various kinds of signals characterized by the particular atom. Figure 9-41 shows the kinds of signals obtained and the approximate depth at which each signal is generated on the surface of the sample.
Obtained signals are chosen to extract necessary information according to measurement purpose, which is then used for analyzing the surface of the sample.

Among the four types of surface analyzers, the scanning electron microscope (SEM) is the most widely used and its structure and principle are illustrated in Figure 9-42.\(^{26}\)

(1)The sample is irradiated by an electron beam to generate secondary electrons which are then collected.

(2)The sample is scanned by an electron beam, just like TV scan.

(3)A gray level image is displayed according to the quantity of secondary electrons.
An electron beam emitted from the electron gun is accelerated at a voltage of 0.5 to 30kV. This accelerated electron beam is then condensed by electromagnetic lens action of the focusing lens and objective lens, and finally formed into a very narrow beam of 3 to 100nm in diameter, irradiating on the surface of a sample. Secondary electrons are then produced from the surface of the sample where the electron beam landed, and detected with a secondary electron detector. The electron beam can be scanned in the XY directions across the predetermined area on the surface of the sample by scanning the electromagnetic lens. A magnified image can be displayed on the CRT in synchronization with the signals of the secondary electron detector. Figure 9-43 shows the structure and operation of the secondary electron detector.

![Diagram of secondary electron detector](image)

**Figure 9-43: Structure and operation of a secondary electron detector**

A typical secondary electron detector consists of a collector electrode, scintillator, light pipe, photomultiplier tube and preamplifier. Voltage is applied to the collector electrode and scintillator at a level required to collect secondary electrons efficiently. Most of the secondary electrons produced from the sample enter the scintillator and are converted into light. This converted light then passes through the light pipe and is detected with the photomultiplier tube. Figure 9-44 shows the images of a broken surface of ceramic, observed with a scanning electron microscope.

![Photographs of ceramic material](image)

**Figure 9-44: Photographs of broken ceramic material taken with a scanning electron microscope**

(2) **Major characteristics required of photomultiplier tubes**

To detect low level light emitted from the scintillator, photomultiplier tubes must have the following characteristics.

a) High stability

b) Low dark current

c) High quantum efficiency
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