

## 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.

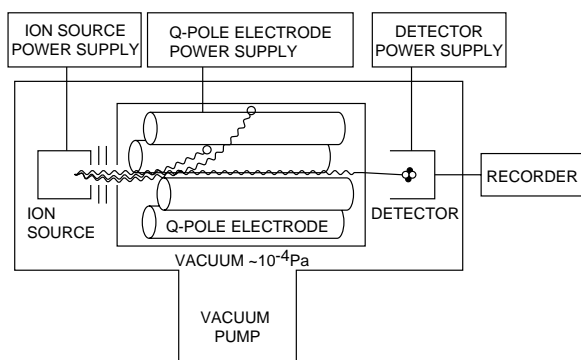
### 9.9.1 Mass spectrometers

#### (1) Overview<sup>23) 24)</sup>

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

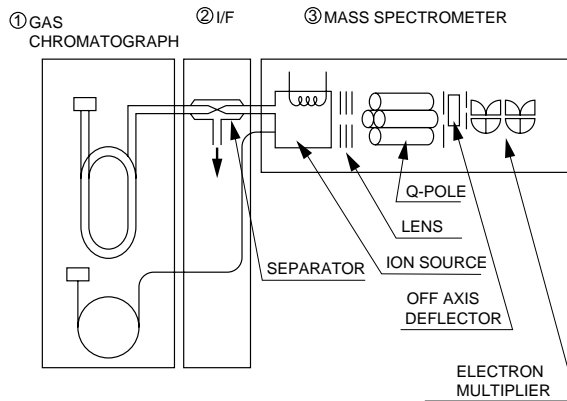
Among these, the quadrupole (Q-Pole) type mass spectrometer is most widely used and its block diagram is shown in Figure 9-39.



**Figure 9-39: Block diagram of a quadrupole (Q-Pole) type mass spectrometer**

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.



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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<sup>25)</sup>

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.

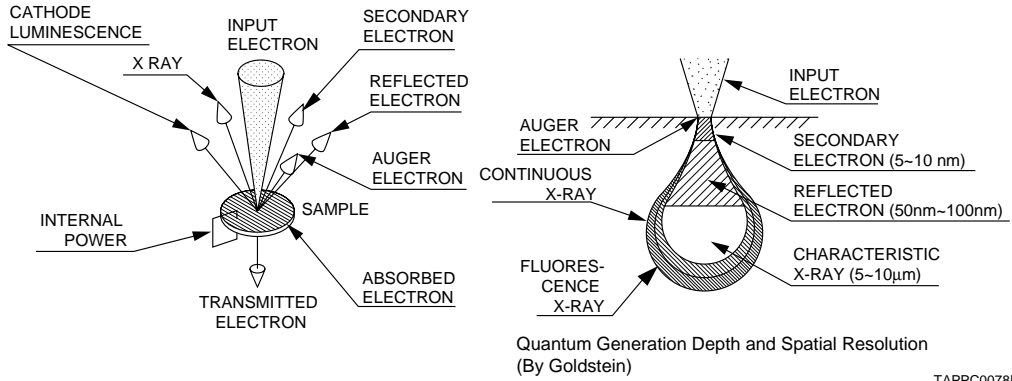


Figure 9-41: Interactions of incident electrons with sample

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.<sup>26)</sup>

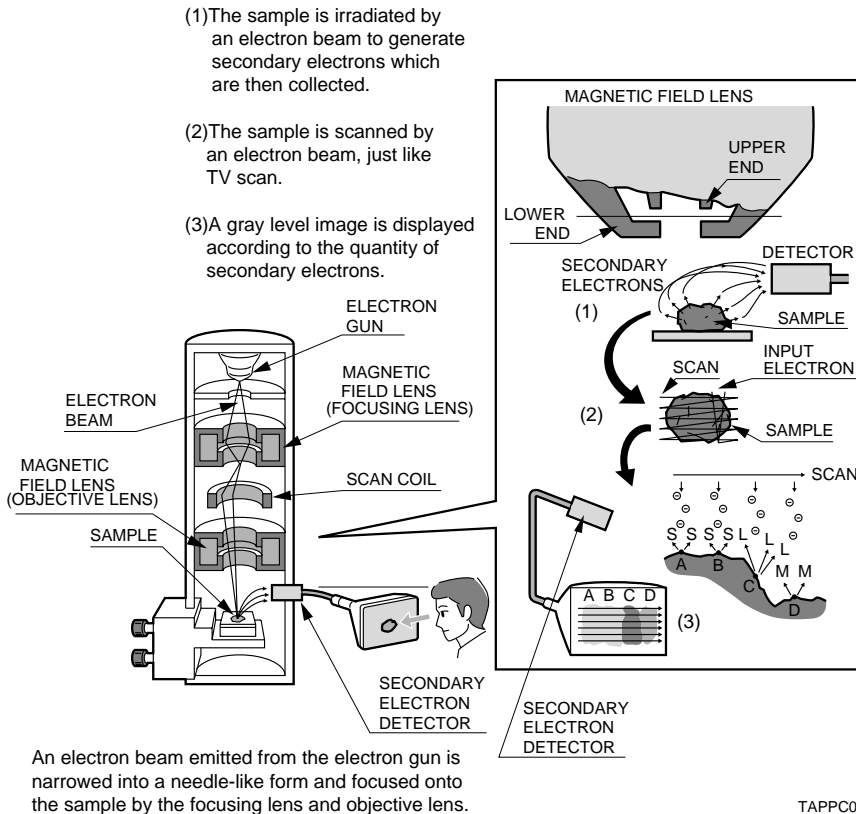
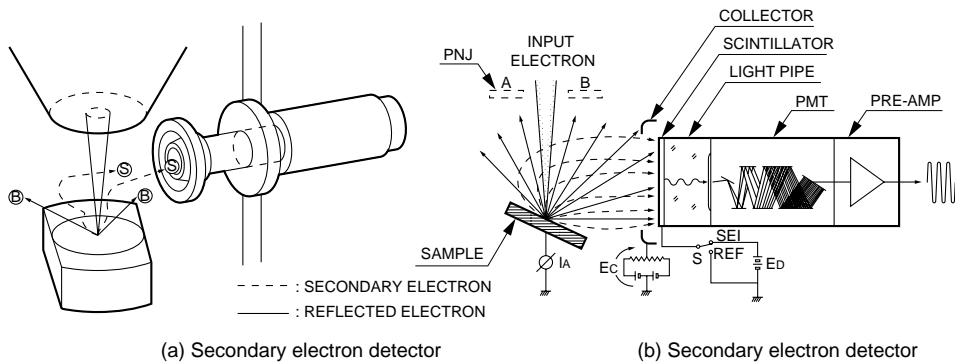


Figure 9-42: Structure and principle of a scanning electron microscope

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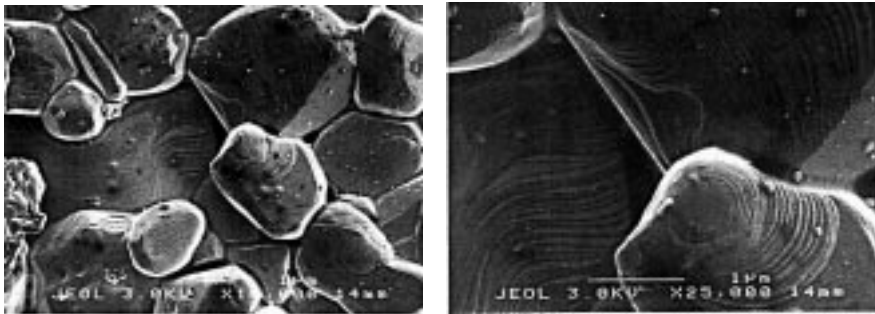
An electron beam emitted from the electron gun is accelerated at a voltage of 0.5 to 30kV. This accelerated electron beam is then condensed by electromagnetic lens action of the focusing lens and objective lens, and finally formed into a very narrow beam of 3 to 100nm in diameter, irradiating on the 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.



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**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.<sup>27)</sup>



**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

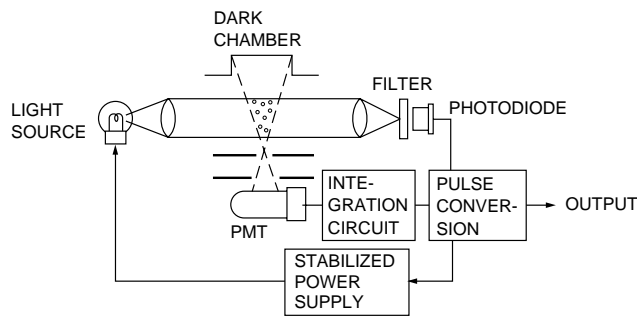
## 9.10 Environmental Measurement

Photomultiplier tubes are also used as detectors in environmental measurement equipment, for example, in dust counters used to detect dust contained in air or liquids, and radiation survey monitors used in nuclear power plants. This section explains some of these applications.

### 9.10.1 Dust counters

#### (1) Overview

A dust counter measures the concentration of floating dust in the atmosphere or inside a room by making use of principles such as light scattering and absorption of beta rays. Figure 9-45<sup>28)</sup> shows the principle of a dust counter using light scattering. If dust is present in the light path, light is scattered by the dust. The quantity of this scattered light is proportional to the quantity of dust. The scattered light is detected by a photomultiplier tube and after being integrated, the output signal is converted into a pulse signal, which then corresponds to the mass concentration. This method offers an advantage that the output signal can immediately follow changes in the concentration, making it suitable for continuous operation to monitor the change over time. However, this method has a disadvantage in that even if the mass concentration is constant, the quantity of scattered light varies with such factors as particle shape and the refractive index.



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**Figure 9-45: Block diagram of a dust counter using light scattering**

Another dust counter makes use of the absorption of beta rays which is proportional to the mass of a substance through which the beta rays are transmitted. A filter paper is used to collect the dust, and the difference in the amount of beta-ray absorption before and after collecting the dust are compared to determine the mass.

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

Since dust counters measure low levels of light, the following characteristics are required of photomultiplier tubes.

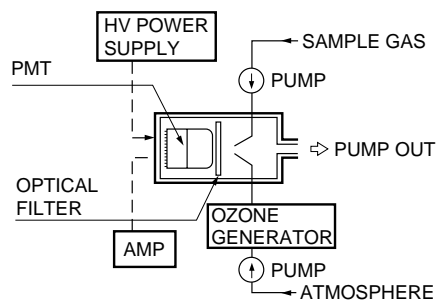
- a) Less spike noise
- b) High quantum efficiency
- c) High gain

## 9.10.2 NO<sub>x</sub> analyzers

### (1) Overview

These instruments are used to measure nitrogen oxide (NO<sub>x</sub>), an air-polluting gas contained in exhaust gases from automobiles and other internal combustion engines. NO<sub>x</sub> is a general term indicating nitrogen monoxide (NO) and nitrogen dioxide (NO<sub>2</sub>) and, in many countries, the concentration of NO<sub>x</sub> is limited by air pollution regulations so that it shall not exceed a certain level.

Figure 9-46 shows the configuration of an NO<sub>x</sub> analyzer making use of chemiluminescence.<sup>29)</sup> When NO gas reacts with ozone (O<sub>3</sub>) to become NO<sub>2</sub> gas, chemiluminescence is released. The intensity of this chemiluminescence is proportional to the concentration of NO<sub>x</sub>. Since other gases contained in the exhaust gas do not produce such luminescence, the NO<sub>x</sub> concentration can be selectively measured by detecting the intensity of this chemiluminescence.



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Figure 9-46: NO<sub>x</sub> analyzer utilizing chemiluminescence

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

The following characteristics are required because this chemiluminescence increases at 600 nanometers and extends into the infrared region.

- a) High quantum efficiency in the infrared region
- b) Low noise

### 9.10.3 Turbidimeters

#### (1) Overview

When floating particles are contained in a liquid, light incident on the liquid is absorbed, scattered or refracted by these particles. It looks cloudy or hazy to the human eye. To express the clarity of such liquid, the term "turbidity" is used. A turbidimeter is a device that numerically measures the turbidity by using light transmission or scattering. There are various methods as explained below:

- |                             |                                       |
|-----------------------------|---------------------------------------|
| 1) Transmitted-light method | a) Transmitted-light method           |
|                             | b) Transmitted/scattered-light method |
| 2) Scattered-light method   | a) Forward scattered-light method     |
|                             | b) Backward scattered-light method    |
|                             | c) Surface scattered-light method     |

The principles of the surface scattered-light method<sup>30)</sup> and the transmitted/scattered-light method<sup>31)</sup> are shown in Figures 9-47 and 9-48, respectively. Either method uses a photomultiplier tube as the photodetector. In the surface scattered-light method, a light beam illuminates the surface of the liquid and the intensity of the light scattered from near the surface is measured. This method facilitates a wide range of measurement points by changing the position at which the light beam is incident. Since the light beam directly strikes the liquid surface, there will be less measurement errors which may otherwise be caused by reflective objects such as a window. However, errors may occur when measuring a colored liquid. The transmitted/scattered-light method measures the ratio between the transmitted and scattered light. No error occurs even when measuring a colored liquid, but dirt or stains on the window may affect the measurement accuracy.

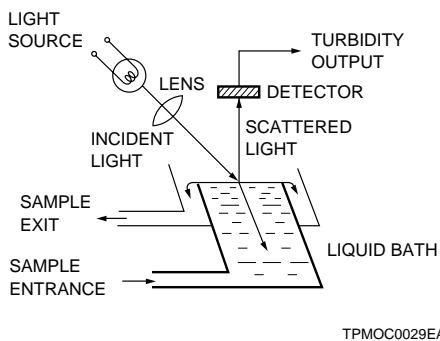


Figure 9-47: Turbidimeter using the surface scattered-light method

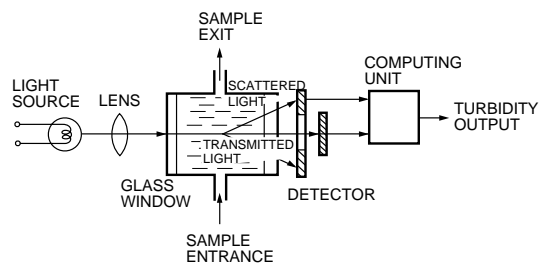


Figure 9-48: Turbidimeter using the transmitted/scattered-light method

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

Photomultiplier tubes used for turbidimeters must provide the following factors.

- a) Low noise
- b) High quantum efficiency
- c) High gain

## 9.10.4 Door monitors

### (1) Overview

As the name implies, the door monitor is installed near the exit door in the monitored area of a nuclear power plant, in order to check the personnel going out of this area for contamination by radioactive material. A photomultiplier tube is used in conjunction with a scintillator to detect radiation released from the radioactive material. An example<sup>32)</sup> of a door monitor is shown in Figure 9-49. The detector section consists of an array of scintillators coupled to photomultiplier tubes, enabling simultaneous measurement of the location and extent of contamination. Since the number of signals to be detected is usually very low, a coincidence counting circuit is used as in the case of scintillation counting to minimize erroneous signal counting.

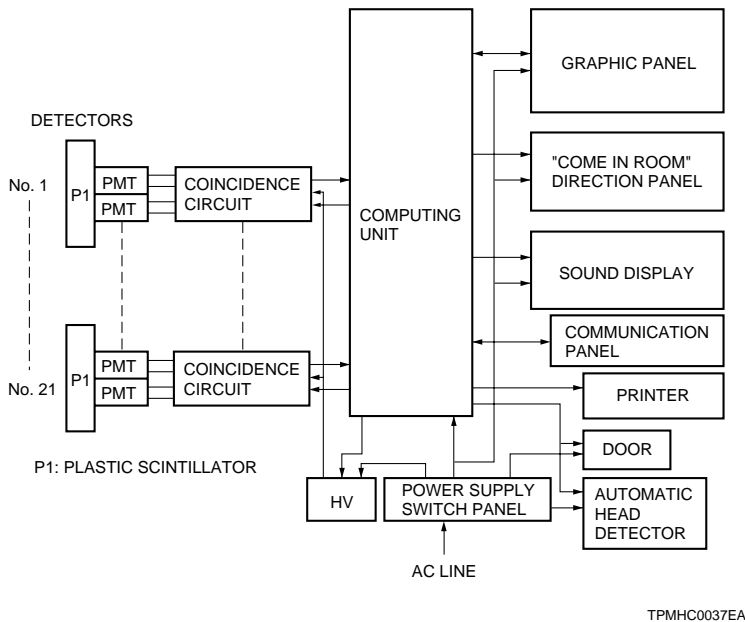


Figure 9-49: Block diagram of a door monitor

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

Because the number of signals to be detected is very low and, further, the amount of light detected by one photomultiplier tube is small, the following characteristics are required of each photomultiplier tube:

- a) High quantum efficiency
- b) Low noise
- c) High energy resolution or pulse height resolution (PHR)
- d) High gain



## 9.11 Applications to Laser Measurement

Recently, lasers are being applied to a wide range of measurement and processing applications owing to their superior advantages such as spatial or temporal coherency and high optical power.

Applications utilizing lasers can be classified as follows:

**1) Measurement**

Rangefinder, laser radar, holography, laser chemistry, medical measurement

**2) Data processing**

Optical communications, optical data processing

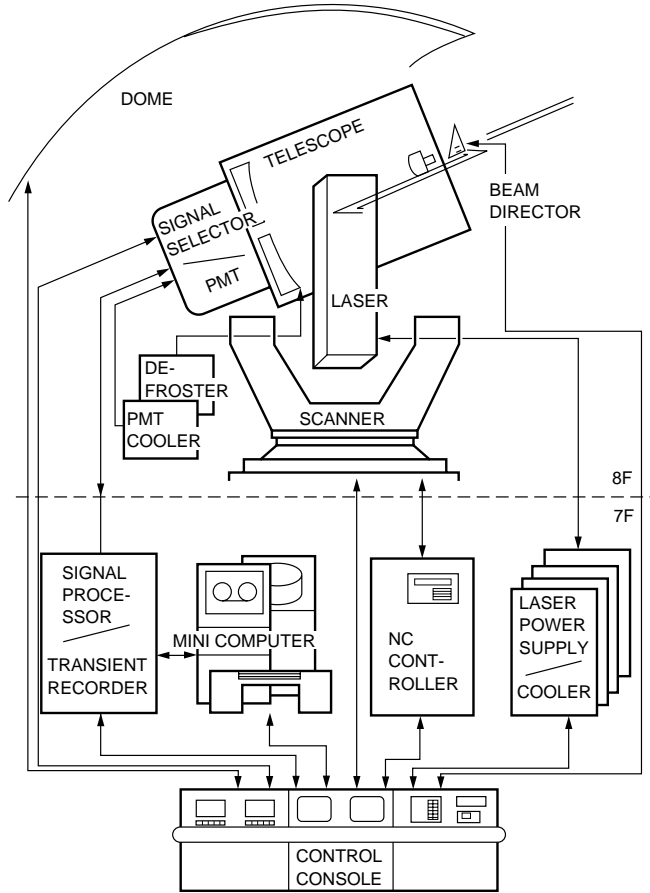
**3) Energy sources**

Laser processing, laser fusion, laser scalpel

This section explains typical applications of photomultiplier tubes used in laser measurements and major characteristics required.

### 9.11.1 Overview

Laser measurement applications using photomultiplier tubes include laser radars for rangefinding and atmospheric observation and laser spectroscopy such as fluorescence lifetime measurement. For signal processing in these measurements, the photon counting mode is widely used rather than analog mode, in order to improve the signal-to-noise ratio and enhance the detection limit. Furthermore, time correlated photon counting (TCPC) technique is employed in picosecond measurements such as fluorescence lifetime determination. Figure 9-50 illustrates the block diagram of a laser radar used for atmospheric observation,<sup>33)</sup> installed at the National Environmental Pollution Laboratory, Tsukuba, Japan.



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Figure 9-50: Schematic construction of a laser radar for atmospheric observation

### 9.11.2 Major characteristics required of photomultiplier tubes

The following photomultiplier tube characteristics are essential in this field.

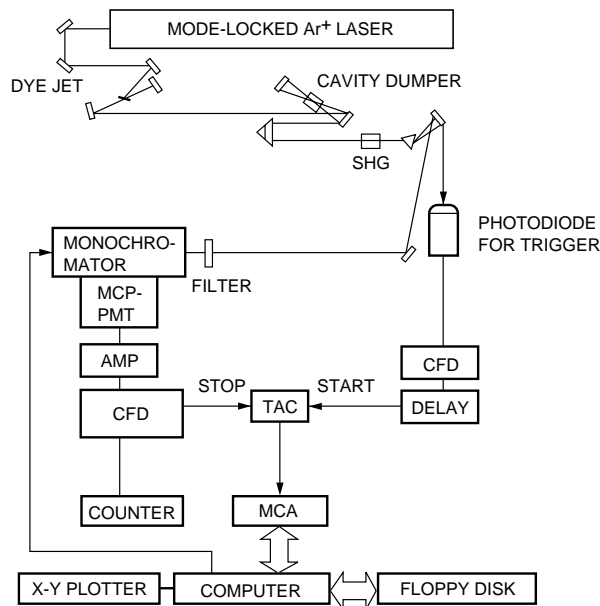
- a) Fast time response
- b) Low noise
- c) High gain

Of these, time response is the most important factor. With the development of laser technology, photomultiplier tubes with faster time response are in greater demand. In particular, electron transit time spread (TTS) is important for picosecond resolution in measuring fluorescence lifetime.

The TTS (transit time spread) is greatly affected by CTTD (cathode transit time difference) and wavelength effects (Refer to Section 3.3.1, "Time characteristics".) These effects sometimes cause significant problems in normal photomultiplier tubes using discrete dynodes, but create very few problems with an MCP-PMT. Normally, noise should be as low as possible to achieve a high signal-to-noise ratio and especially, the dark count must be small.

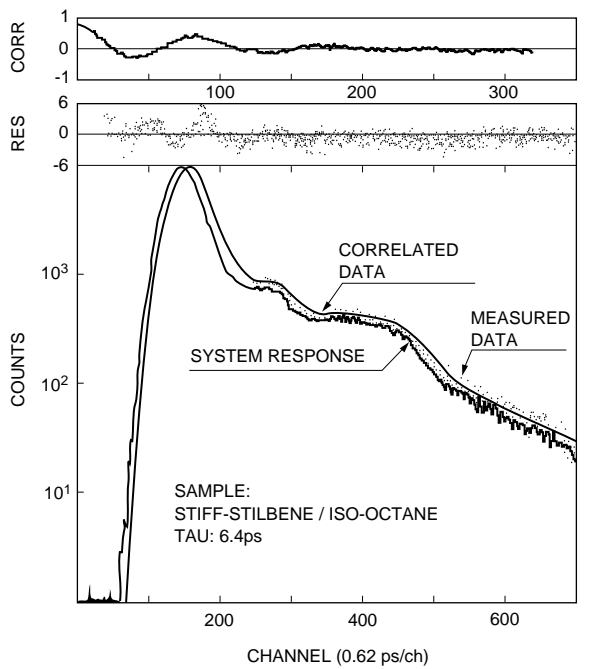
The gain should be high enough to obtain a good pulse height distribution in single photon events, in other words, a distinct valley should exist in the single-photoelectron pulse height distribution. Typically, gain of  $5 \times 10^6$  is necessary.

Figures 9-51<sup>34)</sup> and 9-52<sup>35)</sup> show a system setup for fluorescence lifetime measurement and typical results that were measured. The photomultiplier tube used for this measurement is a high-speed MCP-PMT (Hamamatsu R3809U).



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Figure 9-51: TCPC system for fluorescence lifetime measurement



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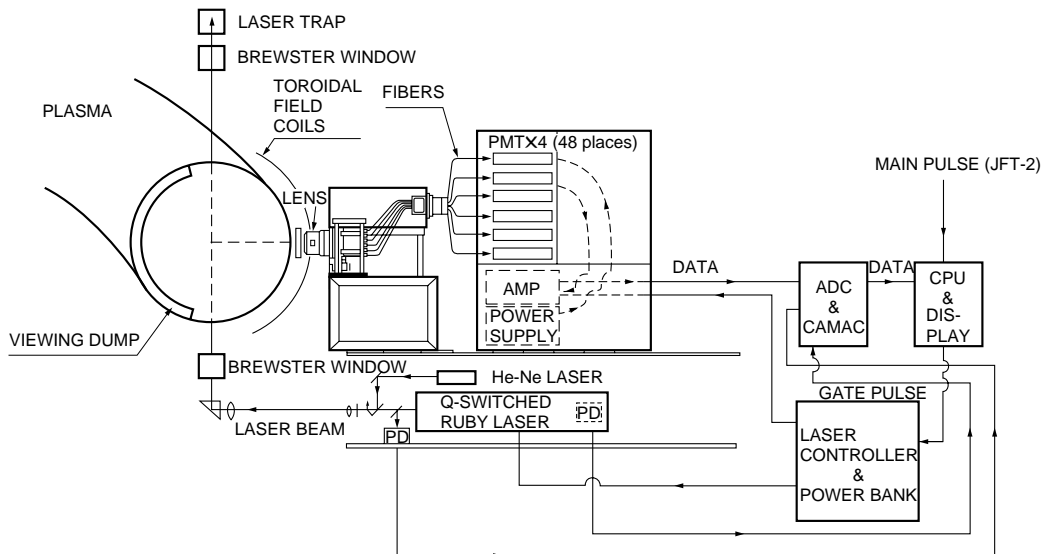
Figure 9-52: Fluorescence lifetime data of stiff-stilbene (courtesy of Prof. Yamazaki, Hokkaido University, Japan)

## 9.12 Plasma Applications

Photomultiplier tubes and MCPs (microchannel plates) are used in plasma measurements, such as plasma electron-density and electron-temperature measurement applications utilizing Thomson scattering or the Doppler effect, plasma spatial-distribution observation and plasma impurity measurements intended for controlling impurities and ions in plasma.

### 9.12.1 Overview

Figure 9-53 shows the construction of a plasma electron-density and electron-temperature measuring system,<sup>36)</sup> actually used in a Japanese tokamak-type nuclear fusion reactor "JFT-2". The detector and signal processing units used in this system are also shown in Figure 9-54<sup>37)</sup>, example of a scattered-light measuring system<sup>38)</sup> using a high-power ruby laser designed for plasma diagnosis is shown in Figure 9-55. In both systems, photomultiplier tubes are used as detectors in the ultraviolet to visible region, while multichannel spectrophotometry using a MCP is performed in the soft X-ray region.



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**Figure 9-53: Schematic construction of a plasma electron-density and electron-temperature measuring system**

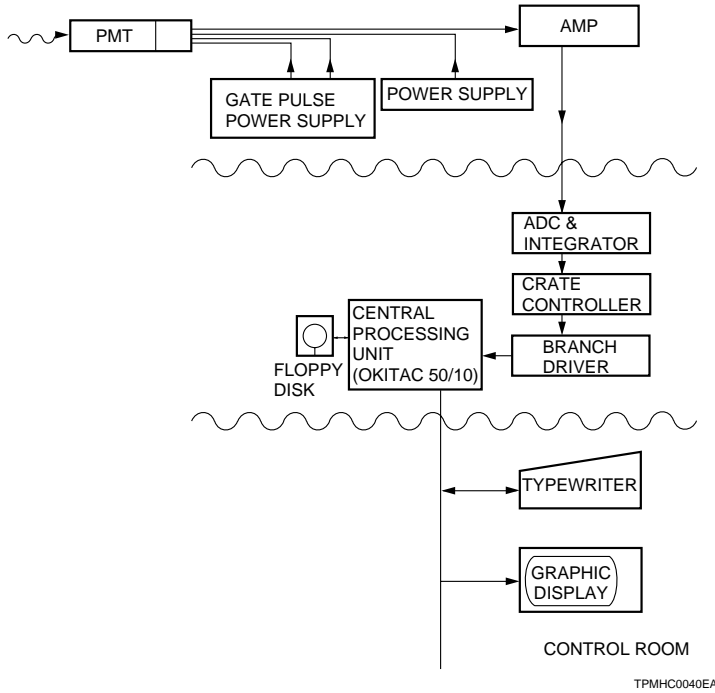


Figure 9-54: Block diagram of the detector and signal processing units used in the above system

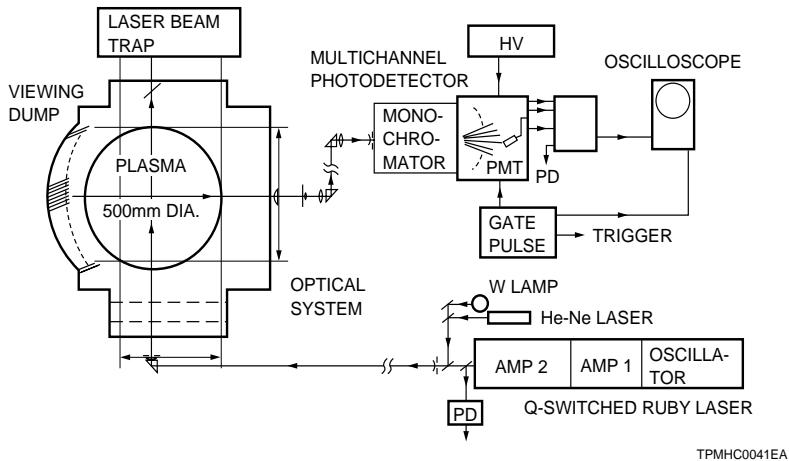


Figure 9-55: Example of a scattered-light measuring system using a ruby laser

## 9.12.2 Major characteristics required of photomultiplier tubes

- a) High photocathode sensitivity
- b) Gate operation

Photomultiplier tubes used in this field must provide gate operation to avoid damage caused by input of intense light from the excitation laser, as well as high sensitivity for detecting low light levels.

## 9.13 Color Scanners

Photomultiplier tubes are used in color scanners in photographic printing applications. The color scanner is a high-precision instrument designed to produce color-analyzed film by photoelectrically scanning an original color film or reflective print and analyzing its color balance.

### 9.13.1 Overview

Figure 9-56 shows the block diagram of a color scanner using a photomultiplier tube for each of three primary (red, green, blue) colors and black. There is another type of color scanner that uses a single photomultiplier tube for analyzing and controlling RGB colors by rotating the drum 3 times faster.

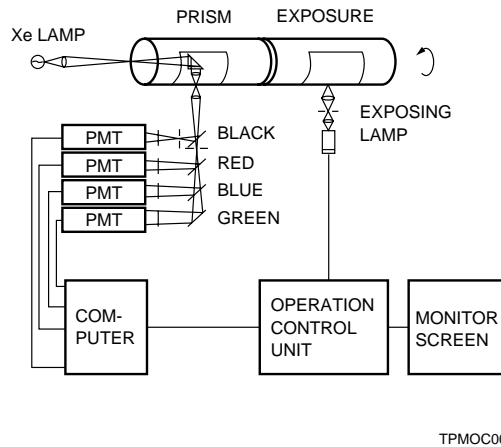


Figure 9-56: Block diagram of a color scanner

### 9.13.2 Major characteristics required of photomultiplier tubes

The following characteristics are required of photomultiplier tubes used in these applications.

- a) High quantum efficiency at each wavelength of RGB
- b) Low noise, especially no microphonic noise
- c) Fast signal-waveform fall time
- d) Good reproducibility with respect to changes in input signal
- e) High stability

Among these, fall time and reproducibility are very important factors that affect color shading and resolution of color scanners.

## 9.14 Industrial Measurement Applications

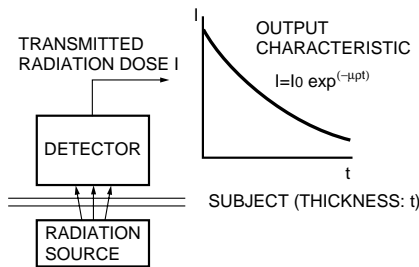
For non-contact measurement on a production line and other industrial measurement applications where rapid measurement with a high degree of accuracy and quality is essential, extensive use is made of various devices having photomultiplier tubes as detectors. These devices include thickness gauges, laser scanners and flying spot scanners, which are briefly discussed in the following paragraphs.

### 9.14.1 Thickness gauges

#### (1) Overview

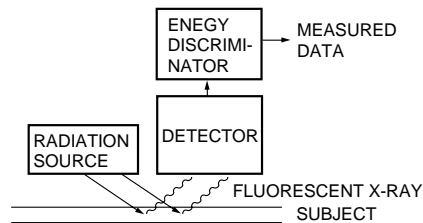
To measure the thickness of paper, plastics and steel plates on a production line, non-contact measurement techniques that use radiation such as beta rays, X rays or gamma rays are favored.

These techniques can be roughly divided into two methods: one measures the amount of beta or gamma rays transmitted through an object<sup>39)</sup> (Figure 9-57) and the other measures the amount of fluorescent X-rays<sup>40)</sup> (Figure 9-58).



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**Figure 9-57: Principle of a transmission-mode thickness gauge**



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**Figure 9-58: Principle of a fluorescent X-ray thickness gauge**

When the intensity of radiation incident on a material is  $I_0$ , the transmitted radiation intensity  $I$  can be expressed in the following relation:

$$I = I_0 e^{(-\mu\rho t)}$$

$t$  : thickness (m)

$\rho$  : density ( $\text{g}/\text{m}^3$ )

$\mu$  : mass absorption coefficient ( $\text{m}^2/\text{g}$ )

Since the transmitted radiation intensity is proportional to the count rate, the thickness of the material can be obtained by calculating the count rate. In general, beta rays are used to measure rubber, plastics and paper which have a small surface density (thickness $\times$ density), while gamma rays are used to measure material with a large density such as metals. In addition, infrared radiation is also used for measurement of films, plastics and other similar materials.

Fluorescent X-rays are used to measure the film thickness of plating and deposition layers. Fluorescent X-rays are secondary X-rays generated when a material is excited by radiation and have characteristic energy of the material. By detecting and discriminating this energy, the quantitative measurement of the object material can be made.



There are a variety of detectors used in these applications, such as proportional counter tubes, GM counter tubes, photomultiplier tubes and semiconductor detectors. Photomultiplier tubes are used in conjunction with scintillators, mainly for detection of gamma rays and X-rays.

## (2) Characteristics required of photomultiplier tubes

Major characteristics required of photomultiplier tubes in these applications are as follows:

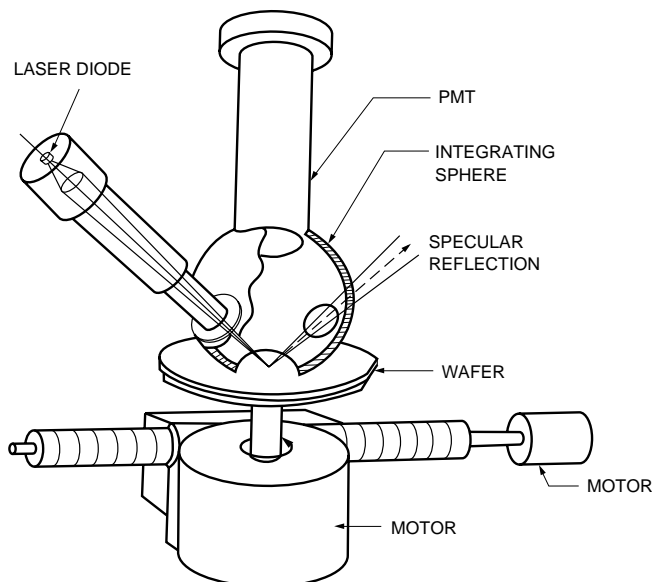
- a) Superior linearity characteristics
- b) Low hysteresis
- c) High energy resolution or pulse height resolution (PHR)
- d) Stability

### 9.14.2 Laser scanners

#### (1) Overview

Laser scanners are widely used in pattern recognition such as defect inspection and mask alignment of semiconductor wafers.

In semiconductor wafer inspection systems,<sup>41)</sup> a laser beam is scanned over the wafer surface or the wafer itself is scanned while a laser beam is focused onto a fixed point. In either case, photomultiplier tubes are commonly used to detect scattered light caused by dirt, stain and defects on the wafer surface. (See Figure 9-59.)



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Figure 9-59: Construction of the optical system for a semiconductor wafer inspection system

## (2) Characteristics required of photomultiplier tubes

The following characteristics are required of photomultiplier tubes used in laser scanners.

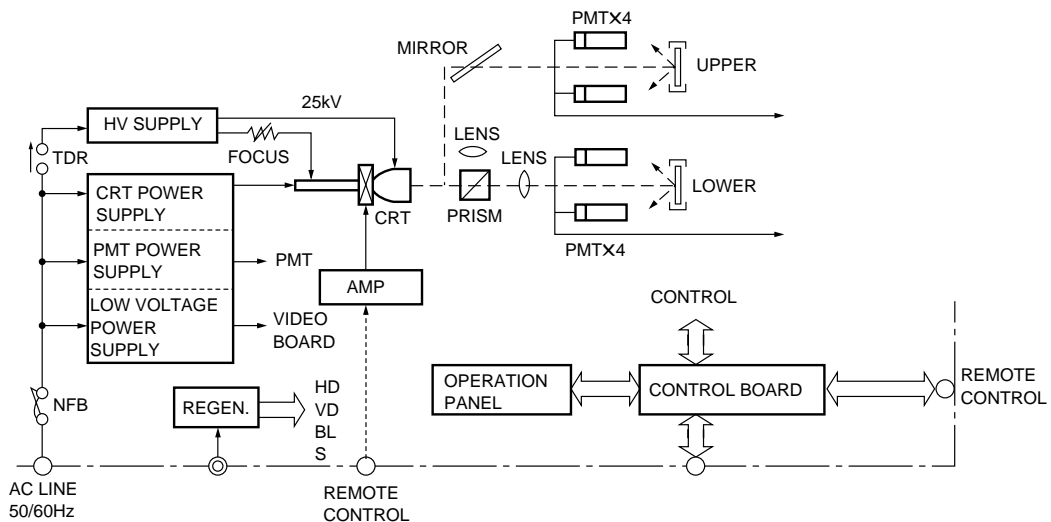
- a) Low dark current and spike noise
- b) High quantum efficiency at wavelengths to be measured
- c) Superior uniformity
- d) Superior linearity
- e) Resistance to relatively large current and good stability

### 9.14.3 Flying spot scanners

#### (1) Overview

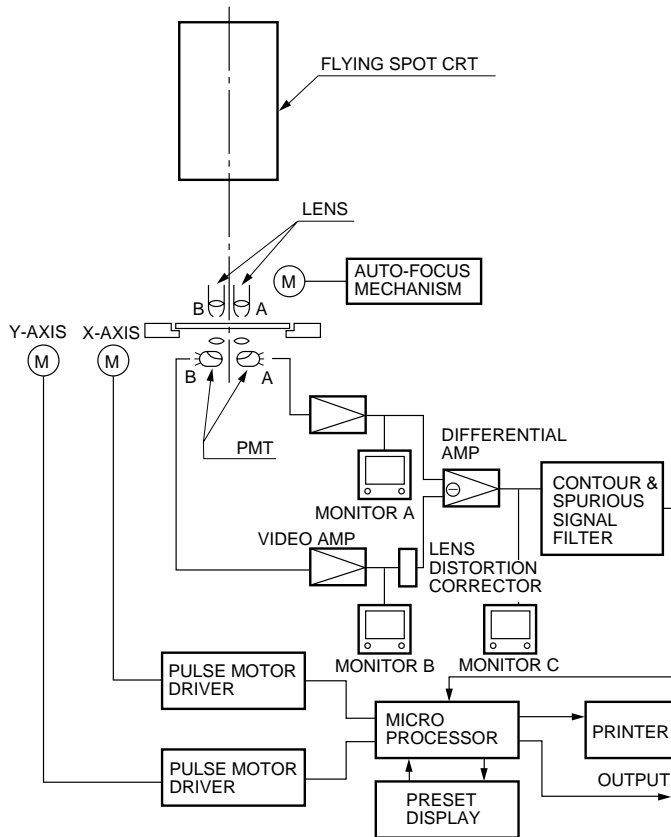
There are several methods for converting the information recorded on photographic film into electrical signals, for example, methods using a camera tube, CCD linear image sensor or flying spot scanning. Of these, flying spot scanning using photomultiplier tubes as detectors has been extensively used thanks to its advantages in processing speed, sensitivity and image quality including resolution and signal-to-noise ratio.

In a typical flying spot scanner, a special low-lag CRT (cathode-ray tube) called a flying spot tube provides a small light spot to form a raster. The raster is focused onto the film, and the transmitted or reflected light is detected by photomultiplier tubes. The block diagram<sup>42)</sup> of a typical flying spot scanner is shown in Figure 9-60. The flying spot scanner is used not only in image processing but also inspection of photolithographic masks used for fabrication of semiconductor devices. Figure 9-61 shows an example of this application.<sup>43)</sup>



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Figure 9-60: Block diagram of a flying spot scanner



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**Figure 9-61: Semiconductor mask inspection system utilizing a flying spot scanner**

## (2) Characteristics required of photomultiplier tubes

Photomultiplier tubes used in flying spot scanners should have the following characteristics.

- a) Low dark current and spike noise
- b) High quantum efficiency (at RGB wavelengths in the case of color operation)
- c) Wide dynamic range

Spike noise may be a cause of a spot-like noise, and low quantum efficiency may result in an increase in shot noise, leading to deterioration of the signal-to-noise ratio.

## 9.15 Space Research Applications

Photomultiplier tubes are widely used in space research applications, for example, detection of X-rays from space, planetary observation, solar observation, environmental measurement in inner or outer space and aurora observation. In addition, photomultiplier tubes are also used for spectral measurements of various radiation in the atmosphere or outer space and measurement of X-rays from supernovas.

### 9.15.1 Overview

Figure 9-62 illustrates the structure of ASUKA launched and placed in its orbit in February 1993, as the fourth astronomical satellite for X-ray observation in Japan. A gas imaging spectrometer (GIS) is used as the detector, which consists of a gas-scintillation proportional counter coupled to a photomultiplier tube (Hamamatsu R2486X).

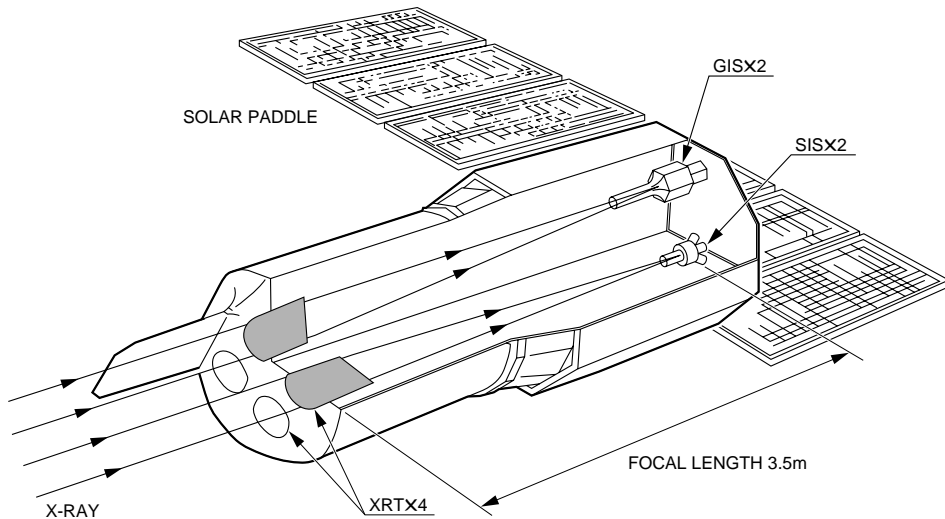
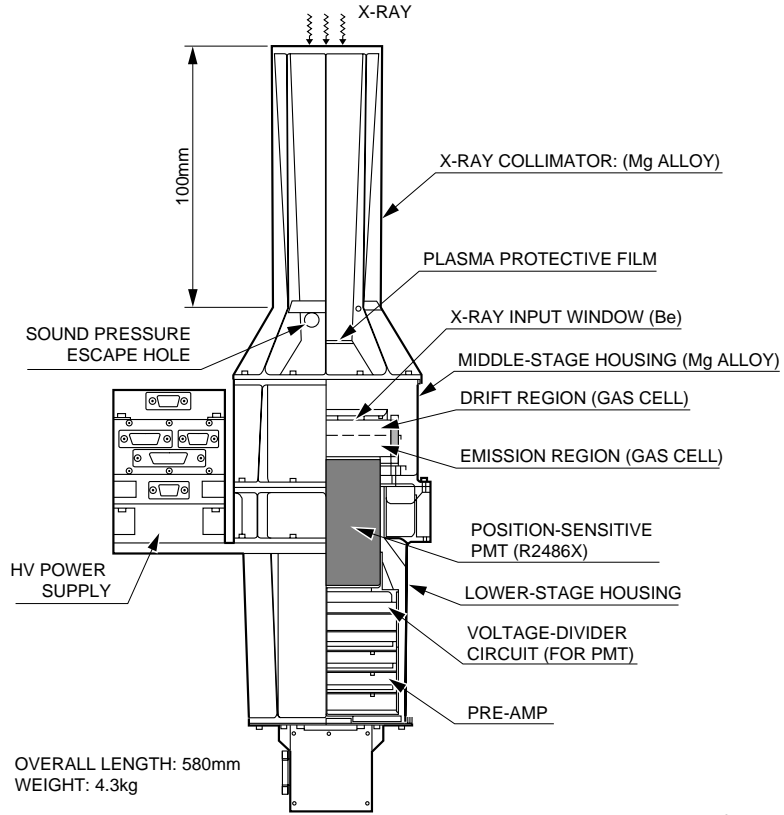
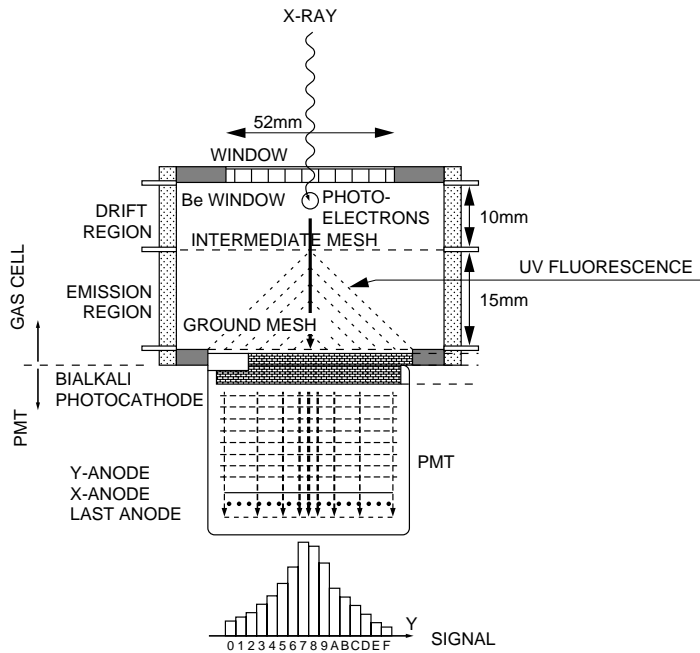


Figure 9-62: Astronomical satellite ASUKA for X-ray observation



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Figure 9-63: X-ray detector (GIS detector) mounted in the ASUKA



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Figure 9-64: Principle of detection in the GIS detector

The ASUKA has succeeded in discovering various interesting facts, beginning from the detection of X-rays travelling from the supernova named "SN1993J", discovery of low-luminosity nucleus in the center of ordinary galaxy, and world's first detection of inverse Compton X-rays coming from a radio galaxy. Furthermore, the ASUKA successfully revealed that the low energy spectrum of CXB (cosmic X-ray background) is extending to 1keV as single photon fingers. This discovery is expected to elucidate the CXB, which is the primary object of the ASUKA.

### 9.15.2 Characteristics required of photomultiplier tubes

Photomultiplier tubes used in these applications must provide the following characteristics.

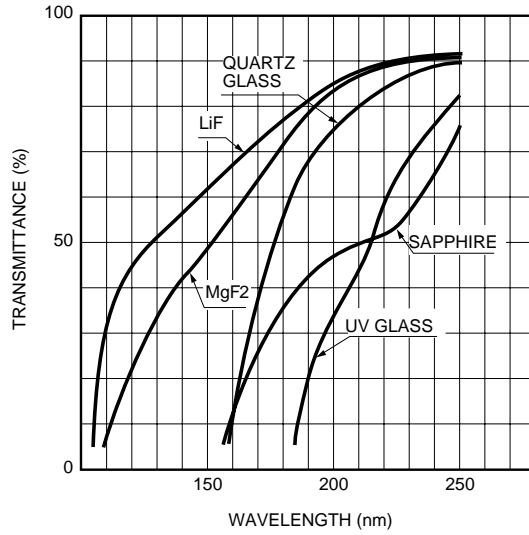
- a) High energy resolution
- b) Resistance to vibration and shock
- c) Solar blind response (in the case of vacuum UV to UV detection)

As discussed in Chapter 8, photomultiplier tube resistance to vibration and shock differs depending on the tube size and dynode structure. Normal photomultiplier tubes are resistant to a vibration of 5 to 10G, while ruggedized tubes can endure up to 15 to 30G. Table 9-5 classifies the grades of measurement conditions. Note that these grades are based on the sinusoidal vibration test, so random vibration tests should also be taken into account as well. Hamamatsu Photonics performs vibration tests according to the user's needs in order to design and manufacture vibration-proof, ruggedized photomultiplier tubes.

Grade	Acceleration G	Frequency	Photomultiplier Tube
A	5.0	10 to 55	Normal type
B	5.0	10 to 500	Normal type
C	7.5	10 to 500	Normal type
D	10	10 to 1000	Normal type
E	15	10 to 2000	Ruggedized type
F	20	10 to 2000	Ruggedized type
G	25	10 to 2000	Ruggedized type
H	30	10 to 2000	Ruggedized type

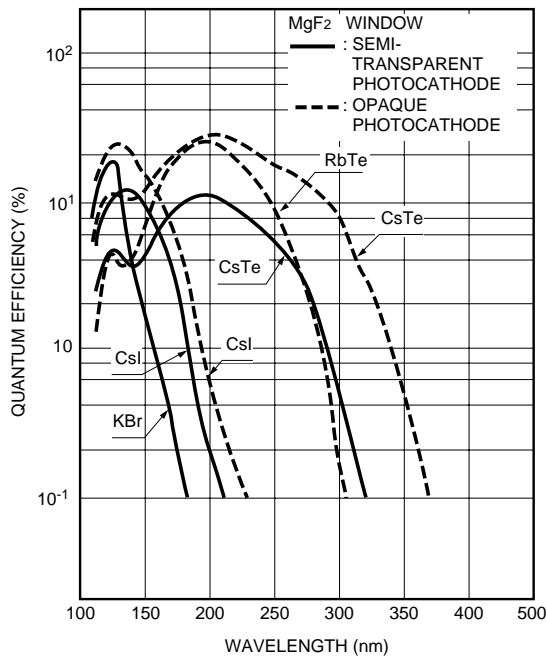
**Table 9-5: Vibration test conditions**

In the measurement of radiation traveling from space, photomultiplier tubes must have high sensitivity in the vacuum UV to UV range but also have a solar blind response. Since the detection limit on the short wavelength side is determined by the transmittance of the window material used for the photomultiplier tube, proper selection of window material is also important. Figure 9-65 shows transmittance characteristics of various window materials and Figure 9-66 shows spectral response characteristics of solar blind photocathodes specifically intended for UV detection.



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Figure 9-65: Transmittance characteristics of various window materials



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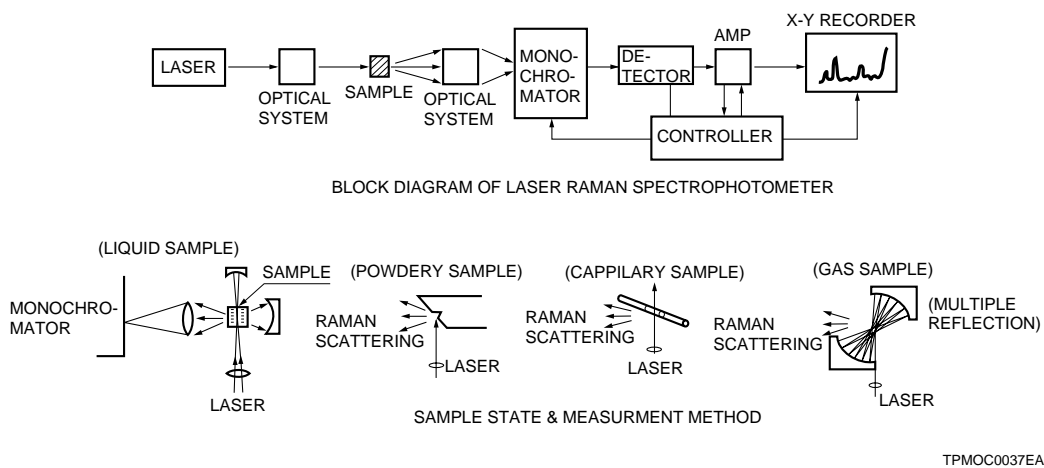
Figure 9-66: Spectral response characteristics of solar blind photocathodes

## 9.16 Low-Light-Level Detection

Lately, low-light-level detection is becoming increasingly important in various scientific fields. In particular, low-light-level detection techniques are in greater demand in such studies as Raman scattering, Rayleigh scattering, biology, analytical chemistry, astronomy and fluorescence analysis. The detection techniques using photomultiplier tubes include the analog DC method, analog pulse method and digital method (photon counting). Of these, the photon counting is extremely effective in low-light-level detection. The excellent characteristics of photomultiplier tubes such as high gain and low noise can be fully utilized in this field.

### 9.16.1 Overview

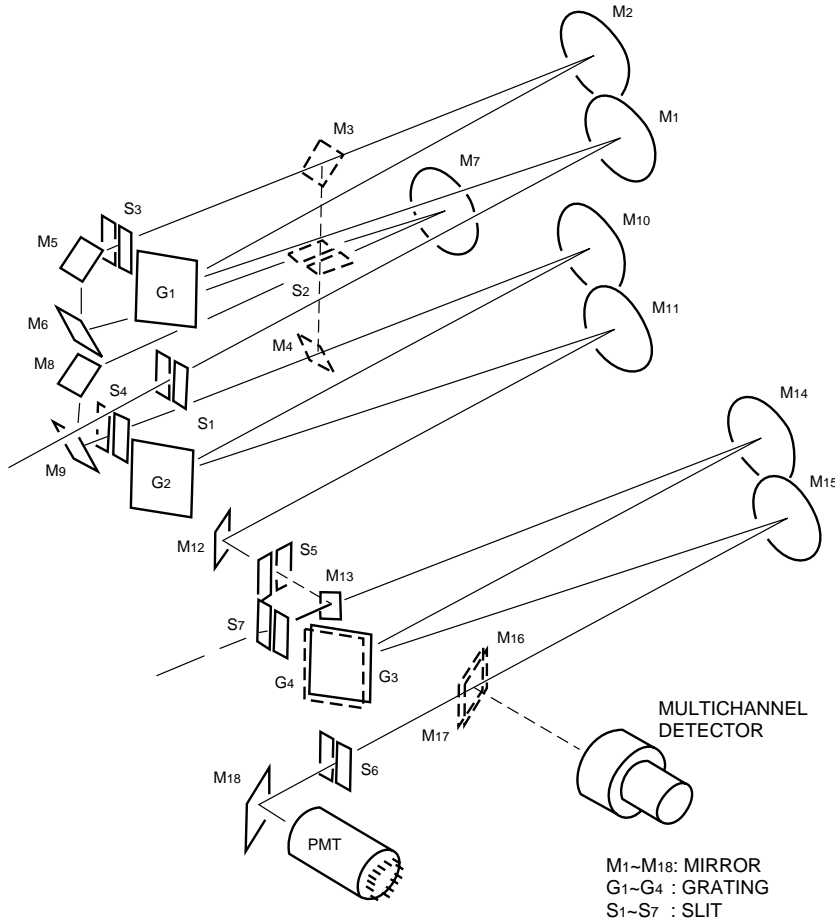
Low-light-level detection utilizing the superior signal-to-noise ratio of photomultiplier tubes is being applied to diverse fields including Raman scattering, biology, chemical analysis and astronomy. Figure 9-67 shows the block diagram of a laser Raman spectrophotometer.<sup>44)</sup>



**Figure 9-67: Block diagram of a laser Raman spectrophotometer**

With recent advancements in laser technology, life science research such as a study of local protein structures utilizing Raman scattering is rapidly progressing. Because Raman scattering has an extremely low light level as compared to Rayleigh scattering (with the same wavelength as that of the excitation light), a high-quality monochromator with minimum stray light and a high-sensitivity detector must be used to separate the Raman scattering from extraneous light. A common monochromator used in Raman spectrophotometry is a double-monochromator equipped with a holographic grating or, in some cases a triple-monochromator with filter mechanism. Raman spectrophotometry requires such a complicated optical system that the incident light on the photomultiplier tube will be exceptionally low. For this reason, the photon counting method which ensures excellent signal-to-noise ratio and stability is frequently used. The monochromator and optical system used in Raman spectrophotometry must provide "minimum stray light", "high resolution" and "good light-collection efficiency". Figure 9-68 shows the optical layout<sup>45)</sup> of a laser Raman spectrophotometer. This instrument usually uses a photomultiplier tube specially selected for photon counting.





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Figure 9-68: Optical layout of a laser Raman spectrophotometer

### 9.16.2 Characteristics required of photomultiplier tubes

The following characteristics are required of photomultiplier tubes used in photon counting.

- a) Less broadening of pulse height distribution, in other words, superior single photoelectron resolution (a sharp valley should exist so that the effects of photomultiplier tube sensitivity drift and supply voltage fluctuation can be reduced when the tube is operated over extended time periods.
- b) Less dark current pulse
- c) High gain

If linear counting is essential up to a high light level, a fast-response photomultiplier tube must be used. In this case, it is recommended that photomultiplier tubes with a linear-focused dynode or circular-cage dynode be used.

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