CHAPTER 12
ELECTRON MULTIPLIER TUBES AND ION DETECTORS

Electron multiplier tubes (EMT) are capable of detecting light at relatively short wavelengths such as soft X-rays and vacuum UV (VUV) radiation and charged particles such as electrons and ions. Ion detectors are designed and optimized for ion detection in mass spectrometers.[1][2][3]

This chapter describes the structures and characteristics of electron multiplier tubes and ion detectors.

12.1 Structure

The structure of an electron multiplier tube is basically identical to the dynode assembly and anode used in photomultiplier tubes. The dynode structure is selected according to the required characteristics, size and shape. (See 4.2.1 in Chapter 4.) Figure 12-1 shows typical electron multiplier tubes.

Figure 12-1: Electron multiplier tubes

An electron multiplier tube is operated in a vacuum, and the ions, electrons, VUV radiation, or soft X-rays to be detected are guided so as to enter the first dynode. The first dynode excited by such particles or radiation emits secondary electrons or photoelectrons. These generated electrons are multiplied in a cascade by the second and following dynodes and a cluster of secondary electrons finally reaches the anode. Electron multiplier tubes come with built-in voltage-divider resistors that supply an optimum voltage between each dynode. A holder is also mounted for holding the electron multiplier tube.

Ion detectors are used for ion detection in mass spectrometers (see 14.10.1 in Chapter 14). As with electron multiplier tubes, ion detectors consist of a dynode section, an anode, voltage-divider resistors, holder, and a Faraday cup or conversion cup needed for various types of mass spectrometers. The dynode type uses linear-focused type dynodes (see 4.2.1 in Chapter 4). Figure 12-2 shows typical ion detectors assembled with a conversion dynode.
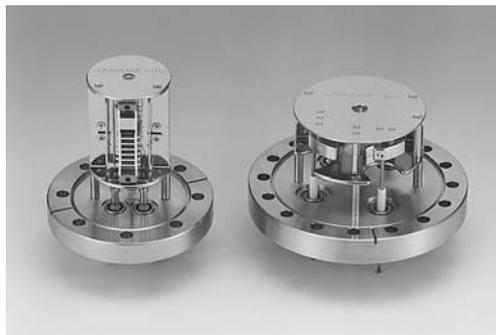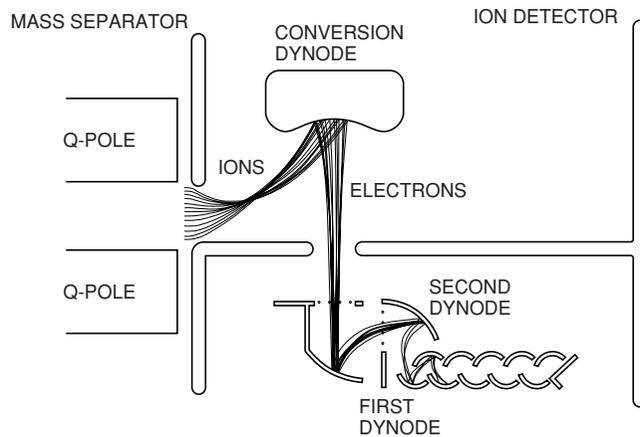

Figure 12-2: Ion detectors with conversion dynode

In a mass spectrometer, ions that have passed through the mass separator are accelerated onto the conversion dynode to which a high voltage is applied. Electrons emitted from the conversion dynode by the incident ions then enter the first dynode where secondary electrons are emitted from the secondary emissive surfaces. These secondary electrons are multiplied by the other dynodes and a cluster of electrons finally reaches the anode. Ion detectors are designed so that these electron conversion and multiplication processes are optimized. Figure 12-3 shows the ion detection mechanism in an ion detector with a conversion dynode.
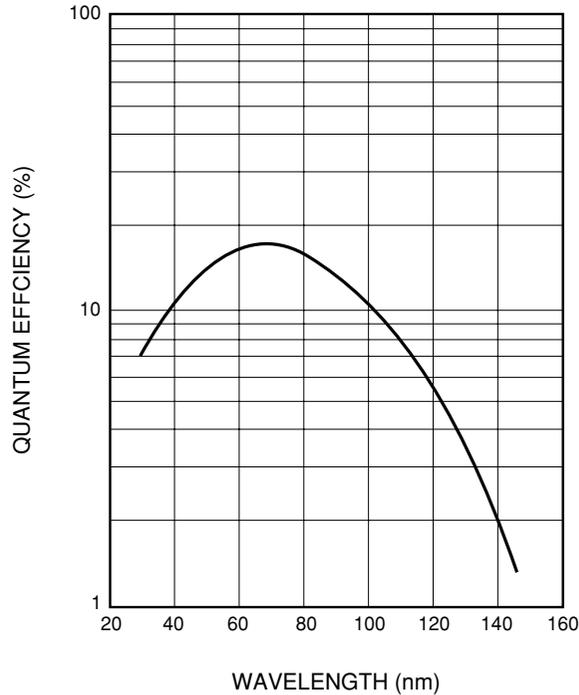

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Figure 12-3: Ion detection by an ion detector with a conversion dynode

The secondary emissive surface of each dynode is activated by special oxidation processing formed on a copper electrode containing several percent beryllium. This secondary emissive surface efficiently emits secondary electrons from the input of soft rays, vacuum UV radiation, electrons, and ions. Another type of dynode uses a secondary emissive surface made of aluminum oxide which provides stable characteristics with extremely low deterioration even if left in air.

12.2 Characteristics

## 12.2.1 Sensitivity to soft X-rays, VUV, electrons and ions

Beryllium oxide (BeO) generally used in the first dynode of electron multiplier tubes is sensitive to soft X-rays to UV radiation at nearly 300 nanometers. Electron multiplier tubes are effective detectors when in a wavelength range shorter than the cutoff wavelength of the MgF_2 window (approximately 115 nanometers). (See 4.1 in Chapter 4.) A typical spectral response for beryllium oxide is shown in Figure 12-4, covering a range from 30 to 140 nanometers.

**Figure 12-4: Spectral response characteristic of beryllium oxide**

Various spectral response characteristics are available by replacing the first dynode of electron multiplier tubes with another type that are evaporated with alkali halide materials such as CsI, CuI, KCI and MgF_2 optimized for the target wavelength range and operating conditions. However, these materials are subject to deliquescence and require careful handling. Typical spectral response characteristics (reference values) of CsI, BeO, RbBr and Au are shown in Figure 12-5.
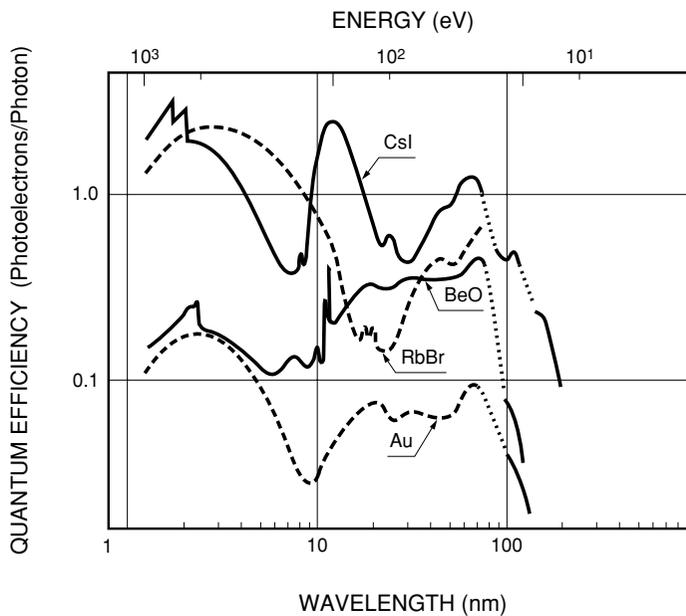
Figure 12-5: Spectral response characteristics of various substances (reference values)

The first dynode of electron multiplier tubes is sensitive to electrons with energy such as Auger electrons, secondary electrons and reflected electrons (see 2.3 in Chapter 2). Figure 12-6 shows typical secondary emission ratio versus primary electron accelerating voltage for beryllium oxide and aluminum oxide. The secondary emission ratio peaks at a primary electron accelerating voltage of about 400 to 500 volts.
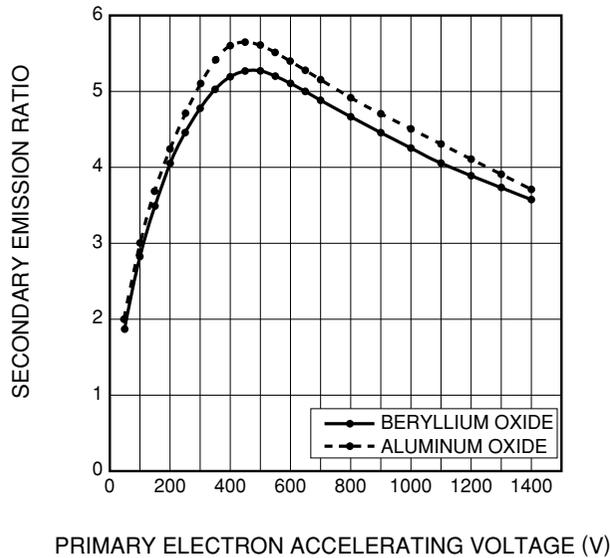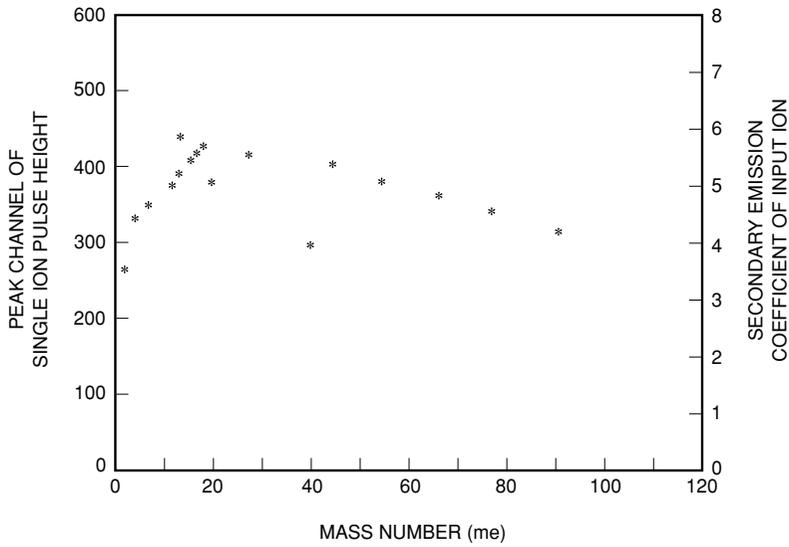

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Figure 12-6: Secondary emission ratio vs. primary electron accelerating voltage

The first dynode of electron multiplier tubes is also sensitive to ions. Typically, several electrons are emitted in response to one ion, although this ratio depends slightly on the state of the secondary electron emissive surface on the first dynode. The number of emitted electrons is also affected by the molecular weight (m/z)[5] and ion accelerating voltage. Figure 12-7 shows the relation between the electron emission ratio and the accelerating voltage for nitrogen ions. In Figure 12-8, typical electron emission ratios at an accelerating voltage of 2,000 volts are plotted for various types of ions.
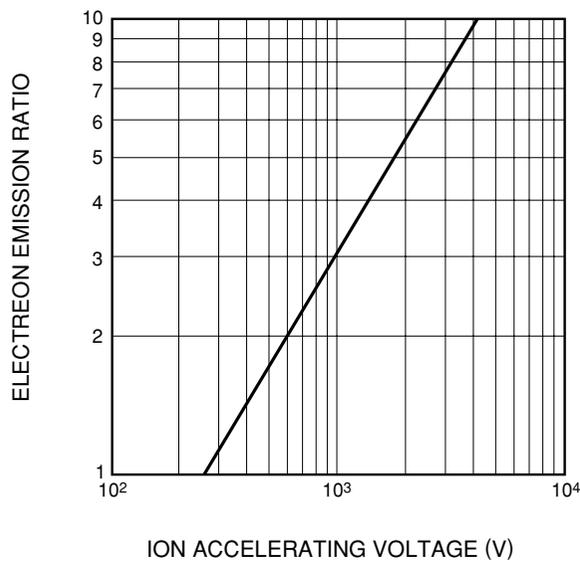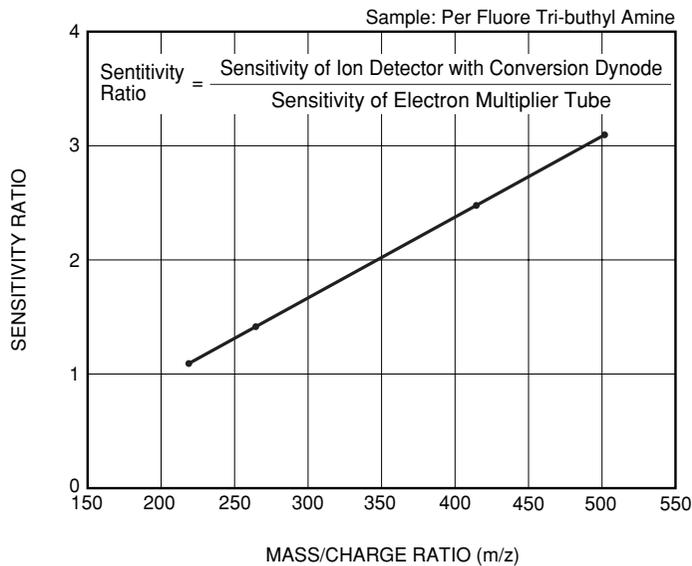

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Figure 12-7: Electron emission ratio vs. accelerating voltage for nitrogen ions

Figure 12-8: Electron emission ratios for various kinds of ions at 2000 V accelerating voltage

Most ion detectors have a conversion dynode applied with a high voltage and positioned before the first dynode. This conversion dynode converts ions into electrons like the first dynode used in photomultiplier tubes does. The ion-to-electron conversion efficiency is proportional to the speed at which ions strike the surface of the conversion dynode.[4] Because of this, the conversion dynode is designed to increase the speed of the incident ions and to enhance the conversion efficiency. Figure 12-9 shows the difference in sensitivity between an electron multiplier and an ion detector with a conversion dynode. The effect of the conversion dynode is more significant in a higher mass/charge ratio region.[5]

Figure 12-9: Sensitivity improvement in ion detector with conversion dynode

12.2.2 Gain

As in the case of photomultiplier tubes, the current amplification or gain of an electron multiplier tube is expressed as follows.
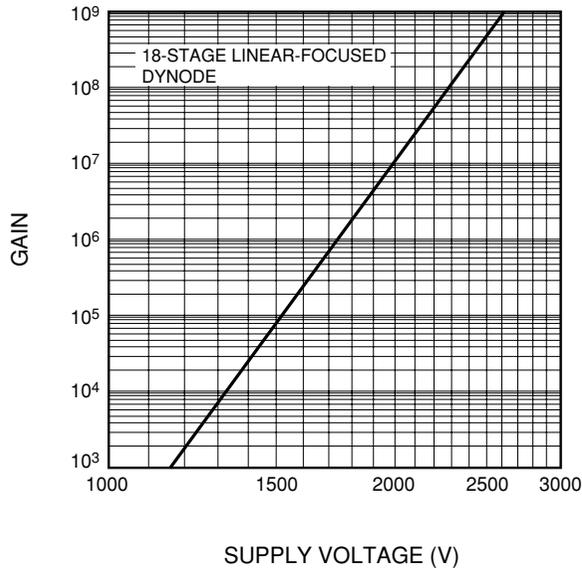
Gain (μ) = $A \cdot E_{bb}{}^{kn}$ .... (Eq. 12-1)

Ebb: supply voltage
  k : constant determined by electrode structure and material
  n : number of dynode stages

It is clear from this equation that the gain μ is proportional to the kn-th power of the supply voltage. Typical gain versus supply voltage is plotted in Figure 12-10.
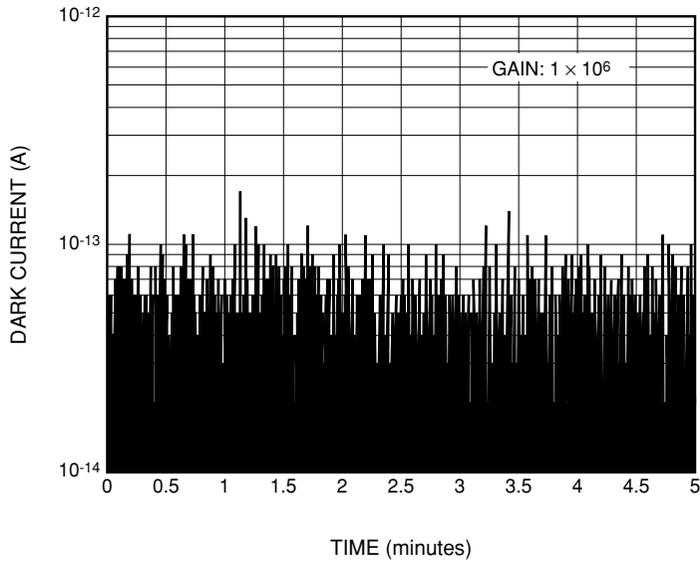

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Figure 12-10: Typical gain versus supply voltage characteristics of electron multiplier tube

12.2.3 Dark current and noise

The secondary emissive surface of dynodes used for typical electron multiplier tubes and ion detectors is made of beryllium oxide or aluminum oxide. These materials have a high work function and therefore exhibit exceptionally low dark current. Even so, small amounts of dark current may be generated by the following factors:

  1. Thermionic emission current from the secondary electron emissive surface

  2. Leakage current from electrode support materials

  3. Field emission current

Typical electron multiplier tubes and ion detectors have very low dark current which is less than 1 picoampere when operated at a supply voltage providing a gain of 10^6. Dark current and noise measurement results are shown in Figure 12-11.

Figure 12-11: Dark current/noise measurement results

An ion source used in mass spectrometers ionizes a sample, but simultaneously produces noise components such as UV radiation and X-rays. These noise components also enter the ion detector along with the sample ions and are then multiplied. This noise is generally regarded as internal ion detector noise, although it is not caused by the ion detector itself. To reduce the noise actually originating from the ion source, the first dynode or conversion dynode of the ion detectors is arranged at a position slightly shifted from the ion input opening. Also an electric field lens created by a special electrode is used to allow only sample ions to enter the ion detector. (This is called an "off-axis structure".) Figure 12-12 shows the ion detection mechanism of an off-axis ion detector and Figure 12-13 shows noise measured with the off-axis ion detector installed in a mass spectrometer. The signal at molecular weight ratios (m/z)[5] where no ions exist appears as noise. This noise level is nearly equal to the intrinsic noise of the ion detector.
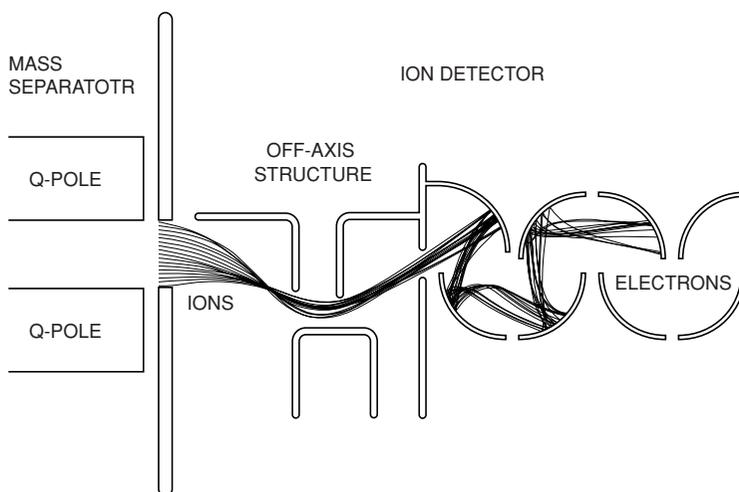

Figure 12-12: Ion detection in an off-axis ion detector
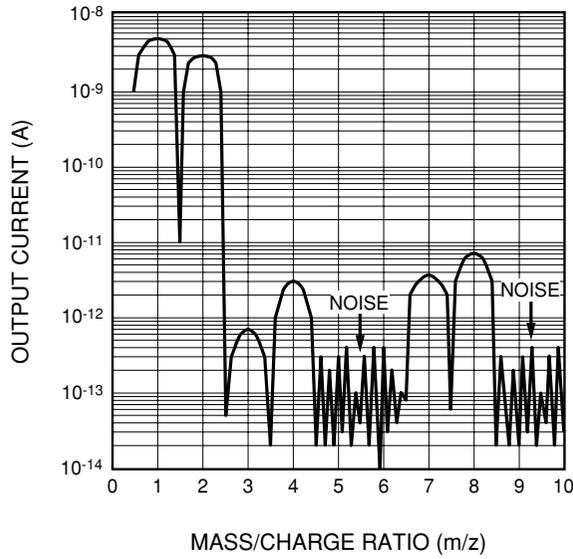
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Figure 12-13: Ion source noise measured with an off-axis ion detector

Because electron multiplier tubes and ion detectors are used in a vacuum, the noise level also depends on the pressure. Generally, the lower the pressure level (for example, 10^{-5} Pa), the less the noise will be, and the higher the pressure level, the greater the noise will be. Figure 12-14 shows the relation between the noise count and the pressure level at which an electron multiplier tube and ion detector are operated.
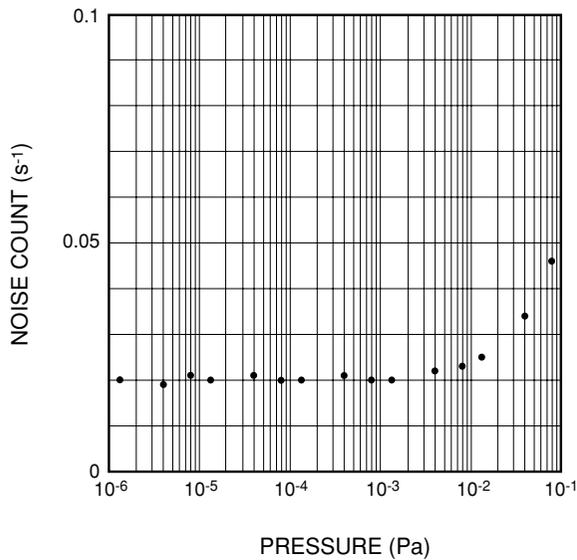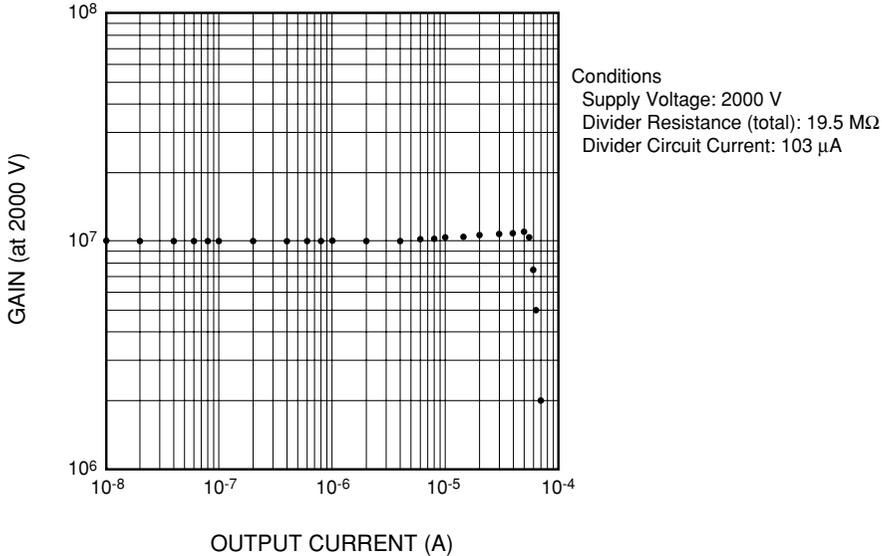

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Figure 12-14: Typical noise count vs. pressure level for electron multiplier tubes

12.2.4 Linearity

Most electron multiplier tubes and ion detectors usually incorporate voltage-divider resistors between each successive dynode. This resistor is about 1 MΩ per stage, so the total resistance comes to 20 MΩ. As in the case of photomultiplier tubes, the value of a linear output current is limited by the current flowing through these voltage-divider resistors. (See 5.1 in Chapter 5.) Figure 12-15 shows the linearity plotted when an electron multiplier tube or ion detector is operated in DC mode.

Conditions
  Supply Voltage: 2000 V
  Divider Resistance (total): 19.5 MΩ
  Divider Circuit Current: 103 μA

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Figure 12-15: Typical electron multiplier tube linearity in DC operation

As the output current increases, the gain abruptly drops after increasing slightly. This is a typical pattern for linearity dependent on the voltage-divider current. The linearity can be improved by reducing the total value of the voltage-divider resistors. To suppress the undesired increase in the gain which tends to occur when the output current becomes large, the resistor value between the last stage and ground should be made smaller.

The linearity in pulse counting mode is generally determined by the time response and voltage-divider circuit current of the electron multiplier tube or ion detector. (See 6.2 in Chapter 6.) To maintain high pulse count linearity, tube types using linear-focused dynodes and smaller voltage-divider resistors should be used.

12.2.5 Life characteristics

The life of electron multiplier tubes and ion detectors is usually affected by the gain, output current and operating pressure level. Two factors that cause gain deterioration are:

    1. Sensitivity deterioration in the first dynode or conversion dynode by incident ions

    2. Contamination on the secondary emissive surface

Figure 12-16 shows typical life characteristics for electron multiplier tubes and ion detectors. This is the supply voltage change required to maintain a preset gain (10^6) measured with the amount of input ions and output current kept constant.
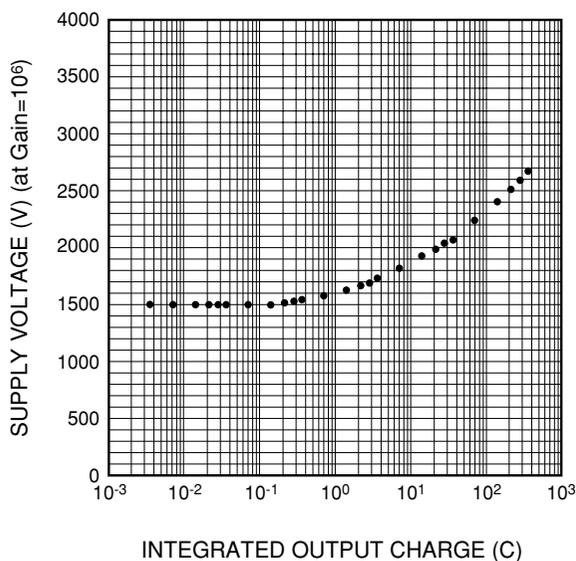
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Figure 12-16: Typical life characteristics for electron multiplier tubes and ion detectors

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4) T. Akashi, M. Takayama, Y. Hashimoto, et al.: "What is mass spectrometry?", International Academic Printing Co., Ltd.

5) K. Okuno, M. Takayama, et al.: Mass Spectrometry Terminology, International Academic Printing Co., Ltd.

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