9.2.4 Detectors

single & multiple detector:

Most mass spectrometers measure one *m/z* value at a time. A single-channel ion detector is used for these instruments, either an **electron multiplier (EM)** or a **Faraday cup**. TOF, ion trap, and FTICR mass spectrometers have the ability to extract ions of many *m/z* values simultaneously, so simultaneous detection of these ions is desirable. One approach to multiple ion detection has been to use multiple detectors. Multiple detectors are also used for high-resolution magnetic sector MS instruments designed for very precise isotope ratio determination and for quantitative analysis using isotope dilution. Instruments with multiple detectors are called "multicollectors." New detector developments in array detectors now permit simultaneous *m/z* measurement over a wide mass range, such as the SPECTRO MS instrument.

9.2.4.1 *Electron Multiplier*

working principle:

The most common detector used for ions in mass spectrometers is the EM. The EM is very similar in concept to the photomultiplier tube for optical detection. It is very sensitive and has fast response. The EM is based on the dynode, which has a surface that emits electrons when struck by fast-moving electrons, positive ions, negative ions, or neutrals. A **discrete-dynode EM** uses a series of 12–24 dynodes, each biased more positively than the preceding dynode. A collision releases several electrons from the dynode surface. These electrons are then accelerated to a second such surface, which, in turn, generates several electrons for each electron that bombards it. This process is continued until a cascade of electrons (an amplified current) arrives at the collector. The process is shown schematically in Figure 9.38. Typically, one ion can produce 10^5 electrons or more; this ratio of electrons measured per ion is referred to as the gain. The gain of the detector can be adjusted, with operating gains of 10^4–10^8 used, depending on the application. An animation of the operation of an EM can be viewed at www.sge.com/products/electron_multipliers. Figure 9.38b shows a commercial discrete-dynode EM. A **continuous-dynode EM**, also called a channel EM (CEM) uses a continuous glass tube, either lead-doped or coated on the inside with a conductive surface of high electrical resistance, such as those shown in Figure 9.39. A potential difference is applied across the tube ends so that the potential varies in a linear manner along the tube. Each incident ion releases electrons that are accelerated and strike the tube again, resulting in the same cascade effect seen in the discrete-dynode EM. The curved or coiled form is designed to reduce electrical noise by preventing positive ions from returning upstream.

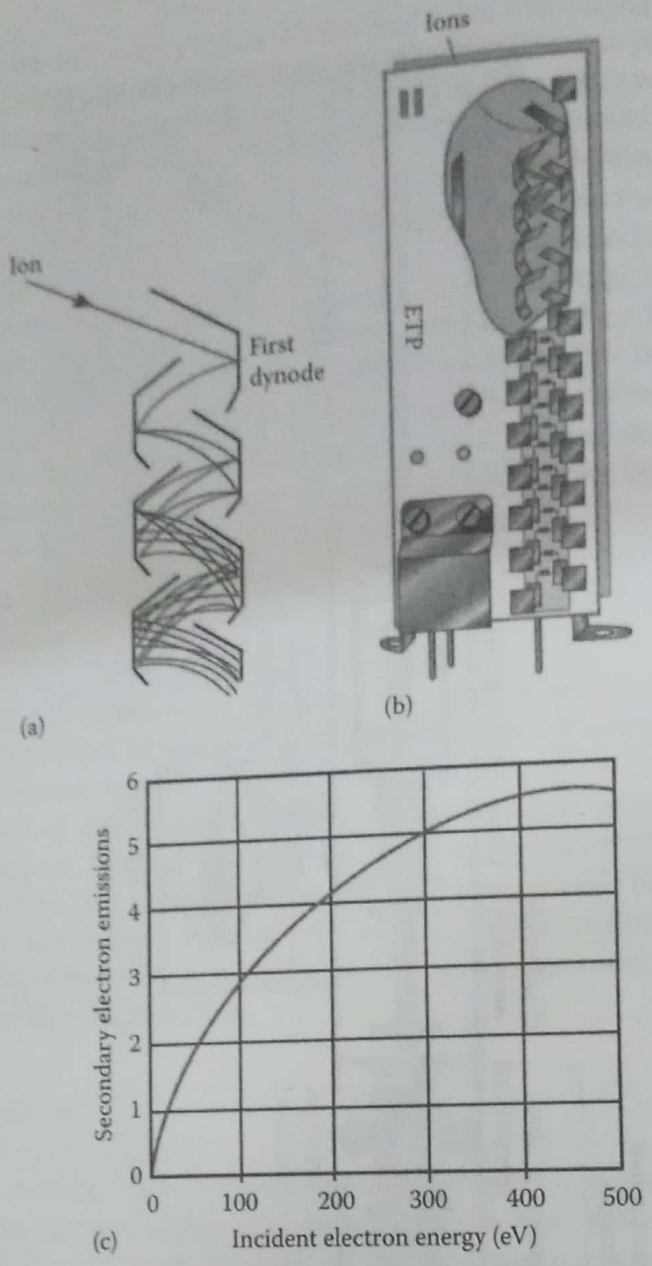


Figure 9.38 (a) A schematic discrete-dynode EM, showing the electron gain at each successive dynode after impact of an ion on the first dynode surface. The electron cascading process results in gains of up to 10^8 being achieved with approximately 21 dynodes. (b) An ETP EM schematic showing the position of the dynodes in the detector. (c) Dependence of the number of secondary electrons emitted on impact energy. (Images courtesy of SGE, Inc., Austin, TX, and ETP Electron Multipliers Pty Ltd, a division of SGE, Sydney, Australia. www.etspci.com and www.sge.com.)

Disadvantage :

A disadvantage to dynode-based detectors is that the number of secondary electrons released depends on the type of incident primary particle, its angle and energy. The dependence of the number of secondary electrons emitted on incident energy is shown for electron impact in Figure 9.38c; the same plot for ion impact would be similar. Therefore, they can exhibit *mass discrimination* due to differences in ion velocity. Heavy ions from quadrupole mass analyzers and from QIT mass analyzers impact the dynode surface at lower velocities than light ions. EM detectors for these instruments must be designed to overcome the difference in velocities, often by accelerating the ions prior to them striking the first electron-emitting dynode. An excellent source of information on how discrete dynode EMs work is the SGE website at www.sge.com, which describes their ETP EMs. Similarly, the Photonis website at www.photonis.com provides technical information on their Channeltron® continuous-dynode EM.

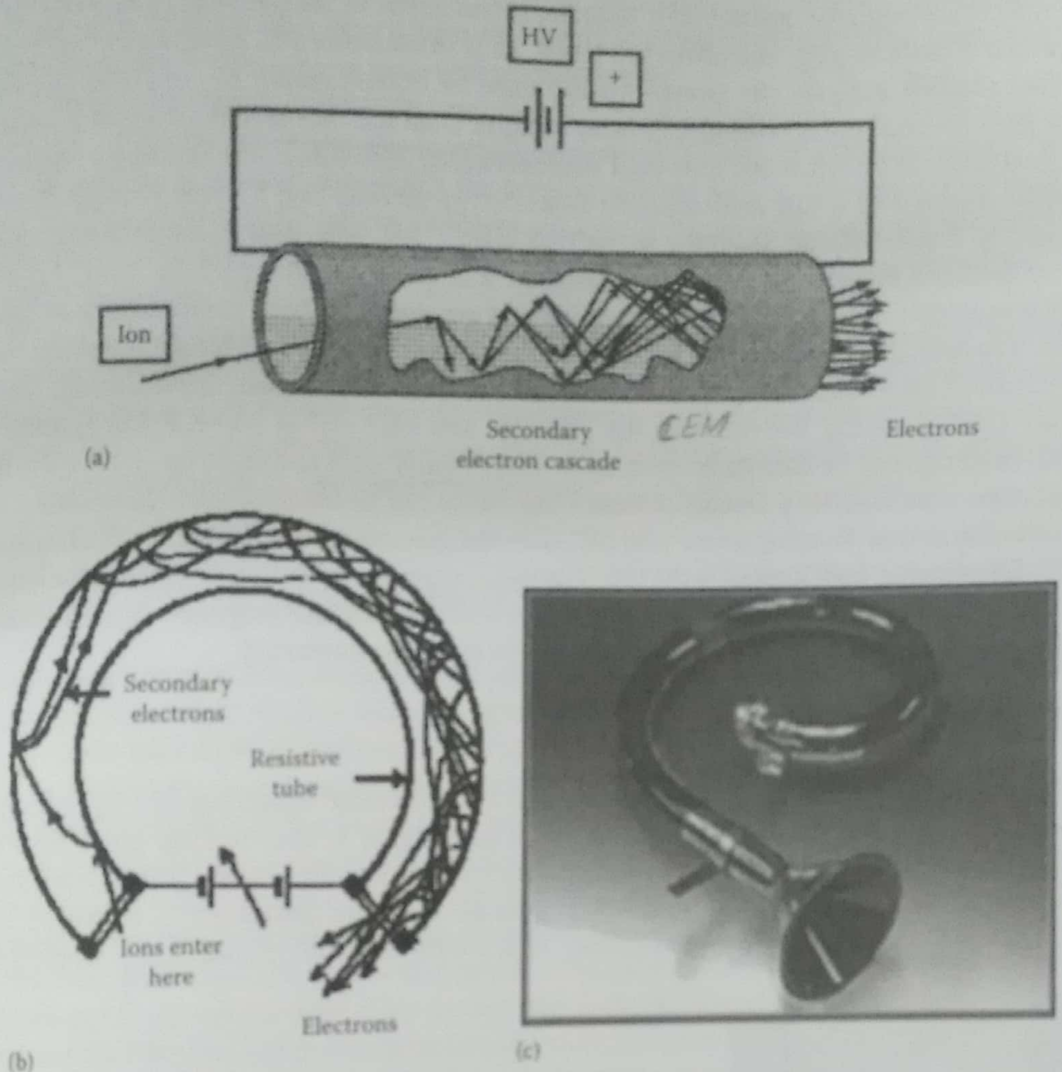


Figure 9.39 (a) A schematic CEM, consisting of a glass or interior-coated ceramic tube that emits secondary electrons upon ion impact. (b) A schematic curved CEM. The curved shape minimizes ion feedback noise. (c) Photo of the Channeltron® EM, showing the curved glass tube without the associated electronics. (Courtesy of Photonis USA, Fiskdale, MA, www.photonisusa.com.)

9.2.4.2 *Faraday Cup*

The least-expensive ion detector is the Faraday cup, a metal or carbon cup that serves to capture ions and store the charge. The resulting current of a few microamperes is measured and amplified. The cup shape decreases the loss of electrons from the metal due to ion impact. The Faraday cup is an absolute detector and can be used to calibrate other detectors. The current is directly proportional to the number of ions and to the number of charges per ion collected by the detector. Unlike dynode-based detectors, the Faraday cup does not exhibit mass discrimination. The detector does have a long response time, which limits its utility. The Faraday cup detector is used for making very accurate measurements in isotope-ratio MS, where the ion currents do not change rapidly. The Faraday cup detector has no gain associated with it, unlike dynode-based detectors. This limits the sensitivity of the measurement. Advantage in SEM:

This low sensitivity can be an advantage when combined with a high-sensitivity discrete dynode secondary EM (SEM) detector. The SEM detector can cover a linear dynamic range of nine orders of magnitude, but at a concentration range equivalent to ppq to ppm. If concentrations of elements

Conditions:

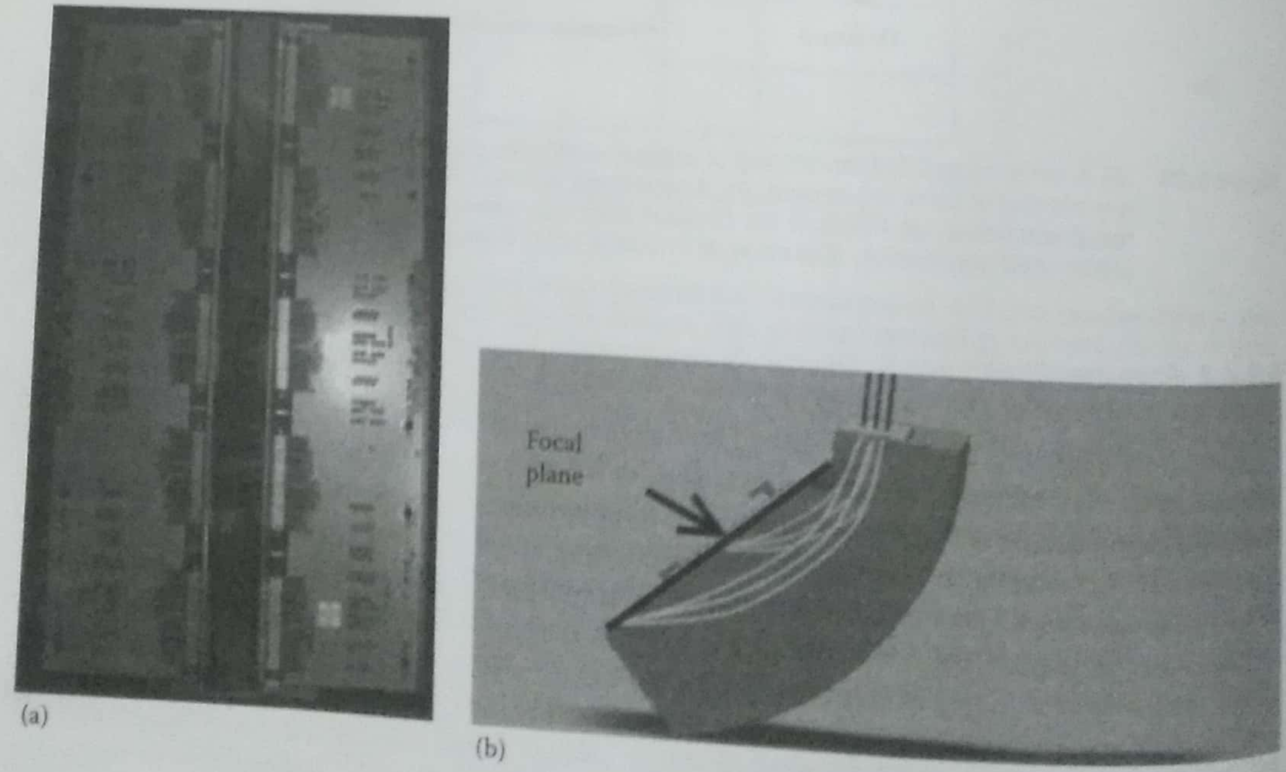
in the sample are high, the detector will saturate. If one wants to analyze matrix elements (usually at % levels) as well as trace and ultratrace levels, as is often needed in geochemical analysis and with laser ablation analysis, the sample usually must be diluted and/or run multiple times under several sets of conditions. By adding a Faraday detector to an ICP-MS system, levels of all elements, % to ultratrace, can be run at one time (still with sequential detection of the elements). Such a high-resolution system with a dual mode discrete dynode-type detector and a single Faraday detector is marketed by Thermo Fisher Scientific as the ELEMENT XR. The system automatically switches between detection modes with <1 ms delay (Figures 9.21 and 9.22). Multiple Faraday

High-precision isotope ratio mass spectrometers are designed with combinations of multiple Faraday cup detectors and multiple miniature EMs (used as ion counters) for simultaneous isotope measurement. These instruments are called multiple ion collector mass spectrometers (e.g., multiple collector [MC]-ICP-MS). For example, the TRITON and NEPTUNE MC-ICP-MS systems from Thermo Scientific can be configured with up to nine Faraday cups and eight ion counters to detect 17 ion beams simultaneously. Details of these instruments can be found at www.thermo.com. Other high precision double-focusing sector field MC-ICP-MS systems are available from Nu Instruments and GV Instruments, both located in the UK. The use of multiple ion collector instruments improves precision by two to three orders of magnitude over a single collector magnetic sector instrument, and this high precision is needed for accurate isotope ratio measurements.

9.2.4.3 Array Detectors

The microchannel plate is a spatially resolved array detector formed of 10^5–10^7 continuous-dynode EMs, each only 10–100 µm in diameter. This detector is used in focal plane mass spectrometers as a replacement for photograph plate detectors and is used in some TOFMS instruments.

A new 12 cm array detector with 4800 separate channels (detectors) is employed in the SPECTRO MS simultaneous double-focusing sector field ICP-MS (Figure 9.40). Each channel



(a)

(b)

Figure 9.40 (a) The 4800-channel array detector in the SPECTRO MS. (b) The detector mounted into the focal plane of the magnet. (Courtesy of SPECTRO Analytical Instruments, Inc., AMETEK® Materials Analysis Division, www.spectro.com, www.ametek.com. Used with permission.)

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consists of two separate detectors with different signal amplification electronics (high and low gain). A non-destructive read-out algorithm adjusts the integration time as needed in real time, permitting low and high intensity signals to be measured simultaneously.

Each detector in high and low gain can cover 4.5 orders of magnitude in signal range, with an overlap of about 1 order of magnitude, resulting in about 8 orders of dynamic range. The non-destructive read-out algorithm also works on transient signals, such as those from HPLC or laser ablation. As seen schematically for two different *m/z* ions in Figure 9.40b, each *m/z* ratio is focused and detected on a different part of the detector. This permits fully simultaneous detection from Li to U with no scanning.

The *focal plane camera* (FPC), still in initial development, consists of an array of 31 Faraday cups, each 145 μm wide. Up to 15 *m/z* values can be measured simultaneously. This detector shows improved precision compared with single channel detectors and has the ability to measure fast transient signals such as those from laser ablation. The detector design is described in the references by Barnes et al. and Knight et al. cited in the bibliography.