Arc and spark excitation sources are still widely used in the analysis of solid materials by emission spectroscopy, especially if the solids are difficult to dissolve or rapid analysis for quality control and production is required. They are still the mainstay of analysis in foundries, where samples are easily cast into electrodes and the range of compositions analyzed is well known.

7.3 PLASMA EMISSION SPECTROSCOPY

A *plasma* is a form of matter that contains a significant percentage (>1%) of electrons and ions in addition to neutral species and radicals. Plasmas are electrically conductive and are affected by a magnetic field. The plasmas used in emission spectroscopy are highly energetic, ionized inert gases. The most common plasma in commercial use is the argon ICP. Other commercial plasma sources are the DCP, also usually supported in argon, the recently introduced nitrogen MP, and the helium microwave-induced plasma (MIP). The temperature of a plasma excitation source is very high, from 6,500 to 10,000 K, so almost all elements are atomized or ionized and excited to multiple levels. The resulting emission spectra are very line rich, which necessitates the use of high-resolution spectrometers to avoid spectral overlap.

7.3.1 Instrumentation for Plasma Emission Spectrometry

7.3.1.1 Excitation Sources

Radio-frequency (RF) ICP source. In ICP-OES, the sample is usually introduced to the instrument as a stream of liquid. The sample solution is nebulized and the aerosol transported to the plasma. In the plasma, the sample undergoes the same process outlined in Table 7.2. The argon plasma serves to atomize, ionize, and excite the elements in the sample. The emitted radiation is sorted by wavelength in a spectrometer and the intensity is measured at each wavelength. A schematic of a typical ICP-OES system is presented in Figure 7.21.

In Figure 7.21, the argon plasma is the flame-like object at the top of the ICP torch, above the coils (the dark lines) from the RF generator. Figure 7.22 depicts a cross section of a typical ICP torch.

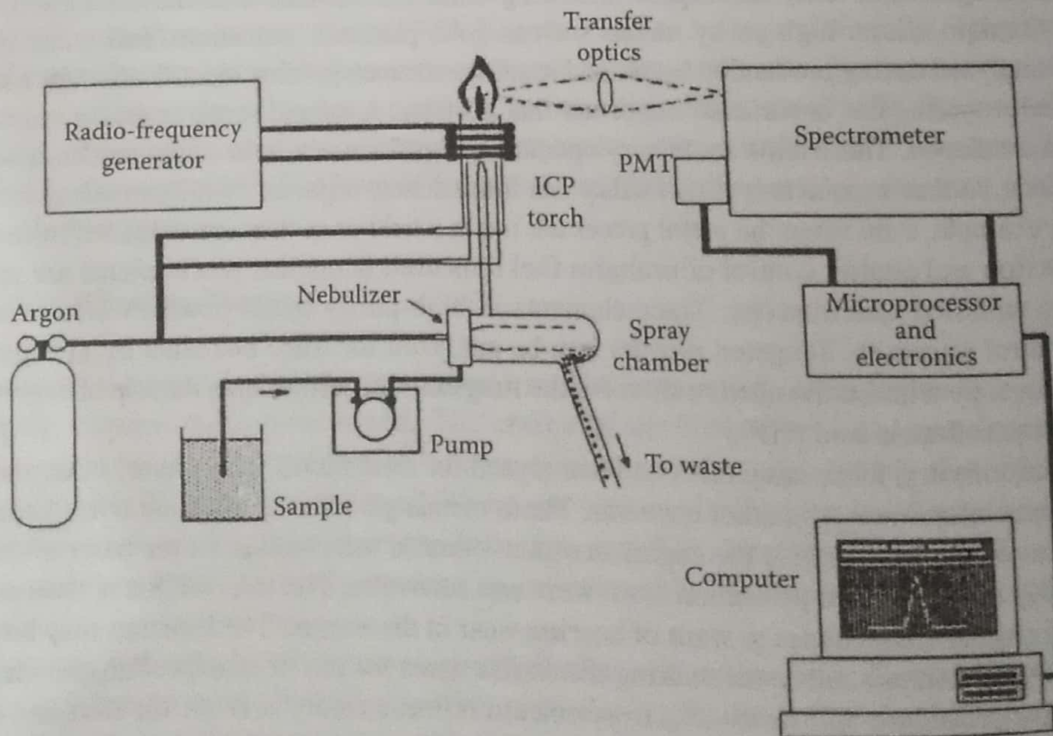

Figure 7.21 Major components and layout of a typical ICP-OES instrument. [**© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).]

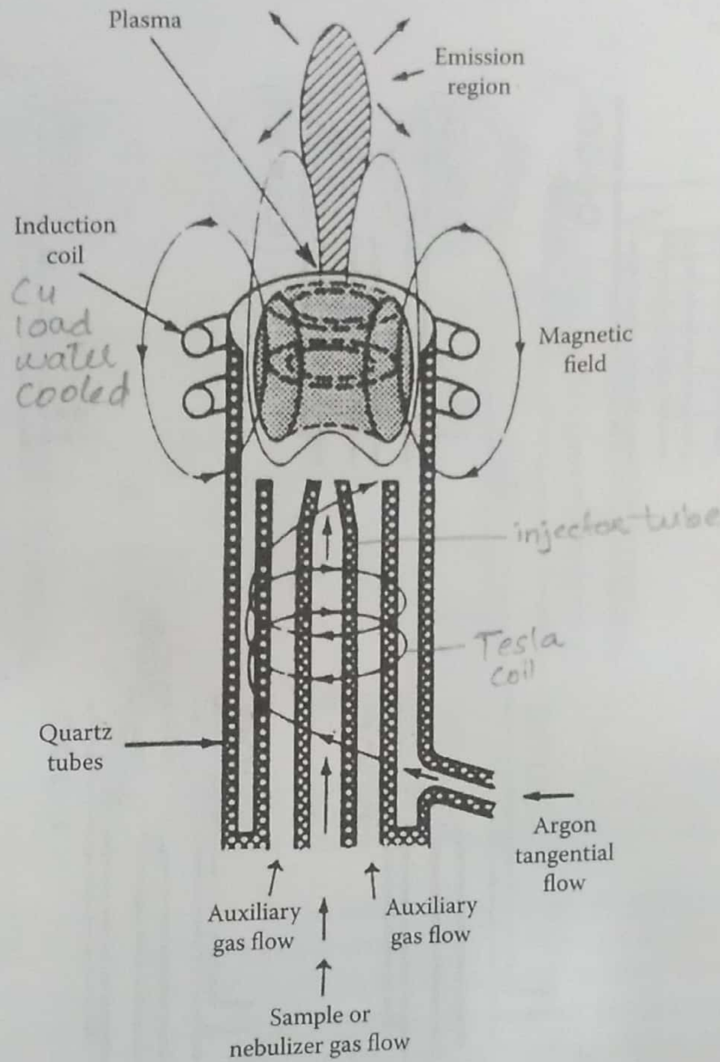

Figure 7.22 Cross section of an ICP torch. The emission is viewed in the region above the coils when the torch is in a radial position.

This torch contains three concentric tubes for argon flow and sample aerosol introduction. The two outer tubes are normally made of quartz. The inner tube, called the injector tube, may be made of quartz, alumina, sapphire, or other ceramic. Surrounding the torch is a water-cooled copper load coil or induction coil, which acts as an antenna to transmit power to the plasma gas from the RF generator. The power required to generate and sustain an argon plasma ranges from 700 to 1500 W. RF generators on some commercial instruments operate at 27.12 MHz; many modern instruments operate at 40.68 MHz, which results in better coupling efficiency and lower background emission intensity. The plasma initiation sequence is depicted in Figure 7.23. When RF power is applied to the load coil, an AC oscillates within the coil at the frequency of the generator. The oscillating electric field induces an oscillating magnetic field around the coil. Argon is swirled through the torch and slightly ionized using a Tesla coil. The few ions and electrons formed are immediately affected by the magnetic field. Their translational motion changes rapidly from one direction to the other, oscillating at the same frequency as the RF generator. The rapid movement in alternating directions is *induced* energy; adding energy in this manner is called *inductive coupling*. The high-energy electrons and ions collide with other argon atoms and cause more ionization. This continues in a rapid chain reaction to convert the argon gas into a plasma of argon ions, free electrons, and neutral argon atoms.

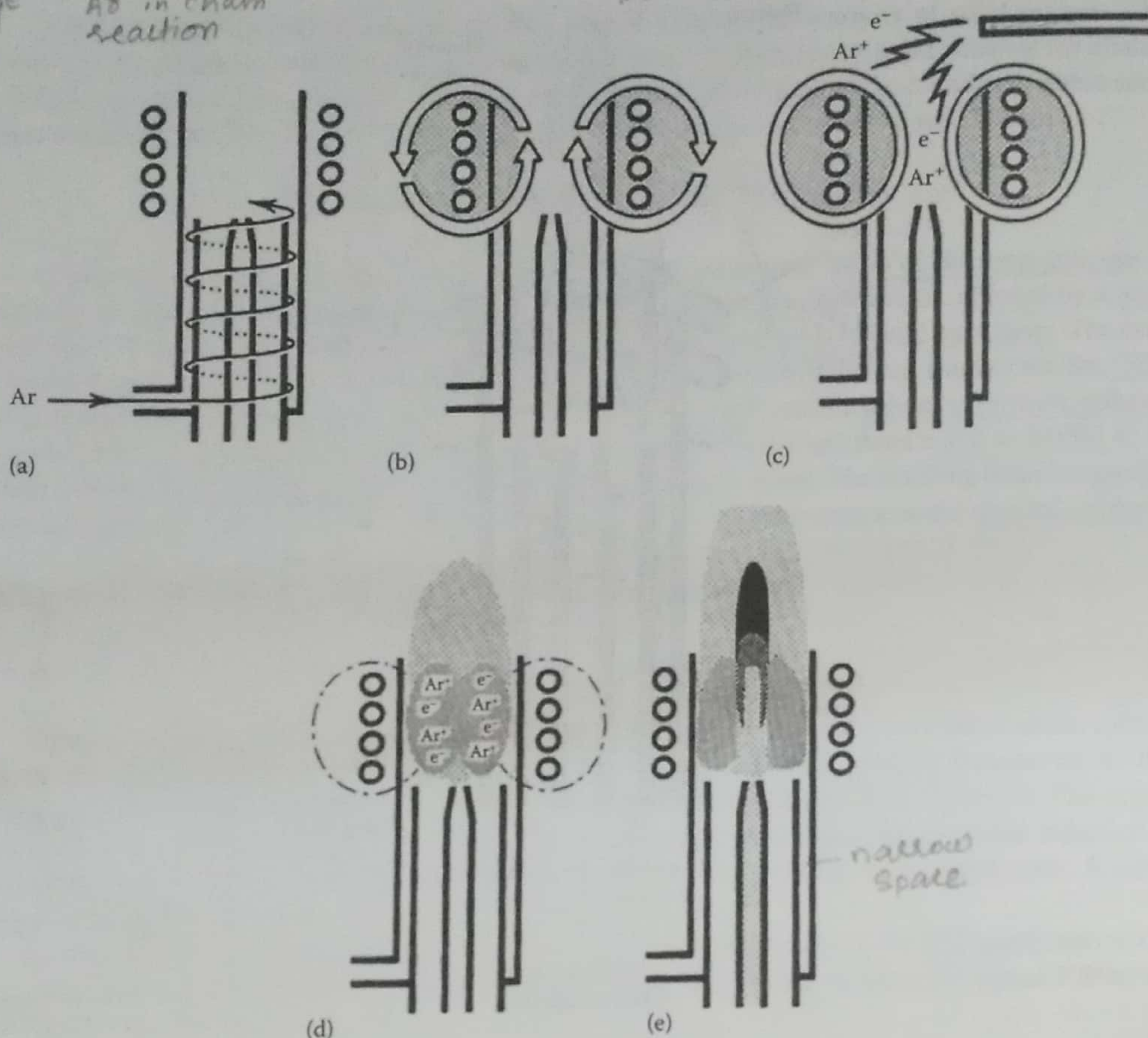

Figure 7.23 Cross section of an ICP torch and the load coil depicting an ignition sequence. (a) Argon gas is swirled through the torch. (b) RF power is applied to the load coil. (c) A spark produces some free electrons in the argon. (d) The free electrons are accelerated by the RF field causing more ionization and formation of a plasma. (e) The nebulizer flow carries sample aerosol into the plasma. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).]

The ICP torch is designed with narrow spacing between the two outermost tubes, so that the gas emerges at a high velocity. The outer tube is designed so that the argon flow in this tube, called the plasma flow, follows a tangential path as shown in Figure 7.22. This flow keeps the quartz tube walls cool and centers the plasma. A typical flow rate for the plasma flow is 7–15 L argon/min. The argon flow in the middle channel is called the auxiliary flow and can be 0–3 L argon/min. The auxiliary gas flow serves several purposes, including that of reducing carbon deposits at the injector tip when organic solvents are being analyzed. The gas flow that carries the sample aerosol into the plasma goes through the center or injector tube. It is called the nebulizer flow or sample flow and is typically about 1 L/min. The tangential or radial flow spins the argon to create a toroidal or doughnut-shaped region at the base of the plasma through which the sample aerosol passes. The temperatures for various regions of the plasma are shown in Figure 7.24a. Immediately above the load coil, the background emission is extremely high. The background signal drops with distance from the load coil, and emission is usually measured slightly above the load coil, where the optimum signal-to-background ratio is achieved. This area is called the "normal analytical zone," shown in Figure 7.24b.

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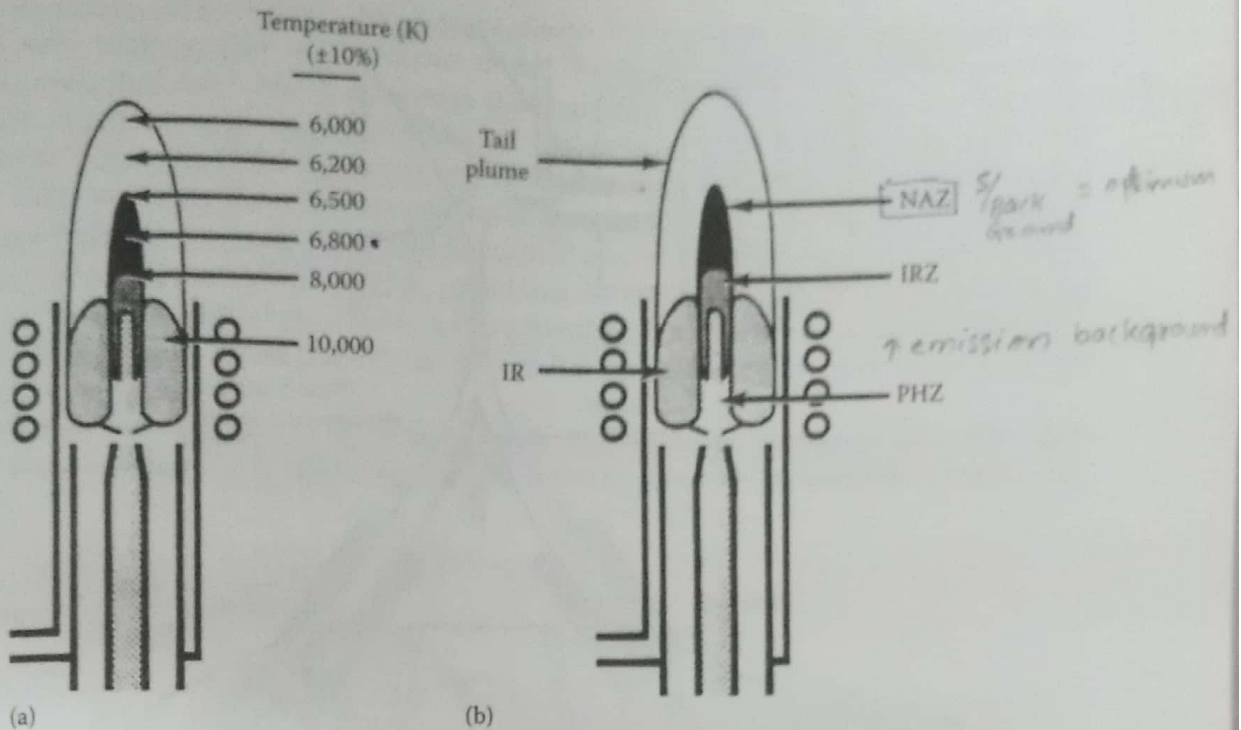

Figure 7.24 (a) Temperature regions in a typical argon ICP discharge. (b) Zones of the ICP discharge. IR, induction region; PHZ, preheating zone; IRZ, initial radiation zone; NAZ, normal analytical zone. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).]

The advantage of the argon ICP as an excitation source lies in its high temperature and its stability. The gas temperature in the center of the plasma is about 6800 K, which permits the efficient atomization, ionization, and excitation of most elements in a wide range of samples. In addition, the high temperature reduces or eliminates many of the chemical interferences found in lower-temperature electrical sources and flames, making the ICP relatively free from matrix effects. Another important advantage of the ICP is that the sample aerosol is introduced through the center of the plasma and is exposed to the high temperature of the plasma for several milliseconds, longer than in other excitation sources; this contributes to the elimination of matrix effects. Elements are atomized and excited simultaneously. The stability of the ICP discharge is much better than arc or spark discharges, and precision of less than 1% RSD is easily achieved. The dynamic range of an ICP source is approximately four to six orders of magnitude. It is often possible to measure major, minor, and trace elements in a single solution with an ICP source. Many ICP systems permit the injection of air or oxygen into the plasma when running organics, to prevent carbon buildup and reduce background.

DCP source. The design of the DCP source is shown in Figure 7.25. Two jets of argon issue from graphite anodes. These join and form an electrical bridge with the cathode, which is made of tungsten. In operation, the three electrodes are brought into contact, voltage is applied, and the electrodes are then separated. Ionization of the argon occurs and a plasma is generated, forming a steady discharge shaped like an inverted letter Y.

As shown in Figure 7.25, the region that is monitored for analytical measurements is at the junction of the anode argon streams. This small region gives good emission intensity from analyte atoms and has a background lower than the regions in the immediate vicinity. The sample is injected into this region with a stream of argon from a separate injection system. In the excitation region, the effective electronic temperature is about 5000 K. This results in spectra that are simpler than ICP emission spectra, with fewer ions lines. Sensitivities are within an order of magnitude of those reported for ICP sources for most elements and for the alkali metals and alkaline-earth elements are as good as ICP. The power supply is less expensive and the quantity of argon required for DCP operation is much less than what is

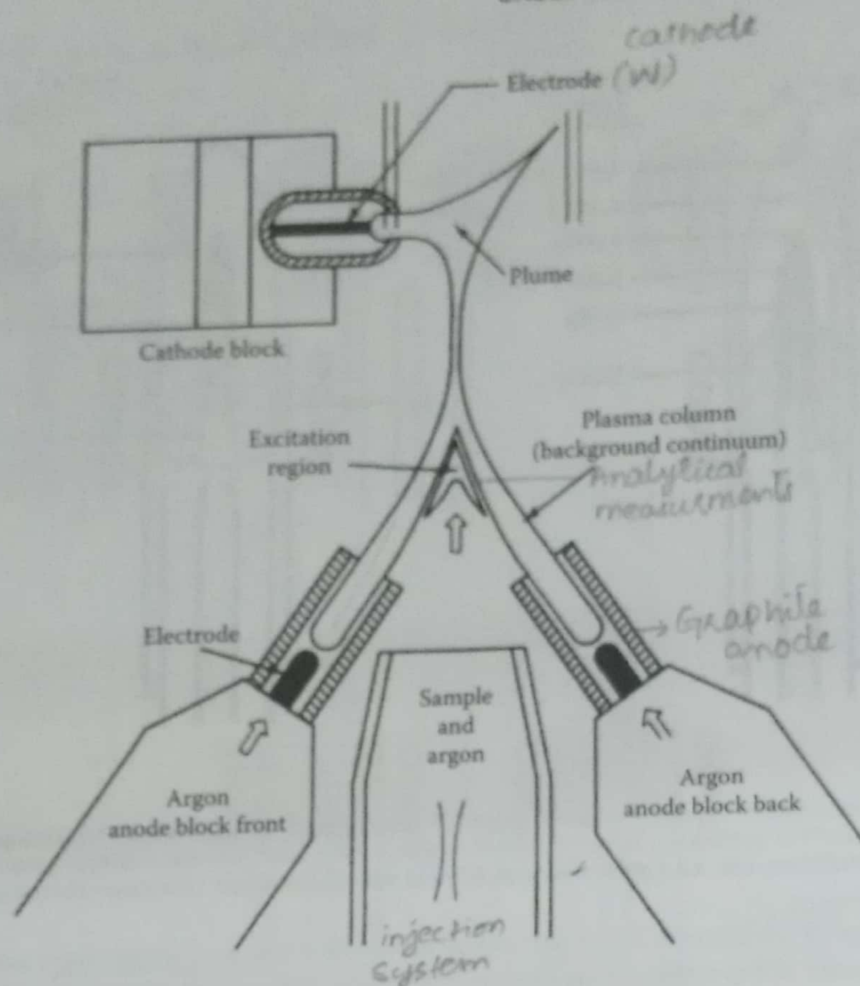

Figure 7.25 The inverted Y configuration of a DCP jet. (© Thermo Fisher Scientific (www.thermofisher.com). Used with permission.)

necessary to operate an ICP. A DCP can be operated for several days on a single cylinder of argon gas; an ICP would use the cylinder up in less than 8 h. Because of the way the sample is introduced into the plasma, the DCP can analyze solutions with high dissolved solids content better than some ICP sample introduction systems. There are several disadvantages to the DCP source. The graphite electrodes must be replaced frequently and the wearing away of the electrodes during analysis contributes to long-term drift in the signal. The dynamic range of a DCP is about three orders of magnitude, less than that of an ICP. The residence time of the sample in the plasma is short because the plasma is small compared to an ICP source, making it difficult to atomize and excite highly refractory elements.

MP source. In 2011, Agilent Technologies, Inc., introduced a unique excitation source for AES. The 4100 MP-AES uses a magnetically excited nitrogen MP (Figure 7.26a). The instrument uses an industrial magnetron, similar to that used in kitchen microwave ovens, and its magnetic field, rather than an electric field, to couple the microwave energy into the plasma. The magnetron is air-cooled and operates at 2450 MHz. It creates a concentrated axial magnetic field around a conventional torch and produces a toroidal plasma. The plasma is ignited using a brief flow of Ar and then automatically switches to nitrogen, either from a cylinder, Dewar (liquid N_2), or produced from air by a nitrogen generator. An external gas control module allows for injection of air into the plasma when analyzing organics to prevent carbon buildup and reduce background.

MIP source. An atmospheric pressure helium MIP is generated using a 2.45 GHz microwave generator and an electromagnetic cavity resonator, called a Beenakker cavity. The helium gas is passed through a discharge tube placed in the cavity, as seen in Figure 7.26b. The plasma is initiated by a spark from a Tesla coil. The electrons produced by the spark oscillate in the microwave field

and ionize the helium gas by collision, producing a plasma. The microwave energy is coupled to the gas stream in the discharge tube by the external cavity. The plasma is centered in the discharge tube and is represented in Figure 7.26b by the shaded spheroid shape.

The MIP operates at lower power than the ICP and at microwave frequencies instead of the RFs used for ICP. Because of the low power, an MIP cannot desolvate and atomize liquid samples. Therefore, MIPs have been limited to the analysis of gaseous samples or very fine (1–20 μm diameter) particles. Helium is the usual plasma gas for an MIP source. Electronic excitation temperatures in a helium MIP are on the order of 4000 K, permitting the excitation of the halogens, C, N, H, O, and other elements that cannot be excited in a flame atomizer. The lower temperature results in less spectral interference from direct-line overlap than in ICP or high-energy sources, but also causes more chemical interference.

A helium MIP has been used as an element-specific detector for gas chromatography (GC). This detector is shown in Figure 7.26c and the use of it for GC will be covered in greater detail in Chapter 12.

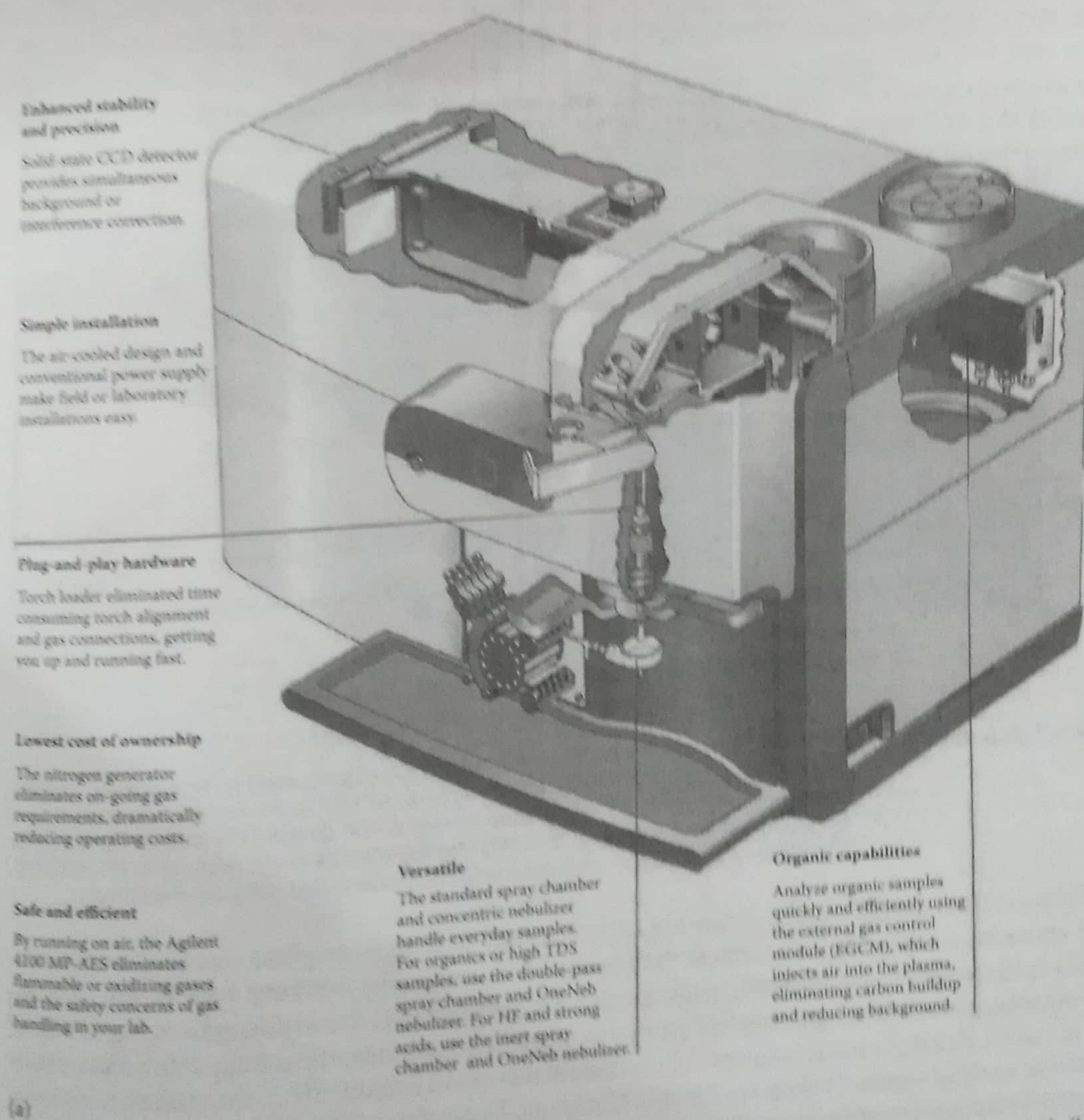

Figure 7.26 (a) The 4100 MP-AES nitrogen-based atomic emission spectrometer. (Courtesy of Agilent Technologies, Inc., Santa Clara, CA, www.agilent.com.)

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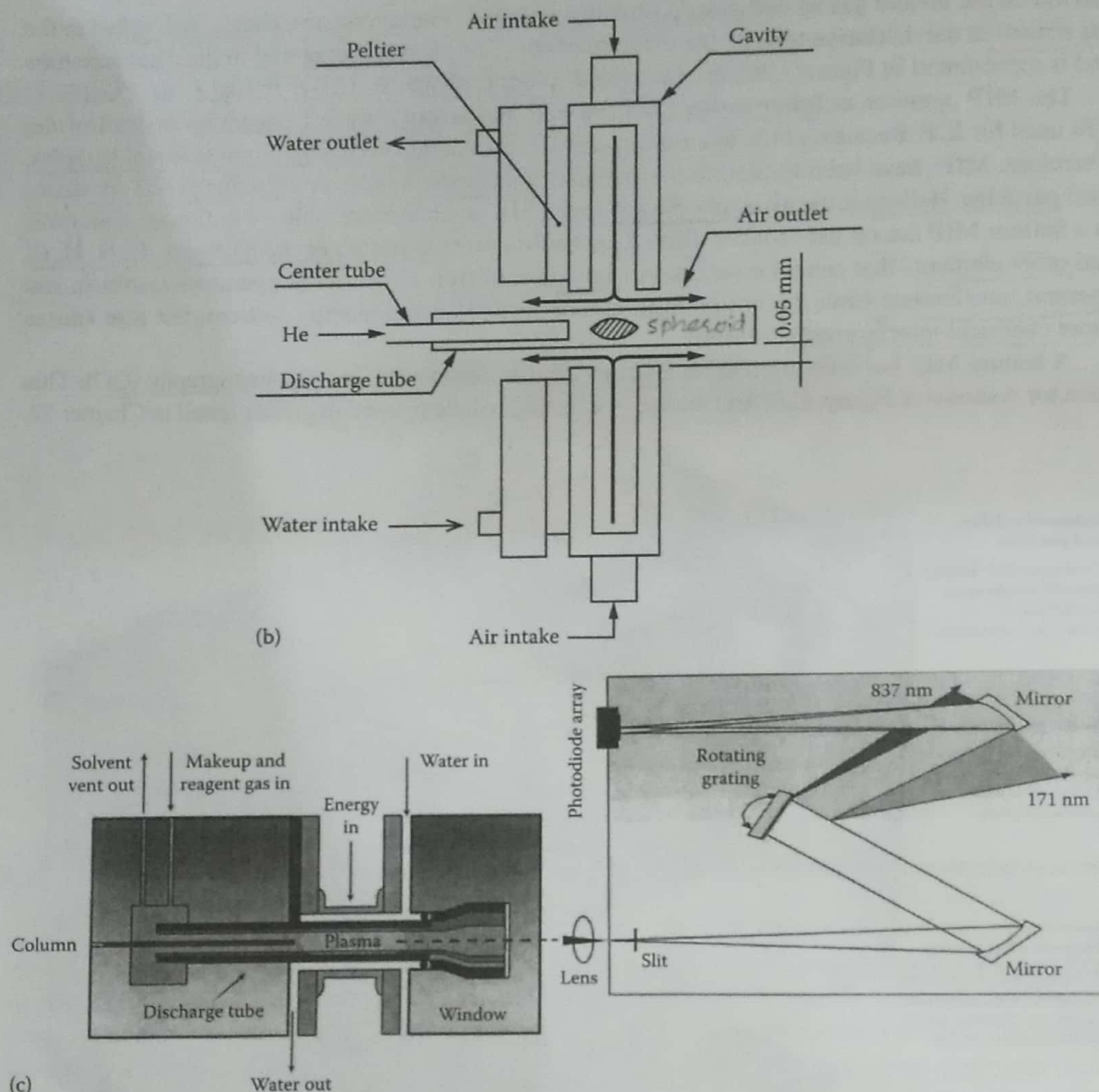

Figure 7.26 (continued) (b) A helium MIP. (Courtesy of Yokogawa Electric Company, Musashino, Japan.) (c) Atomic emission detector for GC using a helium MIP as the excitation source. It uses a scanning diffraction grating spectrometer and PDA detector to measure atomic emission from samples excited in the MIP. The wavelength range covered is 171–837 nm. (Courtesy of Joint Analytical Systems GmbH, Moers, Germany, www.jas.de.)

The effluent from the GC column consists of carrier gas and separated gas-phase chemical compounds. The separated compounds flow through the plasma contained in the discharge tube shown. A compound in the plasma is decomposed, atomized, and excited and emits the wavelengths characteristic of the elements present. The light from the plasma is sent to a grating monochromator with a PDA detector, as shown. Another unique commercial instrument that uses a helium MIP as the excitation source is a particle analysis system (Yokogawa Electric Company, Japan) designed to both count and identify the chemical composition of particles. Particles that have been collected on a filter are "vacuumed" into the He MIP source, where the particles are atomized and excited and emit the characteristic radiation from the elements present. Graphite furnaces (GFs), hydride generation (HG) instruments, and other devices have been used to generate gas-phase samples or desolvated particles for introduction into MIPs.

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