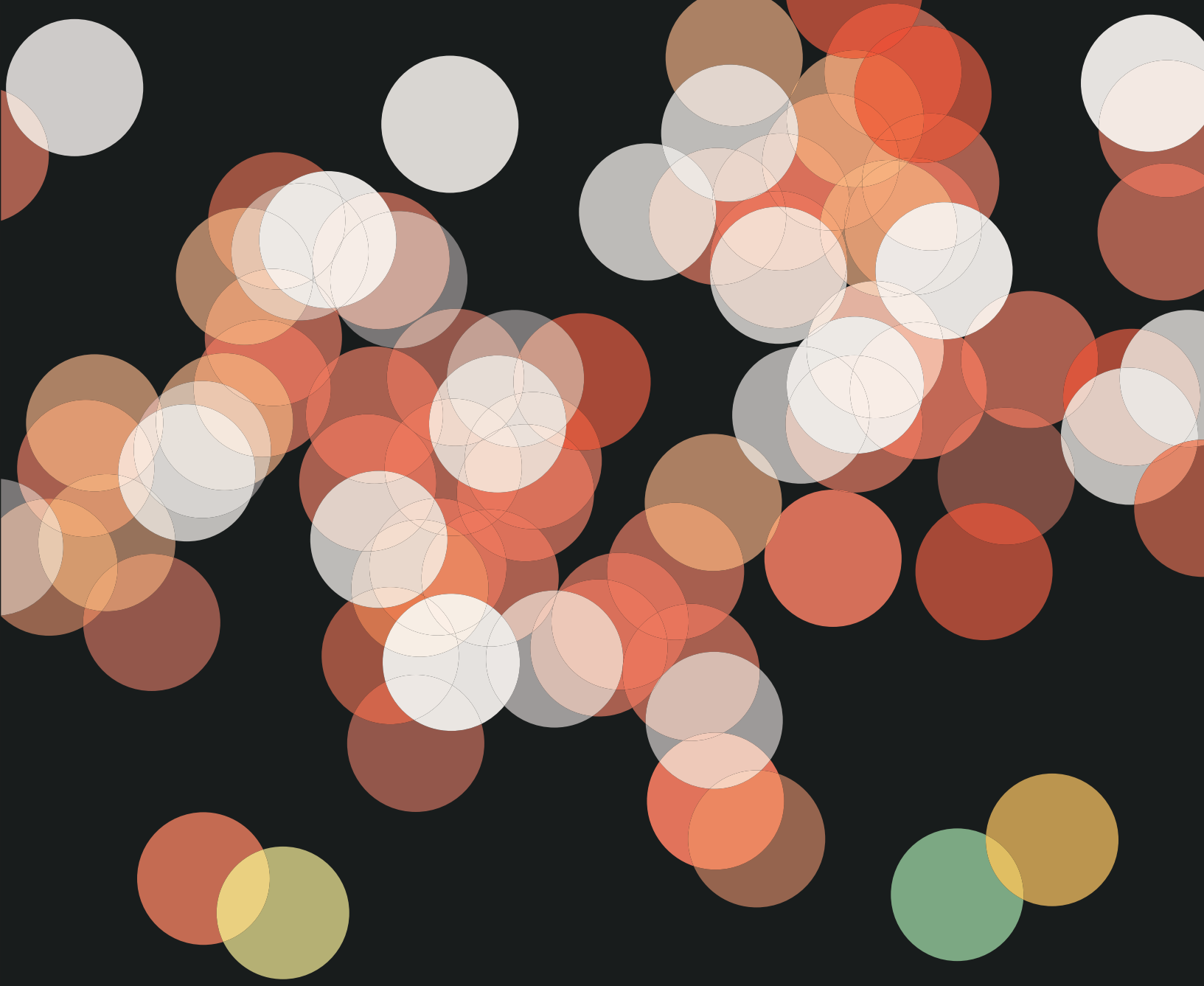

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Suzanne Bell

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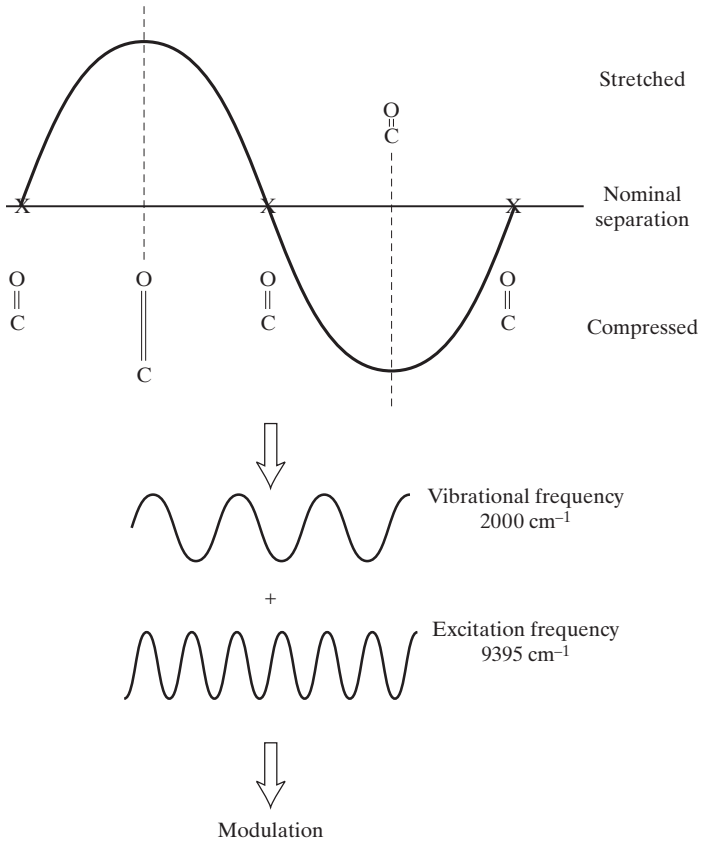

FIGURE 35 Frequency of a hypothetical chemical bond vibration. This bond expands and contracts at a frequency of 2000 cm^{-1}. How polarizable the bond is will determine how it scatters incoming light. At the maximum stretch, the polarizability of the bond will not be the same as when the bond is at maximum compression, so polarizability has the same frequency as the vibration.

and hydrogen are relatively small, and the bonds in water are not easily deformed by interaction with visible light. Because visible light is used for excitation, samples can be mounted on or contained in glass.

Inelastic scattering can result from interactions with the polarizable bond that produce signals (Stokes and anti-Stokes) at the excitation wavelength plus or minus the vibrational mode of the bond, as shown in Figure 36. The Stokes signal is the stronger of the two, but it is still several orders of magnitude weaker than the Rayleigh line. Further problems can arise when higher energy excitation sources, such as those in the visible and UV range, are used. These sources can cause fluorescence (Figure 37), which may produce a signal that will swamp the weak inelastic scattering signal. Despite these issues, Raman spectroscopy is finding a wider niche in forensic applications, given that it provides information that is complementary to absorption IR and is generally nondestructive.

3 MASS SPECTROMETRY

3.1 Overview

The name **mass spectrometer/mass spectrometry (MS)** is somewhat of a descriptive misnomer. Mass spectrometry works on the basis of separation, but not separation of electromagnetic energy into component wavelengths. Rather, a mass spectrometer disperses mass fragments so in this sense, "spectrometer" is a reasonable analogy, since the output is a spectrum of masses across a range of masses; an MS "scans" masses in the same sense that spectrometers scan electromagnetic energy. A good way to visualize

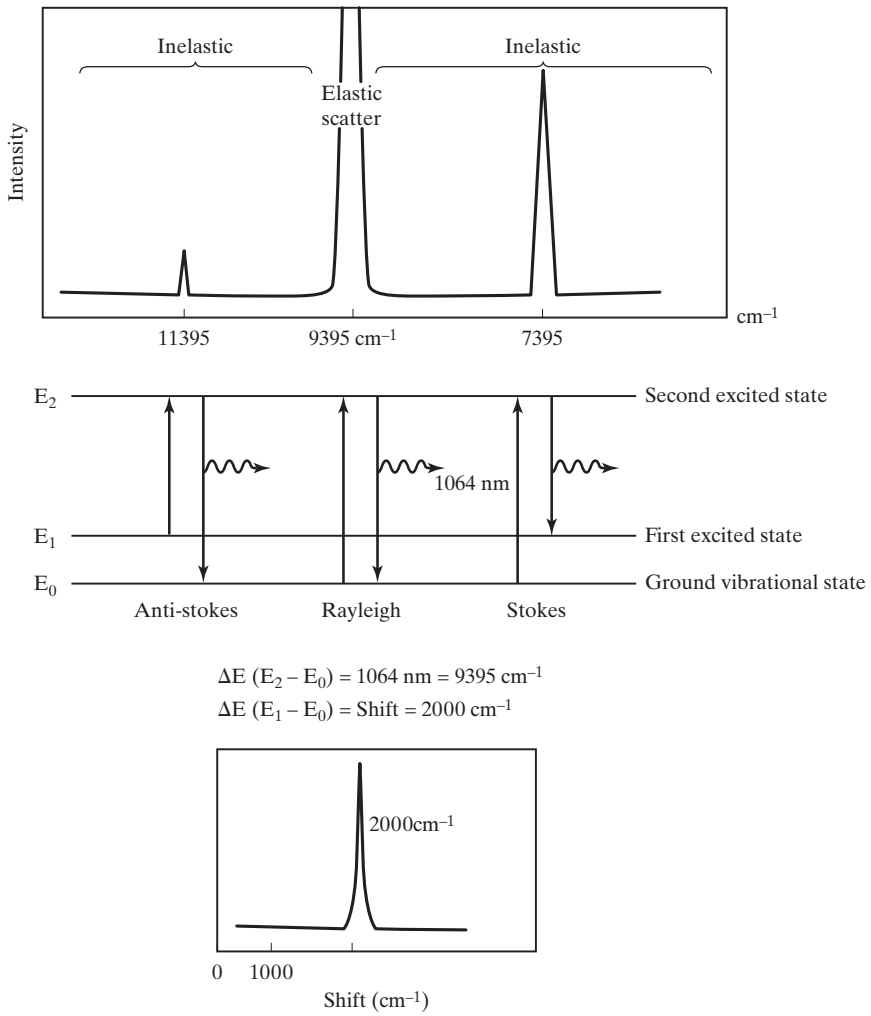

FIGURE 36 A Raman spectrum of a sample bond in a system using a near-infrared laser as the excitation source. Elastic scattering or Rayleigh scattering dominates the spectrum, with inelastic scattering at wave numbers plus or minus the equivalent of the vibrational frequency. The Raman spectrum can also be normalized and plotted as the shift in wavelength of the signal.

a mass spectrometer is as a mass filtering device, as shown in Figure 38. When this device is coupled to the output of some type of sample introduction system such as a gas chromatograph (discussed below), the flow is directed into a vacuum region, where the sample is ionized and fragmented to variable degrees. The ions are then introduced into a filtering device that separates them on the basis of their mass-to-charge ratio. Masses are often specified in units of Daltons (Da) and the ratio of mass to charge is represented by m/z. Ions arrive at the transducer and are converted to electrons. The signal is amplified by an electron multiplier and recorded.

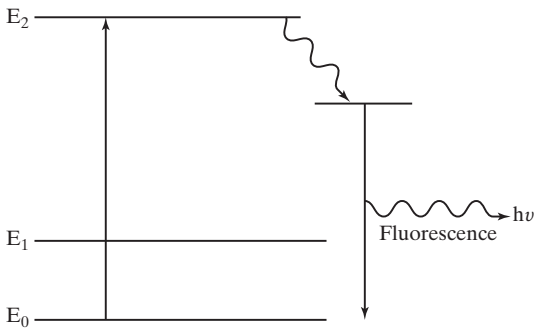

FIGURE 37 The fluorescence problem. If the laser is at a wavelength with sufficient energy to promote the molecule to the next higher state, the molecule can decay to a metastable state and then fluoresce, producing a signal that will swamp the weak scattering signal.

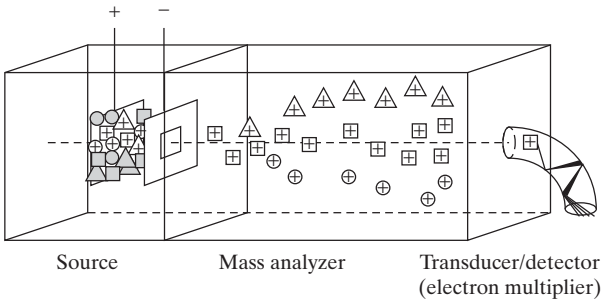

FIGURE 38 A generic mass spectrometer, which does with mass fragments what a grating does to light: filters it and separates it into individual components.

3.2 Basic Designs

There are many types of ionization modes and mass separation filters, the discussion of which is beyond the scope of this book. In forensic science applications, one of the most common MS designs is the **electron impact ionization/quadrupole mass filter** (Figure 39). Ionization and fragmentation are achieved by the collisions between molecules from the sample and electrons generated by a filament, as shown in Figure 40. This ionization technique is referred to as electron impact (EI), and it is considered to be a hard ionization technique. This means the fragmentation is fairly complete as opposed to a soft ionization technique. We will discuss an example of soft ionization shortly. In EI mode, few collisions result in ionization, but enough to generate both positive and negative ions, with positive ions usually being the polarity of interest. The positive ions are pushed into the focusing lenses by a repeller plate kept at a positive potential. The degree of fragmentation depends on the electron energy; standard values are 70 eV. The vacuum is necessary to prevent secondary collisions and combinations. Ions are focused into a tight stream by a series of electronic lenses and introduced into the quadrupoles, where alternating DC and radio-frequency currents determine the field and thus the ion pathways. At a given setting, only ions with a particular mass transit the quadrupoles safely, whereas all others collide with the quadrupoles or are ejected.

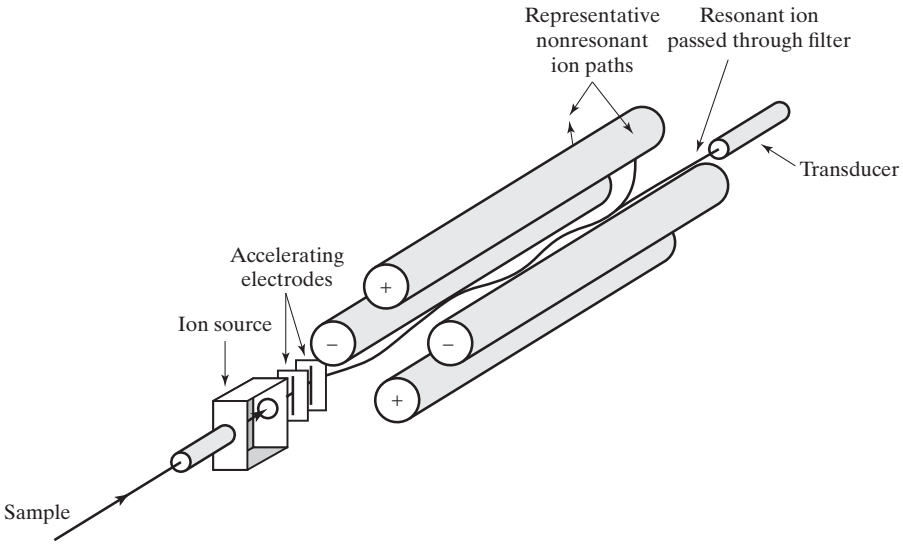

FIGURE 39 A quadrupole mass spectrometer. Alternating DC and radio frequencies applied to the quadrupoles dictate ion paths. At any given setting, only one mass will get through and this is called the *resonant mass.*

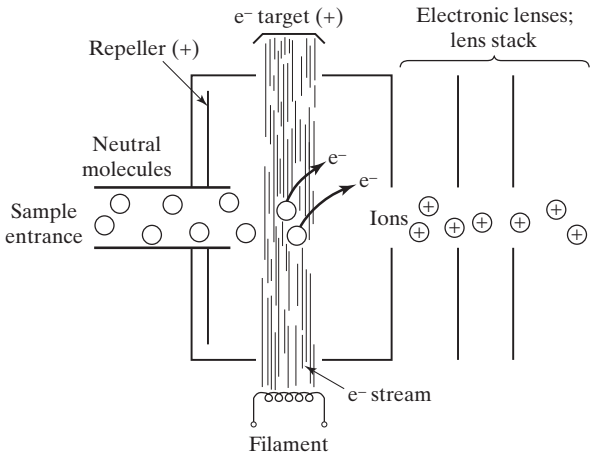

FIGURE 40 The inlet, ionization region, and lens stack of a typical mass spectrometer. The mechanism of ionization shown here is electron impact (EI).

Under standard EI conditions (70 eV), compounds are identified through the mass fragmentation pattern, library matches, and traceable standards. Key to identification is reproducible and controlled instrumental conditions. Electronics must be set such that patterns are reproducible in and across instruments. This is done by an internal calibration or tuning procedure in which a standard compound, usually perfluorotributylamine **(PFTBA)**, is introduced into the mass spectrometer and settings are adjusted or tuned until the resulting mass spectrum meets the required criteria of masses detected and relative abundances. The standard forensic library is the NIST/EPA/NIH Mass Spectral Library, which was acquired under instrumental conditions for PFTBA. Because the electronic settings alter mass intensities, if an instrument is out of tune (i.e., if it cannot produce a PFTBA spectrum with the required mass peaks and intensities), any calibration curves obtained under those tuned conditions have to be redone.

3.3 ICP-MS

For elemental analysis, particularly of the metals and semimetals, a mass spectrometer has obvious appeal; the challenge is in ionizing the sample prior to introducing it into the quadrupole (or other mass filter). The solution was the development of **inductively coupled plasma (ICP) torches**, which were described in the 1970s and became available as ionization sources for mass spectrometers in the 1980s. A schematic of an ICP torch is shown in Figure 41. Within the torch, there are three concentric quartz tubes. Argon flows through the tubes as shown, consuming several liters a minute of the gas. At the top of the torch are water-cooled induction coils that are powered by a radio frequency generator. The torch is ignited by a spark from a Tesla coil, which generates ions that then flow through the rapidly oscillating magnetic field generated from the coil. Frictional and collisional interactions heat the plasma (consisting of Ar^+ and electrons) to temperatures in excess of 6000 K. Sample that flows with argon through the center of the coil experiences temperatures of ~6500 K, resulting in rapid de-solvation, dissociation, atomization, and ionization.

The plasma stream cannot be directed into the mass spectrometer owing to the high temperature and flow rates. Thus, the design of the interface region is a primary technical challenge in ICP-MS. As shown in Figure 42, a differentially pumped design is used. The plasma is directed onto an orifice into a region that is maintained at a vacuum of about 1 torr. The sample cone allows a small stream of the plasma to enter, where it then passes through a second orifice called the skimmer cone and on into the high vacuum region. The beam is focused by a series of electronic lenses, some of which may direct the ion beam **off-axis**. This reduces the number of neutral species in the beam.

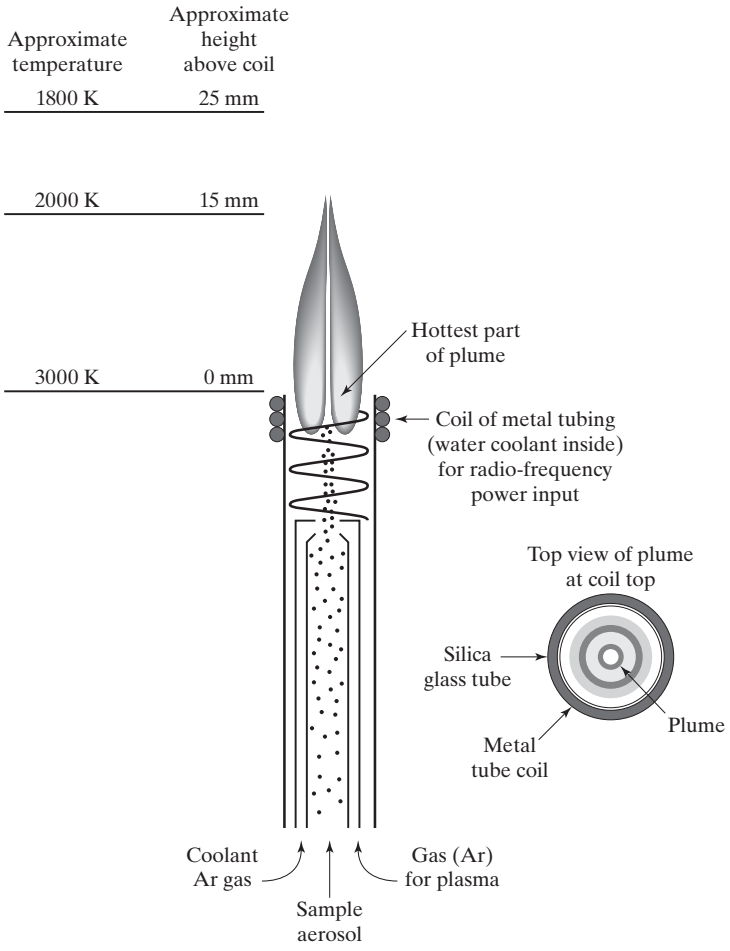

FIGURE 41 A plasma torch for ICP. A radio-frequency generator ionizes argon in the tube and accelerates the ions, maintaining heat by sustained collisions. Once the generator is off, the plasma stops forming.

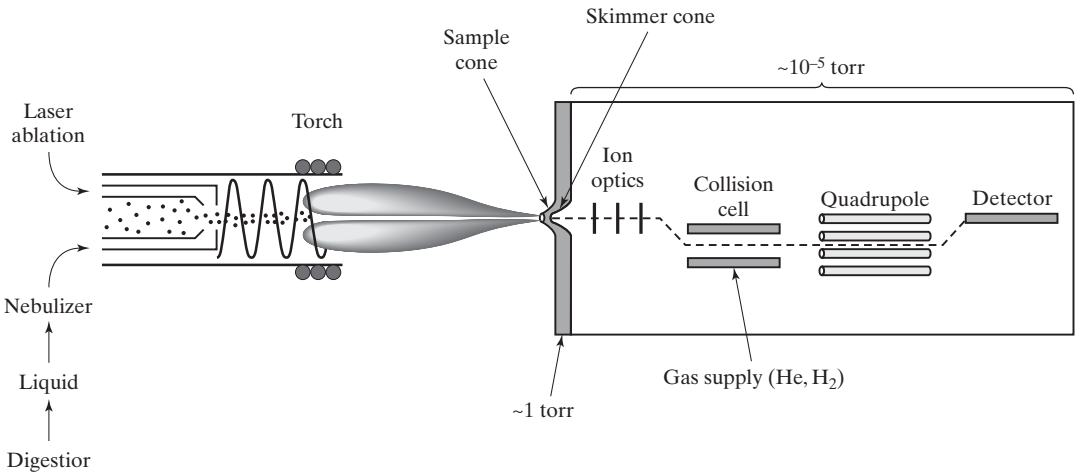

FIGURE 42 Schematic of a generic ICP-MS instrument. Sample can be introduced into the torch via pumping of liquid samples or by laser ablation. Note the collision cell is off-axis.