4.2. IR INSTRUMENTATION

Until the early 1980s, most IR spectrometer systems were double-beam dispersive grating spectrometers, similar in operation to the double-beam system for UV/VIS spectroscopy described in Chapter 2. These instruments have been replaced almost entirely by FTIR spectrometers because of the advantages in speed, signal-to-noise ratio, and precision in determining spectral frequency that can be obtained from a modern multiplex instrument. There are NIR instruments that are part of double-beam dispersive UV/VIS/NIR systems, but many NIR instruments are stand-alone grating instruments.

The first requirement for material used in an IR spectrometer is that the material must be transparent to IR radiation. This requirement eliminates common materials such as glass and quartz for use in mid-IR instruments because glass and quartz are not transparent to IR radiation at wavelengths longer than 3.5 μm. Second, the materials used must be strong enough to be shaped and polished for windows, samples cells, and the like. Common materials used are ionic salts, such as potassium bromide, calcium fluoride, sodium chloride (rock salt), and zinc selenide. The final choice among the compounds is determined by the wavelength range to be examined; for example, sodium chloride is transparent to radiation between 2.5 and 15 μm. This wavelength range was therefore termed the *rock salt region* when an ionic salt prism was used as the wavelength dispersion device in early instruments. Potassium bromide or cesium bromide can be used over the range of 2.1–26 μm, and calcium fluoride in the range of 2.4–7.7 μm. The wavelength ranges of some materials used for IR optics and sample holders are given in Table 4.3.

The major problem with the use of NaCl, KBr, and similar ionic salts is that they are very soluble in water. Any moisture, even atmospheric moisture, can dissolve the surface of a polished salt crystal, causing the material to become opaque and scatter light. Optics and sample containers made of salts must be kept desiccated. This limitation is one of the reasons salt prisms are no longer used in dispersive IR spectrometers.

4.2.1. Radiation Sources

A radiation source for IR spectroscopy should fulfill the requirements of an ideal radiation source, namely, that the intensity of radiation (1) be continuous over the wavelength range used, (2) cover a wide wavelength range, and (3) be constant over long periods of time. The most common sources of IR radiation for the mid-IR region are *Nernst glowers*, *Globars*, and *heated wires*. All of these heated sources emit continuous radiation, with a spectral output very similar to that of a blackbody radiation source. Spectral curves for blackbody radiators at several temperatures are shown in Fig. 4.5. The normal operating temperatures for IR sources are between 1100 and 1500 K. The range of light put out by mid-IR sources extends into both the NIR and far-IR regions, but intensity is at a maximum in the mid-IR region from 4000 to 400 cm^{-1}.

4.2.1.1. Mid-IR Sources

The two main types of sources for mid-IR radiation are electrically heated rigid ceramic rods and coiled wires.

The Nernst glower is a cylindrical bar composed of zirconium oxide, cerium oxide, and thorium oxide that is heated electrically to a temperature between 1500 and 2000 K. The source is generally about 20 mm long and 2 mm in diameter. The rare earth oxide ceramic is an electrical resistor; passing current through it causes it to heat and glow,

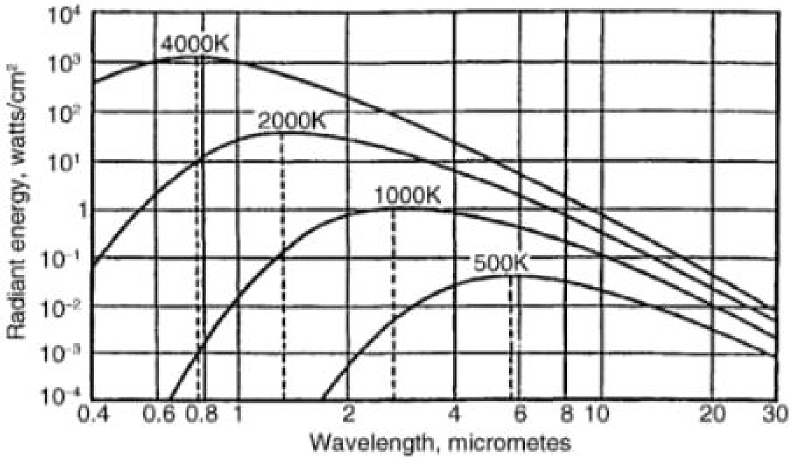


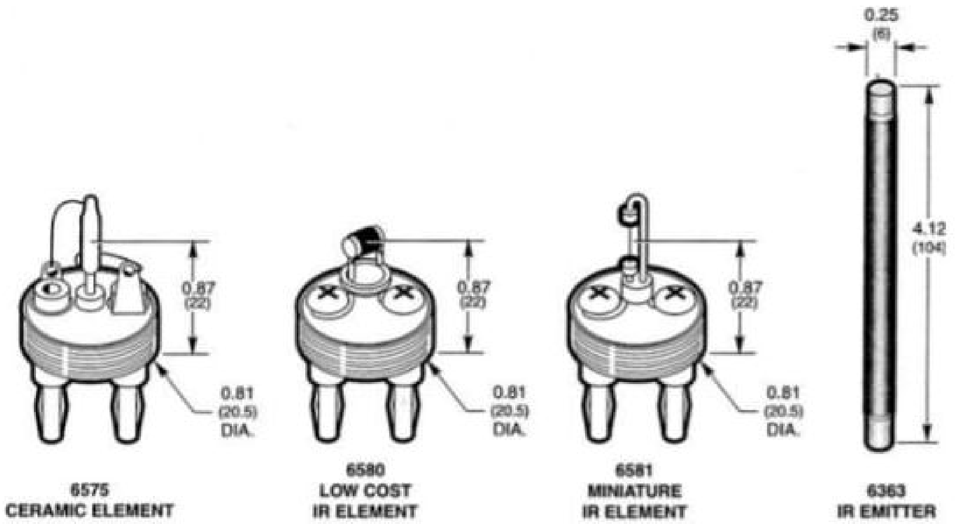
Figure 4.5 Radiant energy distribution curves for a blackbody source operated at various temperatures. (From Coates, used with permission.)

giving off continuous IR radiation. The Nernst glower requires an external preheater because of the negative coefficient of electrical resistance; it only conducts at elevated temperature. In addition, the Nernst glower can easily overheat and burn out because its resistance decreases as the temperature increases. The circuitry must be designed to control the current accurately. A related source, the Opperman, consists of a bar of rare earth ceramic material with a Pt or other wire running coaxially through the center of the ceramic. Electrical current through the wire heats the wire, and that heats the ceramic, providing a source similar to the Nernst glower without the preheating requirement. The Globar is a bar of sintered silicon carbide, which is heated electrically to emit continuous IR radiation. The Globar is a more intense source than the Nernst glower. These rigid cylinders were designed so that their shape matched the shape of the slit on a classical dispersive spectrometer. Modern FTIRs do not have slits, so the geometry of the source can now be made more compact. Commercial ceramic IR sources are available in a variety of sizes and shapes, as seen in Fig. 4.6. Typical spectral outputs from these commercial ceramic sources are compared with a blackbody radiator in Fig. 4.7.

Electrically heated wire coils, similar in shape to incandescent light bulb filaments, have also been used successfully as a light source. Nichrome wire is commonly used, although other metals such as rhodium are used as well. These wires are heated electrically in air to a temperature of ~1100°C. The main problem with these wire coils is "sagging" and embrittlement due to ageing, resulting in fracture of the filament, exactly the way a light bulb filament "burns out". Some coiled wire sources are wound around a ceramic rod for support; this results in a more uniform light output over time than that from an unsupported coil.

Modern sources for the mid-IR region are variants of the incandescent wire source or the Globar, but generally in a compact geometry. Commercial furnace ignitors and diesel engine heaters such as the silicon carbide tipped "glo-plug" have been adapted for use as IR sources because of their robustness, low operating voltage, and low current requirements.

Sources are often surrounded by a thermally insulated enclosure to reduce noise caused by refractive index gradients between the hot air near the source and cooler air in the light path. Short-term fluctuations in spectral output are usually due to voltage fluctuations and can be overcome by use of a stabilized power supply. Long-term changes occur as result of changes in the source material due to oxidation or other high temperature reactions. These



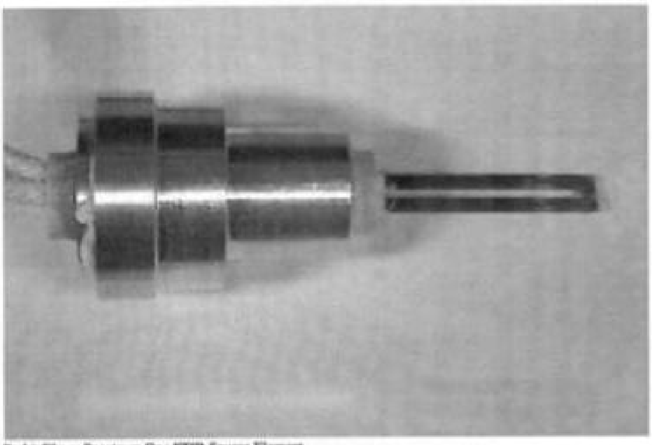


Figure 4.6 Commercial IR radiation sources. (Top) A variety of designs from ThermoOriel. Dimensions given are in inches (mm). Courtesy of Newport Corporation, Irvine, CA (www.newport.com). (Bottom) FTIR source element used in the PerkinElmer Spectrum One instrument. It is made of a proprietary ceramic/metallic composite and is designed to minimize hot spots to the end of the element. Only the last 5 mm on the end lights up. [Courtesy of PerkinElmer Instruments, Shelton, CT (www.perkinelmer.com).]

types of changes may be seen as hot or cold "spots" in the source, and usually require replacement of the source.

4.2.1.2. NIR Sources

As can be seen in Fig. 4.5, operating a mid-IR source at higher temperatures (>2000 K) increases the intensity of NIR light from the source. Operation at very high temperatures is usually not practical, due to the excessive heat generated in the instrument and premature burn-out of the source. For work in the NIR region, a quartz halogen lamp is used as the source. A quartz halogen lamp contains a tungsten wire filament and iodine vapor sealed in a quartz envelope or bulb. In a standard tungsten filament lamp, the tungsten evaporates from the filament and deposits on the lamp wall. This process reduces the light output as a result of the black deposit on the wall and the thinner filament. The halogen gas in a tungsten-halogen lamp removes the evaporated tungsten and redeposits it on the

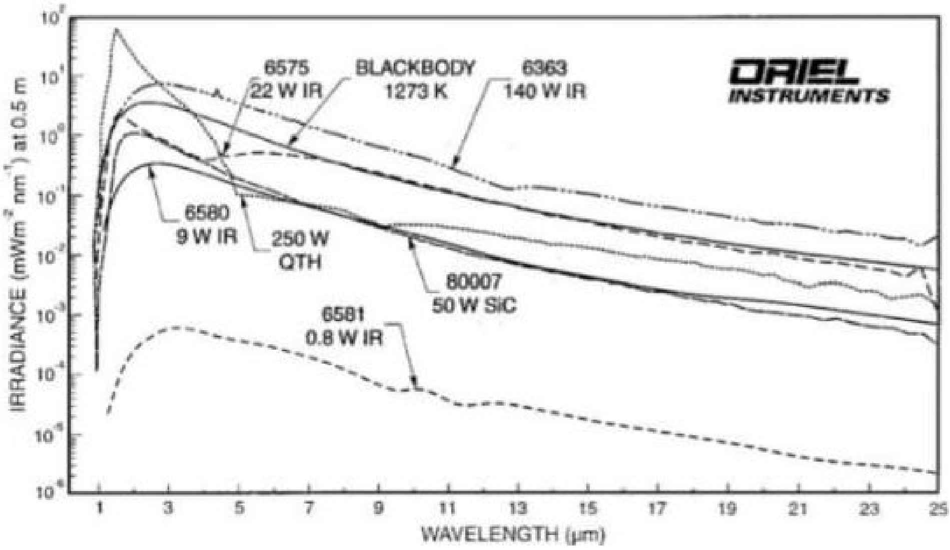


Figure 4.7 Spectral output of a variety of commercial IR radiation sources, including a silicon carbide source (dashed line marked SiC) and an NIR quartz tungsten-halogen lamp (the dotted line marked QTH). A blackbody curve at 1273 K is included for comparison. [Courtesy of Newport Corporation, Irvine, CA (www.newport.com).]

filament, increasing the light output and source stability. The intensity of this source is very high compared to a standard tungsten filament incandescent lamp. The range of light put out by this source is from 25,000 to 2000 cm^{-1}. Figure 4.8 shows typical commercial quartz tungsten-halogen lamps and a plot of the spectral output of such a source.

4.2.1.3. Far-IR Sources

While some of the mid-IR sources emit light below 400 cm^{-1}, the intensity drops off. A more useful source for the far-IR region is the high pressure mercury discharge lamp. This lamp is constructed of a quartz bulb containing elemental Hg, a small amount of inert gas, and two electrodes. When current passes through the lamp, mercury is vaporized, excited,

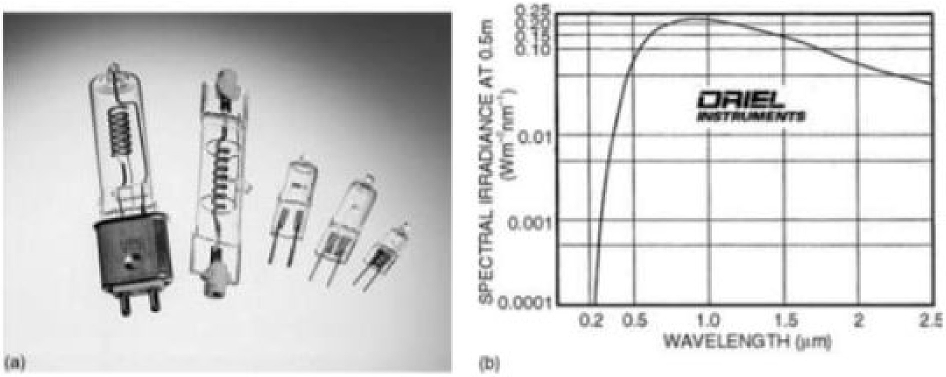


Figure 4.8 (a) Commercial quartz tungsten-halogen lamps for use in the NIR region. The lamps are constructed of a doped tungsten coiled filament inside a quartz envelope. The envelope is filled with a rare gas and a small amount of halogen. (b) The spectral output of a model 6315 1000 W quartz tungsten-halogen lamp. The location and height of the peak depend on the model of lamp and the operating conditions. [Courtesy of Newport Corporation, Irvine, CA (www.newport.com).]

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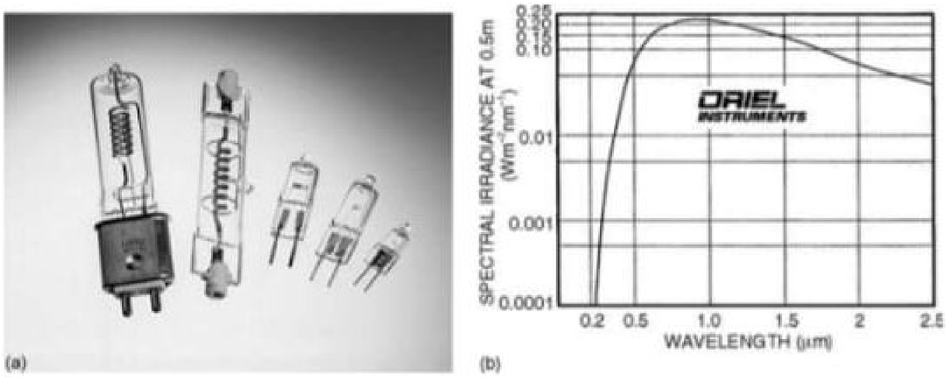

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and ionized, forming a plasma discharge at high pressure (>1 atm). In the UV and visible regions, this lamp emits atomic Hg emission lines that are very narrow and discrete, but emits an intense continuum in the far-IR region.

4.2.1.4. *IR Laser Sources*

A laser is a light source that emits very intense monochromatic radiation. Some lasers, called tunable lasers, emit more than one wavelength of light, but each wavelength emitted is monochromatic. The combination of high intensity and narrow linewidth makes lasers ideal light sources for some applications. Two types of IR lasers are available: gas phase and solid-state. The tunable carbon dioxide laser is an example of a gas phase laser. It emits discrete lines in the 1100–900 cm^{-1} range. Some of these lines coincide with the narrow vibrational–rotational lines of gas phase analytes. This makes the laser an excellent source for measuring gases in the atmosphere or gases in a production process. Open path environmental measurements of atmospheric hydrogen sulfide, nitrogen dioxide, chlorinated hydrocarbons, and other pollutants can be made using a carbon dioxide laser.

Tunable gas phase lasers are expensive. Less expensive solid-state diode lasers with wavelengths in the NIR are available. Commercial instruments using multiple diode lasers are available for NIR analyses of food and fuels. Because of the narrow emission lines from a laser system, laser sources are often used in dedicated applications for specific analytes. They can be ideal for process analysis and product quality control, for example, but are not as flexible in their applications as a continuous source or a tunable laser.

4.2.2. Monochromators and Interferometers

The radiation emitted by the source covers a wide frequency range. However, the sample absorbs only at certain characteristic frequencies. In practice, it is important to know what