MOLECULAR SPECTROSCOPY WORKBENCH

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Common Sources and Signal Processing Techniques Used in Vibrational Spectroscopy

It's holiday time again — Festival of Lights, Christmas lights, New Year's fireworks, and so on. What better topic for this column, then, than light sources for vibrational spectroscopy? (Okay, it's a stretch, but you try being clever every month for five years!) In this column, I continue to describe components available to instrument manufacturers. Of course, there are more specialized or individually fabricated components available, but these are better relegated to later pages under the heading, "Research."

Don't toss out your back issues of *Spectroscopy* just yet, folks. You'll need all the pieces later when I tie all of these parts together. In a subsequent column, we'll look at the puzzle and see how a manufacturer puts all the components into a box to solve your particular problem. I'll use case histories to show how "the right tool is chosen for the right job" (as Mr. Scott stated in "Star Trek IV").

As I've said before, it is wasteful to build the most sensitive (read "expensive") research-grade instrument to measure water in methanol. It is equally silly to try to perform research with a twenty-year-old dispersive model that only cost $5000 new. Let's look at some more pieces of the puzzle. There aren't quite as many sources as there are means to detect and crunch infrared (IR) radiation, so sources are a good starting point for this epistle.

RADIATION SOURCES

While you may never be called on to actually choose the source type for your instrument, knowing the rationale behind a manufacturer's decision can be helpful. Sources for vibration, rotation, and bending are essentially pseudo-blackbody radiators. They are heated to 1500–2000 K and emit light between 1000 and 15,000 nm (or 10,000 and 667 cm^{-1}). The maximum intensity at these operating temperatures is between 1700 and 2000 nm (5900 and 5000 cm^{-1}). The shape of the intensity curve is somewhat asymmetric, with a gradual falloff toward the longer wavelengths to about 1% of maximum at 15,000 nm. A steeper falloff is seen toward shorter wavelengths with the minimum occurring at about 1000 nm. The reduction is related approximately to the fourth power of the wavelength.

The main variations in the sources are based on cost, range of maximum intensity, and instrument lifetime. Ease of replacement and cost are often the two main factors in choosing a source. The monochromator will also dictate certain parameters for light sources: interferometer and diode array–based instruments are single-beam spectrometers and demand extremely stable sources. Most dispersive instruments are dual-beam, wherein small drifts may be tolerated.

Incandescent wire. A closely wound spiral of Nichrome wire around a ceramic core is a low-intensity yet durable source. At temperatures of 1100 K, a black oxide coating is formed and acts as a blackbody. That is, throughout the range of emitted radiation, a continuum of energy exists. No cooling is required other than radiation losses to ambient. This source is rugged and long-lived enough for classroom or quality-control instruments and is decidedly simple to replace.

Because the wire is sturdy albeit not very intense, it is recommended for in-process, filter-type and nondispersive spectrometers. The initial low energy is further diminished if gratings and mirrors are used, thus the simpler applications. A rhodium wire heater sealed in a ceramic cylinder may be used in all the applications recommended for Nichrome and will have similar characteristics. There is definitely a trade-off in cost versus intensity for these two sources.

Nernst glower. The Nernst glower consists of a cylinder of rare earth oxides (zirconium, yttrium, and thorium) 1–3 mm wide and 2–5 cm long. The glower is heated through platinum leads sealed in the ends of the cylinder and is fairly fragile. The glower has a negative temperature coefficient of electrical resistance. That is, as it is heated, the resistance to current goes down. In fact, an external heater is required to lower the resistance before the material can conduct enough current to heat itself.

This necessitates a circuit with a current-limiting device, otherwise burnout will occur. The glower may be operated between 1200 and 2000 K and may be twice as intense as the other sources described here. The higher temperature necessitates ventilation, but the glower must be protected from drafts, because the poor conductivity of the oxides causes stress fractures with rapid cooling.

Glowbar. A glowbar consists of a silicon carbide rod ~5 cm long × 5 mm in diameter. The advantage of the glowbar is its positive coefficient of resistance, allowing simple control of intensity and temperature. Unlike the glower, it needs no booster. One drawback is that the electric contacts of the glowbar need water cooling to prevent arcing, adding to the complexity of any unit it fuels.

The spectral output of the glowbar is ~80% that of a theoretical blackbody radiator. It is a better choice than the glower below 5000 nm and beyond 15,000 nm. It has been used out to 50,000 nm (200 cm^{-1}).

Mercury arc. Simple blackbody sources lose enough intensity beyond 200 cm^{-1} that other types must be used in the far-IR range. High-pressure mercury arc lamps, jacketed with extra layers of quartz for thermal stability, produce intense energy in the far-IR. The overall output is similar to other blackbodies, but the plasma created by the arc through the mercury vapor emits fairly large amounts of long wavelength radiation.

Incandescent lamps. Using a filament composed of tungsten, incandescent lamp sources are used primarily for near-IR work. The output is mostly between 780 and 2500 nm (12,800 and 4000 cm^{-1}). Most commercial near-IR instruments use this source, as it is reliable for 1000 to 2000 h of continuous use and is quite inexpensive. Because this type is similar to car headlamps, high-quality units may be produced for about \$100.

As with any other source, the intensity may be increased by increasing the voltage. The maximum wavelength is blue shifted with increasing temperatures, and lamp life is shortened in the process. Because most near-IR instruments are single-beam types, careful voltage regulation is required. This is mandated by the low noise inherent in near-IR detectors — they will see defects in lamp intensity immediately.

LASERS

Tunable laser diodes. A direct offspring of the fiberoptics communication age, tunable laser diodes are solid-state creations. They are mostly used in nondispersive spectrometers in process environments to monitor a small number of specific components. The laser diode emits radiation over a very narrow band of wavelengths at surprisingly high intensities.

Because common tunable diodes are used at cryogenic temperatures, the wavelength emitted may be selected by varying either the diode current or the operating temperature. This sensitivity demands careful temperature control and voltage stability.

Carbon dioxide lasers. Tunable CO_2 lasers have been used for measuring concentrations of atmospheric pollutants and various species in water. The CO_2 laser produces radiation in the 9000–11,000-nm range (1100–900 cm^{-1}), consisting of ~100 closely spaced discrete lines. These lines are extremely strong and pure and, at the same time, occur where many materials have absorption bands.

Some typical applications of a tunable laser source are for ammonia, butadiene, benzene, ethanol, nitrous oxide, and trichloroethylene. The power is amenable to the extremely long pathlengths used in environmental monitoring. The source and detector may be separated by many meters, allowing for incredibly low concentrations of materials to be quantified and qualified.

ASSORTED AND SUNDRY ELECTRONICS

Two things that most transducers (a transducer is a device that transforms a physical or chemical change into an electric signal) have in common are 1) a small signal output and 2) a continuous or analog output. One or both of these conditions must usually be changed before useful information is obtained from an analytical instrument. That is, the signal must be amplified and/or digitized for an integrator or computer to crunch the numbers.

We will examine these two steps as if they were independent, although anyone who has ever turned a radio louder because of static knows that the static also becomes louder. The last thing, then, that one needs from an amplifier is additional noise. This is another area where price versus performance comes into consideration. We'll look at some components used in the signal processing of instruments and then look at S/N enhancement techniques.

Operational amplifiers. Don't look now, but we don't use tubes in our equipment anymore — everything is solid-state electronics. We won't bother with the theory of transistors and other solid-state electronics and will instead jump right to integrated circuits. Integrated circuits and components such as operational amplifiers (op-amps) are used in place of discrete transistors, resistors, and capacitors.

A simple comparison circuit, seen in Figure 1, uses a single op-amp for both detectors. The meter can easily be replaced by any other measuring device. The point here is that any "noise" the detectors produce or any stray radiation they pick up is simply amplified without discrimination.

An op-amp used for mathematical operations (for example, logarithms, as seen in Figure 2) also passes along noise without filtering effect. To understand how a filtering device (passive or active) may be added to eliminate much of the noise present in a signal, the nature of the noise must be reviewed. Without going into much detail, the common noise(s) may be either low or high frequency and of short or long duration. In other words, noise varies all over the playing field. How, then, might it be avoided?

Let us assume that some of the line current at 60 Hz is being picked up by the detector. Compared with the typical frequencies observed in the IR, this is low. A simple capacitance/resistance (CR) circuit, as shown in Figure 3, will passively and effectively block signals below a frequency determined by the values for R and C. It is called a *high-pass filter*.

High-frequency noise, possibly generated by a high-speed motor or rf source, may be blocked by a resistance/capacitance (RC) circuit, as seen in Figure 4. Again, by choosing proper values for R and C, high-frequency signals are effectively blocked. This type is referred to as a *low-pass filter*. A combination of high- and low-frequency interferences may be treated with an impedance/resistance (LC) circuit, as seen in Figure 5, and is called a *band-pass filter*.

A simple, active filter may be affected by periodically sampling the same portion of a signal over a fixed interval. It then averages the samples using a low-pass filter. This device, a boxcar integrator, provides reasonably good S/N enhancement.

Digital electronics. All of the above manipulations are on the raw, or as-is, signal. The signal arising from most detectors is continuous, whether or not the beam is modulated or chopped. Computers and integrating devices work on discrete points of data. To turn a continuous or analog signal into a series of pulses or a digital signal, an analog-to-digital converter is used.

This is simply a device that samples a signal at predetermined intervals for predetermined periods of time. The time intervals are usually chosen to provide the maximum amount of useful infor-

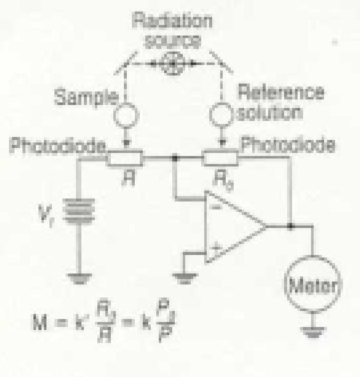

Figure 1. A simple comparison circuit with a single op-amp for both detectors.

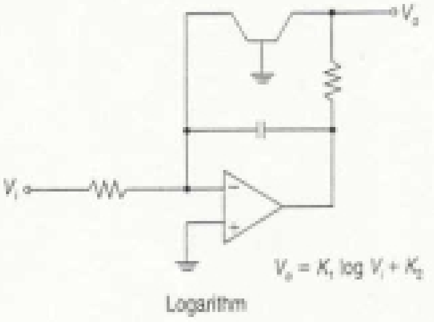

Figure 2. An op-amp used for logarithms.

mation using the minimum amount of computer space and time. If an interferometer is being used to generate a signal, it is obvious that a rapid sampling rate is required to avoid losing important portions of the spectrum. If a chemical process is being followed, often data points may be up to minutes apart. Once the sampling rate has been optimized for the measurement, further noise reduction may be used.

Ensemble averaging. Used in all forms of science, the concept of ensemble averaging is based on the statistical assumption that noise, like assay errors, is random. The reason we perform titrations in triplicate is to assure random error averaging and to minimize its effect.

In ensemble averaging, the same signal (for example, spectrum) is measured *n* times and co-added point by point. The summed signal is then divided by *n* and used. If the noise is truly random, the signal will cause "destructive interference" and the signal will "constructively interfere," significantly enhancing the S/N

The limit to this technique is that the noise is diminished by roughly $\sqrt{n}$ (barring chemical or physical interferences, carbon dioxide or water in the path of a single-beam instrument, or detector drift). Thus, to halve the noise generated by 10 co-added scans, the instrument must scan 100× and co-add the results.

Smoothing (weighted digital filtering). Assigning different levels of importance (weights) to points as a function of their position relative to the central point of a moving average may produce better filtering than mere co-adding or equally weighted moving averages.

The number of times smoothed and the relative weightings are open for discussion, but most statisticians agree that the procedure works. The smoothing usually occurs after the signal has been captured, because it usually takes longer than scanning the data.

Boxcar averaging. For situations in which the signal changes relatively slowly with respect to, say, wavelength, this procedure is worth trying. In some IR spectra of liquids or near-IR spectra of almost anything, the peaks are wide and relatively featureless. Loss of resolution is balanced against loss of noise.

In this process, also called *n-point averaging*, equally spaced groups of data points or "boxcars" are averaged and replaced by a single data point. The resultant spectrum is simplified by the number of points in each boxcar (for example, ⅙ as large if the boxcar contains six points). The enhancement of the S/N is calculated by the equation

$$S/N = \sqrt{n}\,(S/N)_0$$

where $(S/N)_0$ is the signal-to-noise ratio of the untreated data and *n* is the number of points averaged in the boxcar.

The cost of S/N enhancement is loss of resolution. Only by using enhanced data in real situations to predict analyte values can the "correct" amount of averaging be determined.

Fourier transformations. This is the heart of interferometric-based instruments, but may be used with "normally" generated data as well. One common application is in collecting spectrophotometric data at a much greater than normal rate. In essence, data are rapidly collected in the time domain and converted to the conventional frequency domain.

Because spectra are gathered so rapidly, smoothing is more easily performed on multiple scans. Conventional signals may be converted by a Fourier transform (FT) operation, the signal modified as needed, then an inverse FT converts it back to a usable signal.

This column is not the place for detailed math treatments, but an example of an FT pair is

$$F(\nu) = \int_{-\infty}^{\infty} f(t)\, e^{-i2\pi\nu t}$$

(frequency-amplitude function)

$$f(t) = \int_{-\infty}^{\infty} F(\nu)\, e^{i2\pi\nu t}\, 2\pi\, d\nu$$

(time-amplitude function).

The most common functionality is based on cosines, for example:

$$f(t) = A \cos 2\pi \nu_0 t$$

but may include square waves of most common repeating forms.

SUMMARY

Many types of detectors are available for the infrared spectrum. Manufacturers have to balance lifetimes with cost and ease of operation. In multiple-process monitors, it is necessary to choose a durable instrument, but the cost of a large number of instruments cannot make the process nonprofitable. In a laboratory setting, an analyst might well choose the best available instrument, because he or she will normally only have the one instrument for method development and QC use. These facts must be taken into consideration in the initial engineering of equipment.

We also see that a number of commonly used data treatments are used to enhance the accuracy of the data. These will also depend on the type of work being performed. After we discuss monochromators in next month's column, we'll tie all these components together.

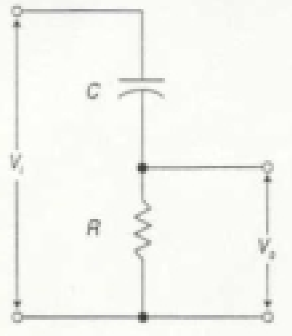

Figure 3. A high-pass filter, or simple capacitance/resistance circuit.

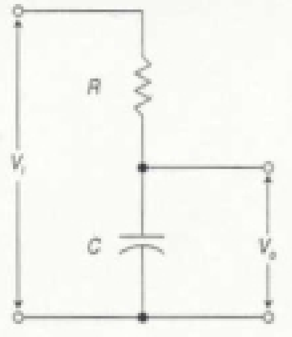

Figure 4. A low-pass filter, or simple resistance/capacitance circuit.

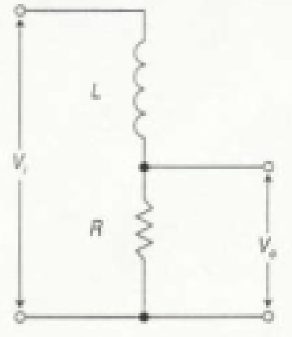

Figure 5. A band-pass filter, or impedence/resistance circuit.

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