White paper: The highs and lows of working with your benchtop spectrometer at extended sample cuvette temperatures

By Jeanne Small, PhD, Chief Information Officer, Quantum Northwest, Inc.

1 Introduction

When a scientist wants to measure spectral properties of a sample at temperatures far removed from room temperature, problems arise. This white paper discusses the issues that come with thermostatting a liquid sample in a cuvette at temperatures other than room temperature.

2 Problem

A standard spectrophotometer for UV-Vis-NIR absorbance or fluorescence comes with a cuvette holder for the liquid sample and often a second one for the reference sample. The cuvette holders are housed in the structure of the spectrometer on a lab bench. "Room temperature" is often cited when specifying the temperature at which a sample was held when a spectrum was measured. For many situations, this is adequate. For sensitive measurements – either because the sample is chemically different at different temperatures, or its spectra are different at different temperatures – it is necessary to control the temperature of the sample to a precisely set value.

Altering the sample temperature of a cuvette holder requires a temperature-controlled circulating water bath (containing water or a mixture of water and another solvent), and a cuvette or cuvette holder that allows the flowing water to directly cool or heat the cuvette. Alternatively, a Peltier cuvette holder can be used. A Peltier unit uses thermoelectric cooling/heating to alter the sample temperature. With a Peltier cuvette holder, the circulating water bath is used to remove heat from the Peltier's heat exchanger rather than directly influencing the temperature of the sample in the cuvette. Air-cooled Peltier units use air rather than liquid for removing heat from the heat exchanger, and have more limited temperature ranges available to them.

Problems arise at both hot and cold temperatures. As a sample in a cuvette gets warmer, bubbles are likely to form in the cuvette. Left in place, they scatter incident light and create artifacts in spectra. Cold samples are problematic at or below the dew point of the ambient air, as condensation forms on the surface of the cuvette. This condensation also scatters incident light, creating artifacts in spectra. As the temperature is lowered, the condensed water may freeze, causing issues with icing on the cuvette holder and subsequent damage to the spectrometer.

3 Solution

Work at any temperature benefits from having the sample in the cuvette stirred gently using a magnetic stirrer built into the cuvette holder and a stir bar placed in the cuvette. This facilitates more rapid equilibration of the sample to the temperature set for the circulating water or Peltier unit. For high sample temperatures, up to +150 °C, magnetic stirring also helps dislodge bubbles that may form inside the cuvette as dissolved gases become less soluble with increasing temperature.

Low temperature work must address the condensation of water on cuvette surfaces that are exposed to the atmosphere. The condensation can be limited by the application of a flow of dry gas (dried air, nitrogen, or argon, for example) to the surface of the cuvette while the sample is chilled. For cuvette holders used inside the sample chamber of a spectrometer, the whole sample compartment can be purged with dry gas.

How low can you go? For low-temperature spectroscopy with a benchtop spectrometer, many factors come into play. With Peltier cuvette holders, achieving low temperatures can be aided by the circulation of precooled liquid through the Peltier heat exchanger. For example, when using ice water at 0.0 °C, Peltier cuvette holders will approach -30 °C or so. To go lower, circulation of precooled fluids below 0.0 °C is required. The use of 30% methanol-water as the circulating liquid is recommended, since it has ample heat capacity and low viscosity, permitting adequate flow through the heat exchanger. It should be possible to achieve a sample holder temperature about 25 °C lower than that of the circulating fluid.

The final consideration for achieving high and low extended temperatures with a benchtop spectrometer is the amount of insulation that can be positioned around the cuvette holder without obstructing the light beam in and out of the cuvette, and while maintaining normal operation of the spectrometer itself. Typically, spectrometer manufacturers do not provide either the insulation or the guidance on how to craft a well-insulated sample chamber for their products. This is left to the operator, and is often the final factor on whether or not an extended temperature can be reached. Creativity is required in using foam packing material or other foam products, often with tape and rubber bands, to provide the insulation required for the temperature desired.

4 Application to Quantum Northwest Products

Quantum Northwest's Peltier cuvette holders provide not only temperature control, but also stirring and dry gas purging.

Extended temperature spectroscopy ranges are available for UV-Vis-NIR absorbance, fluorescence, fiber optic, flash photolysis, photoacoustic and circular dichroism applications:

- Versa 20 family of products for UV-Vis-NIR spectrophotometry
- Luma 40 and TLC 50 Legacy families of products for fluorescence spectroscopy
- qpod cuvette holder for fiber optic spectrometers
- Flash 300 stand-alone device for laser flash photolysis and pulsed-laser photoacoustics
- CD 250 cuvette holder for circular dichroism spectrometers

These cuvette holders can be specially built to extend their temperature ranges from their normal range of -40 to +105 °C. Choosing the extended temperature option – denoted by /E – extends this control range to -55 °C to +150 °C. This requires the use of materials that are stable at the high and low temperatures, sensors with extended range, and design details that protect the delicate magnetic stirring motors. The Versa 20, Luma 40 and Flash 300 can be provided with windowed jackets to trap dry gas around the cuvette, thus greatly extending their range downward.

The lowest measured temperature reached to date at Quantum Northwest's manufacturing facility in Liberty Lake, WA, USA, was -52.7 °C with an extended temperature Flash 300/E, considerable added insulation, and circulating fluid of -20 °C. This is short of the -55 °C claimed for the extended temperature (/E) products. Why is this?

In short, with an extended temperature product, the user can send a control command to the unit to go to -55 °C; but, whether the unit will actually go to -55 °C depends on whether cold circulating fluid is used, and how well insulated the sample holder is. This situation is analogous to trying to chill a room to 15 °C with a powerful air condition unit, but if the user keeps the windows open on a hot summer day, the room will not likely get to 15 °C. The scientist's ability to customize and maximize the foam insulation around the cuvette holder is usually the key determinant to achieving low temperature spectroscopy without specialty cryogenic devices.

5 CONCLUSION

Sample temperatures from -55 °C to +150 °C are possible in a standard benchtop spectrometer. Magnetic stirring is required for extended temperature work. The temperature of the circulating water bath needs to be controlled, and it may be necessary to blend the water with another solvent such as methanol to reach the required temperatures. For cold temperature work, dry gas must flow onto the surface of the cuvette to reduce condensation and ice build-up, and additional insulation must be added to surround the cuvette holder without obstructing the light beam.

For Quantum Northwest Peltier products that operate at extended temperatures, the following temperatures are achievable under the approximate conditions:

5 °C – lowest temperature in the open air (with typical humidity), no dry gas flow;

-10 °C – lowest temperature in an exposed environment but with dry gas flow;

-25 °C – lowest temperature in an enclosed, dry environment, with 0 °C circulating fluid;

-40 °C – lowest temperature with a windowed jacket surrounding the cuvette holder, -15 °C circulating fluid, some added insulation;

-55 °C – lowest temperature with a windowed jacket surrounding the cuvette holder, -30 °C circulating fluid, and maximum added insulation.