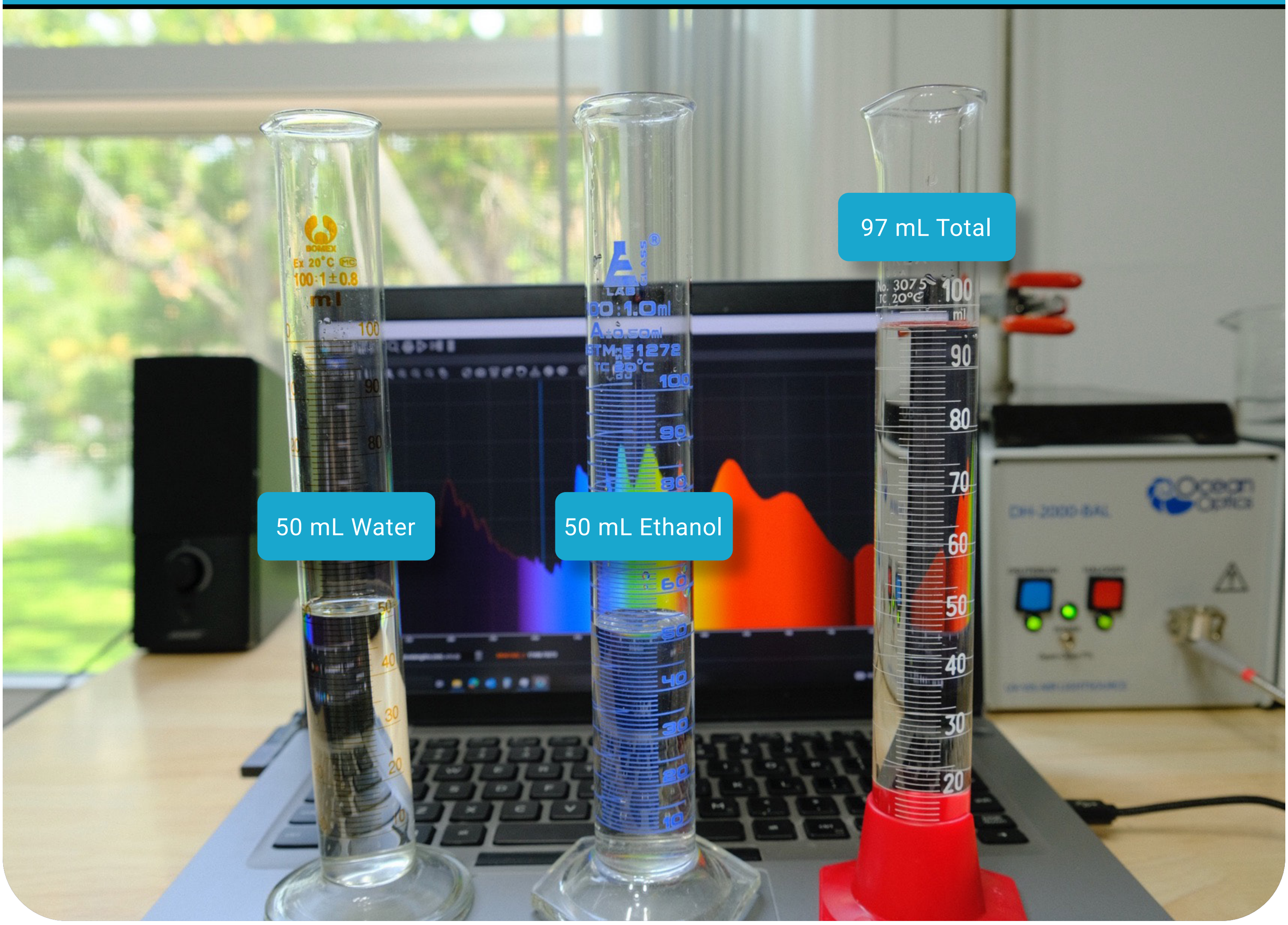
Volumetric Accuracy with Broadband Spectroscopy

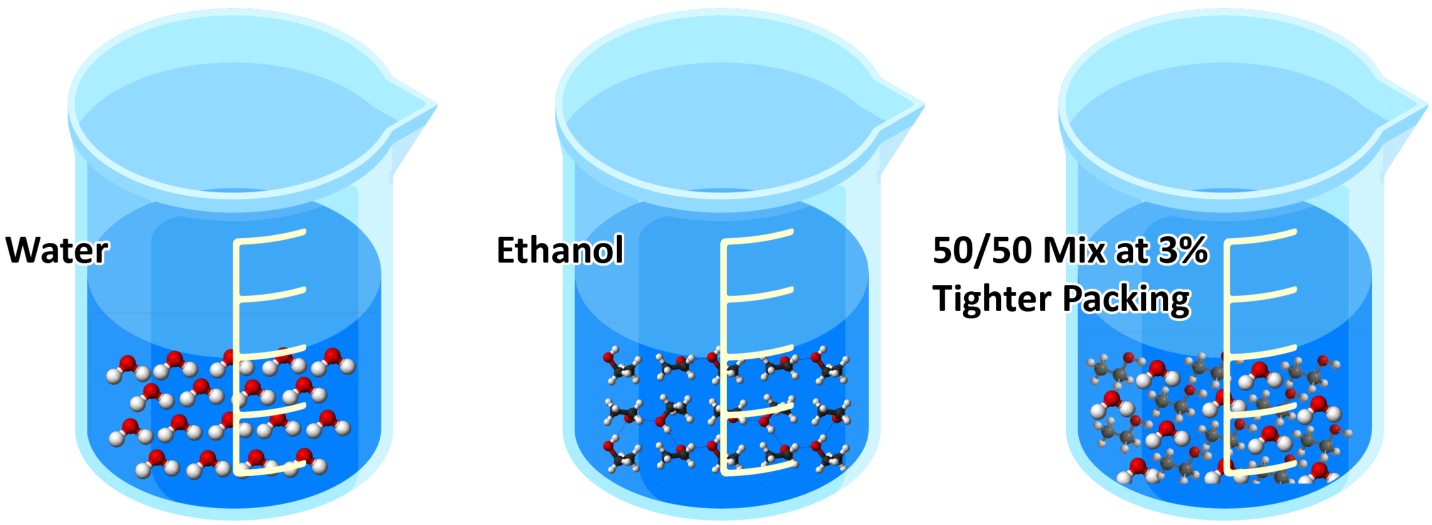
Detecting Subtle Deviations in Water Composition



50 + 50 = 97. This isn't just how we tally our golf scores—it's scientifically accurate! And you can test it yourself by mixing 50 mL of water with 50 mL of ethanol.

So what's going on here? Are we just losing those 3mL in the transfer? That's an entire cuvette's-worth of fluid! What's actually happening is a change in molecular packing, where the mix of water and ethanol molecules can fit tighter together like puzzle pieces than they can alone.

OceanOptics



This is a cool phenomenon of physical chemistry where we can see molecular interactions on a macroscopic scale.

Physical Chemistry Meets Analytical Chemistry

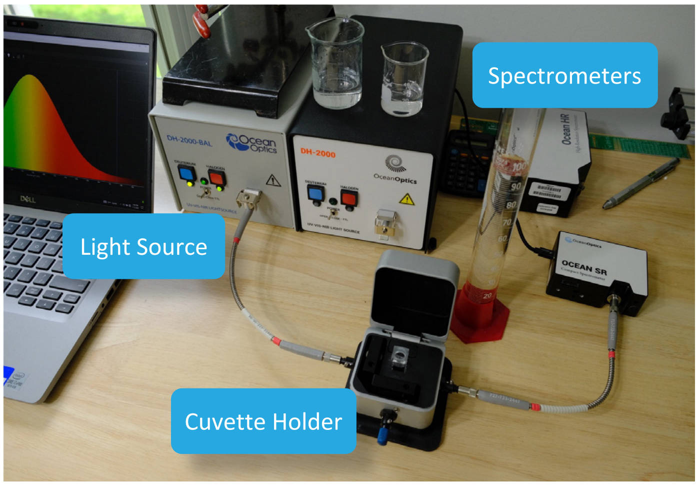
But what if we wanted to make a solution of 50vol% ethanol in water? A high school chemistry student would likely do what we just did above, mixing 50 mL with 50 mL and calling it a day. But a good analytical chemist knows to fill a 100 mL volumetric flask with 50 mL solute (in this case ethanol) and Q.S.* with solvent (in this case water).

We know from our 97 mL result that it will take more than 50 mL water to get up to 100 mL, so this solution of 50vol% $EtOH_{(aq)}$ will be slightly water-heavy. Shoe on the other foot, a solution of 50vol% $H_2O_{(EtOH)}$ will be slightly ethanol-heavy.

This may seem like a negligible difference, but for processes that require exact concentrations to achieve optimized yields, such as pharmaceutical syntheses, getting this right is critical. UV spectroscopy offers an instant way to differentiate these solutions and determine their precise concentration.

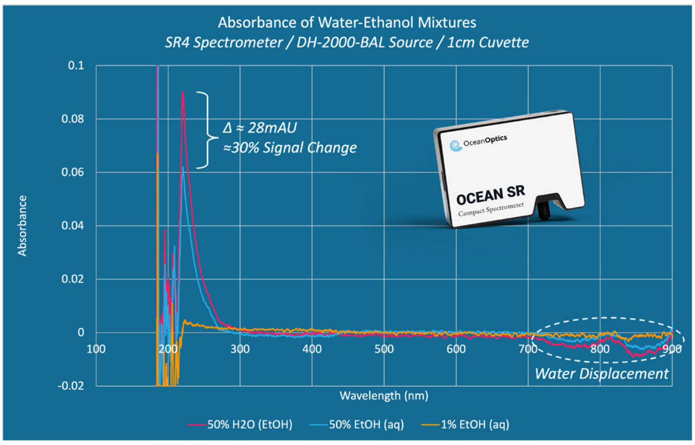
Experimental Setup

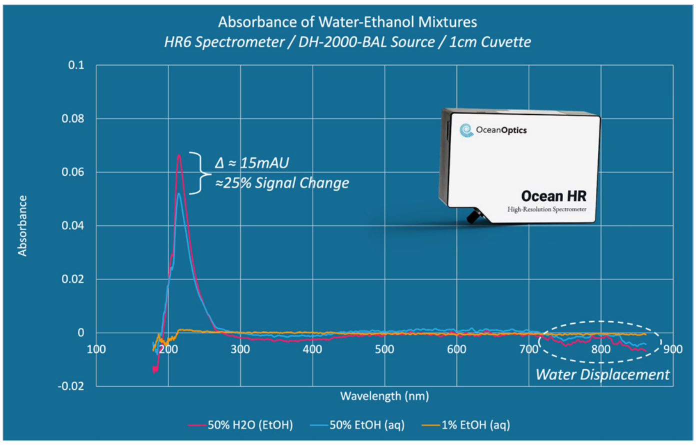
We made the two 50vol% solutions described above, along with a 1vol% $EtOH_{(aq)}$ standard for comparison, and we observed these in a 1cm quartz cuvette. A broadband deuterium-halogen source was used to get clear absorbance signals well down into the 200 nm range. Readings were taken with both the SR4 and HR6 spectrometers; the SR4 is known for its high spectral resolution, while the HR6 offers enhanced sensitivity.



Results

Each system showed clear ethanol activity around 220 nm, highlighting the need for the deuterium source.





The peak absorbance for these small changes in ethanol content registered around 25-30% signal change for each system, allowing for clear differentiation of which is which. While these are only milli-absorbance changes, this is well within the operational sensitivities for such a system. The 1% solution registered between 1.5mAU and 4.5mAU for the two spectrometers, showing that each can be used for low-level detection; but this also shows each system requires its own concentration regression to provide accurate correlations between absorbance and ethanol content.

While discussing the UV range, the other obvious difference is the noise seen at the lowest wavelengths, where the SR4 shows more noise than the HR6. This comes back to the sensitivity aspect, since the more-sensitive HR6 can coherently calculate absorbance values at the very low light levels seen at the end of the spectrum, whereas the SR4 struggles to decipher signals below a certain threshold.

Moving up from the UV into the VIS range, we naturally do not see any activity since these are visibly clear fluids. But moving higher into the NIR range we see some dips in the 750-900 nm range that stack like a mirror-flip of our UV trends. This negative absorbance often leads to head-scratching, but it is nothing but the simple displacement of water. Water absorbs in this region, and when we take a reference in pure water this sets everything to zero in absorbance mode. But then as we add ethanol (or any other non-water species) in our limited 1cm pathlength, this displaces some of the water's real estate and we start seeing negative values in that range. Some researchers see this as an annoyance or unwanted artifact, but it can serve as an extremely useful secondary indicator of impurities that are not optically active elsewhere in your spectrometer's range. If you can't see the impurity directly, you can at least see that something is there displacing the water.

Conclusion

Analytical chemistry is all about getting things right to the smallest detail, and broadband spectroscopy is an invaluable tool to instantly measure at that level of precision. Whether determining exact concentration levels or just checking for trace impurities, these modular systems offer affordable and customizable platforms to accommodate aqueous and non-aqueous samples. Get a handle on your own fluid compositions by chatting with a spectroscopy expert today.

*Q.S. is an abbreviation for *quantum sufficit* or *quantum satis* that's used as a traditional notation meaning "as much as suffices." It's a fancy way to say "fill to the mark" that's rarely used anymore.