# ChemCorrect™

Successfully flag chemical impurities in isotopic water analyses with the unique, information-rich quality data from CRDS

PICARRO

## Introduction

The Picarro L21x0-*i* analyzers are a series of Cavity Ring-Down Spectroscopy (CRDS) instruments that deliver high-performance stable isotope data for liquid, vapor and matrixed water samples. CRDS is a laser optical technique especially suited to high precision measurements. The analyzer simultaneously records values for $\delta D$, $\delta^{18}O$ and $\delta^{17}O$ from the optical spectra of specific stable isotopologues of water ($H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$ and HDO). A typical optical spectrum is shown in the figure below.
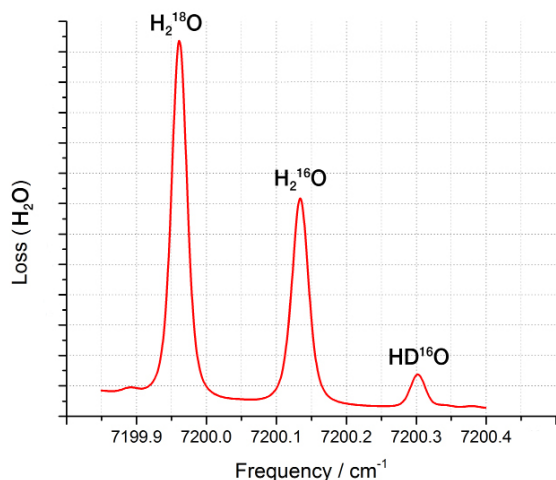


**Figure 1.** Near-IR spectrum of the isotopologues of water used to measure $\delta^{18}O$ and $\delta D$

Fundamentally, CRDS quantifies the optical absorption by measuring the rate of decay (the ring-down curve) of laser light in a cavity containing a gaseous sample. Increased sample concentration leads to faster decay mechanisms (via molecular rotation & vibration) and a faster ring-down time. To measure the delta values, the laser is tuned across the spectrum. At specific spectral points a ring-down curve is collected and once the full spectral range has been scanned, the suite of ring-down curves are then transformed into an absorption spectrum. This signal is significantly more precise that that gained from constant transmission techniques such as FT-IR and OA-ICOS for two reasons. First, only in CRDS is the laser switched off

during data acquisition. This removes the highest source of noise in laser spectroscopy and thereby substantially improves signal sensitivity and stability. Second, CRDS acquires data in the time domain, a more precise measurement than available in the frequency domain. This level of performance enhancement results in incredibly stable spectra as well as highly quantitative concentration and isotopic analyses. The ease-of-use, lower cost, small footprint, and reliable performance have made these instruments an appealing alternative to Isotope Ratio Mass Spectrometers (IRMS), previously the only existing technique for such analyses. Picarro CRDS water analyzers and other laser optical systems have rapidly found success in geoscientific applications such as 1) ice core for paleoclimatology, 2) surface, groundwater, and rain water for hydrology 3) seawater for oceanography.

## Contamination Irregularities

However, as geoscientists expanded the applications and the types of water analyzed through such devices, they encountered the potential issue of organic interferences that could compromise the isotopic measurement. Indeed, it was shown in peer-reviewed publications[1],[2] that certain organics, including some of those found in plant water, can shift the baseline of the water spectral curve or have their own spectral features which overlap with a water characteristic resulting in deviation of the $\delta D$, $\delta^{18}O$ or $\delta^{17}O$ isotopic reading. The ability of a spectrometer to record shifts or features from all molecules in a sample is a ubiquitous feature of molecular spectroscopy. Such molecules can fall into one of the following three categories, based on the nature of the distortion to the optical spectrum:

1.  Typically, larger compounds of >8 atoms do not affect the isotopic water spectrum (at concentrations up to 10-20% of the water sample). In the presence of these contaminants, Picarro analyzers will report accurate and precise isotope values without bias or increase in noise.

[1] Brand et al., Cavity ring-down spectroscopy versus high-temperature conversion isotope ratio mass spectrometry; a case study on delta (2)H and delta (18)O of pure water samples and alcohol/water mixtures, 2009, Rapid Comm. in Mass Spec: RCM . DOI:10.1002/rcm.4083

[2] West et al, Discrepancies between isotope ratio infrared spectroscopy and isotope ratio mass spectrometry for the stable isotope analysis of plant and soil water, 2010, Rapid Comm. in Mass Specs: RCM . DOI:10.1002/rcm.4597

2. Compounds with about 6-8 atoms can contribute a broad, spectrally unresolved absorption baseline beneath the target molecules. To first order, this baseline shift will cause no systematic bias to the reported values. Because optical absorption is a linear, additive process, the water spectrum will 'float' on top of the contaminant baseline. The linear dynamic range of CRDS makes the technique particularly insensitive to these baseline offsets. In some cases, however, this baseline offset is accompanied by a tilt or curvature of the spectrum with wavelength. This larger offset can cause bias in the measurements and degrade the precision of the instrument.

3. Small compounds (with fewer than 6-8 atoms) may have spectrally resolved absorption lines that can interfere with the lines from the observed water vapor. This can lead to systematic errors in the reported isotope ratios. One example of such a molecule is methanol, which has a particularly complex absorption spectrum in this spectral region and causes particularly large shifts in reported isotope values.

In order to manage these different situations, Picarro developed ChemCorrect, a data interpretation and data processing software program available to users of L21x0 instruments. The data processing aspect manages standards and calibration and will be treated separately. However, ChemCorrect also takes advantage of data derived from the mathematical transformation of the ring-down decay data which can aid in interpretation beyond deriving isotopic values. This mathematical process requires that the recorded data is fit to attributes of a pure water spectrum at a specific gas temperature and pressure. This ensures that spectral line narrowing and other terms, including the baseline constant, slope, tilt are optimized for the application. Hence, the recorded data are acquired at a fixed temperature and pressure also; within +/- 0.005°C and +/- 0.0002 atm. Further, Picarro's wavelength monitor, an in-line optical wavemeter, has a resolution of better than 0.0001 wavenumbers, thereby assuring the frequency position of the measured line to unprecedented levels of accuracy. These two key attributes of the real, acquired data mean that we can generate a highly accurate residual variance of the lineshape and baseline of the measured spectrum compared to that of the pure water spectrum. The higher the residual variance, the greater the likelihood

of underlying contaminating features, either from underlying spectral characteristics of small molecules or from baseline contributions from larger molecules. Constant transmission laser optical analyzers such as FT-IR or OA-ICOS have neither the pressure and temperature control of the Picarro CRDS systems, nor the wavemeter frequency accuracy. Therefore they cannot, with any similar degree of certainty, develop a set of least-square residual data comparing actual versus pure spectra to confirm the presence of potential contaminants.

The specific statistical tests that ChemCorrect uses to determine how those spectral features differ between the samples and the standards are:

- **RESIDUAL:** the root mean squared residual of the least-squares fit to a spectrum, is used to screen for potential small molecule contaminants, e.g., methanol.
- **BASELINE SHIFT:** the spectral baseline is a good early indicator of a potential issue with a sample. The baseline shift term is a change in the constant term of a fitted baseline.
- **BASELINE CURVATURE:** the spectral baseline is also good early indicator of a potential issue with a sample. The baseline curvature parameter is a change in the quadratic term of a fitted baseline.
- **SLOPE SHIFT:** the slope of the spectral baseline, or change in the linear term of the fitted baseline, although not unique is also a useful indicator for moderately-sized molecules, e.g., ethanol, that can interfere with nearby spectral features.

The ChemCorrect software then displays green, yellow and red flags if the data above, acquired from any sample, deviates in a statistically significant way. For example, a red flag can be triggered by any of the following:

- the sample residual being 1.5 σ away from the mean of the standards residual
- the sample baseline shift being 18 σ away from the mean of the standards baseline shift
- the sample baseline curvature being 3 σ away from the mean of the standards baseline curvature

## Conclusion

Picarro's implementation of CRDS provides a suite of tools that not only yields high quality stable isotope data, but also generates data that can be used to assess the potential of interferences from organic contaminated water samples, a well-known and documented concern for users of laser optical systems.