

Plant Water: Accurate Water Stable Isotope Analysis of Organic Contaminated Water

PICARRO

APPLICATION NOTE (AN040) CHEMCORRECT™ MICRO-COMBUSTION MODULE™ (MCM)

Introduction

Picarro's Cavity Ring-Down Spectroscopy (CRDS) instruments have become a globally accepted standard for the analysis of water stable isotopes from discrete liquid water samples, ambient water vapor and water extracted from solid matrices. 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 (LAS) 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. However, as geoscientists expanded the applications and the types of water analyzed through such devices, they encountered interferences from organic molecules that compromised the isotopic measurements. 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 water characteristics resulting in deviation of the δD , $\delta^{18}O$ or $\delta^{17}O$ isotopic reading.

There are two potential methodologies for removing the effect of organics contamination of water samples. First, the spectroscopic treatment of signals attributed to organics. Second, the physical removal of organic compounds. Both possibilities have received significant interest, either alone or in tandem. Neither technique or combination of techniques have yielded straightforward methods applicable to all samples possibly contaminated with organics. However, Picarro has developed two products that are capable of making a significant contribution to scientists' efforts in recording accurate water isotope data from plant waters and similarly composed samples.

ChemCorrect is a software tool that analyzes the spectral features of each sample and uses data extracted from that information to determine whether the analysis is compromised by trace hydrocarbons. This is extremely useful information in deciding whether further methods have to be applied to a sample. Currently, although some spectroscopic information derived from organics in water samples is available to laser spectroscopists, it is not yet convincingly possible to use this data to correct the water isotope delta values for these contributions. Efforts to date have required extremely time-consuming training sets and post data analysis and are generally considered to be too demanding for routine analytical experiments. However, using the data to flag problematical samples is a valid and useful tool for any suspect data set.

The **Micro-Combustion Module (MCM)** is a unique peripheral that oxidizes organic contaminants entrained in the water vapor prior to entering the analyzer. Although several methods to remove organics compounds using,

¹West et al (2010), RCM, 24, 1948-1954

²Brand et al (2009), RCM, 23, 1879-1884

for example activated carbon or solid phase extraction, have been tried none of these methods have yielded organics-free waters. The extraction techniques are generally too specific to catch all organics, or are susceptible to fractionation of the isotopic species. However, combustion of the organics while they are in the analyzer's flow path has been proven to generate satisfactory results for plant water samples.

In this application note, we will describe these unique solutions and their demonstrated efficacy through the analysis of synthetic plant water.

ChemCorrect

Organic contaminants 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 spectrum (at concentrations up to 10-20% of the water sample). Most compounds fall into this category. In the presence of these contaminants, Picarro analyzers will report accurate and precise isotope values without bias or increase in noise.
2. Compounds with about 6-8 atoms that contribute a broad, spectrally unresolved absorption baseline beneath the target molecules. To first order, this baseline will cause no systematic bias to the reported values. Because optical absorption is a linear, additive process, the water vapor spectrum will 'float' on top of the contaminant baseline. The linearity 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.

The **ChemCorrect** software platform derives statistical data from spectral parameters acquired from each sample as part of the process of converting raw ring-down data into the highly accurate, temperature and pressure controlled spectral curves from which all Picarro concentration and isotope data are calculated. During data acquisition, the analyzer calculates both residual fits of the raw data points to the final spectral output, as well as fundamental baseline characteristics such as the slope and curvature to assess data quality. Since the mathematical algorithms that define the data conversion for water isotope measurements incorporates parameters associated with the pure gas species, small organic molecules can contribute an appreciable and measurable difference in peak width and height compared to those of pure water. Larger organic molecules will noticeably affect the baseline. These changes will be apparent in the residual fit and baseline parameters calculated for these organic-contaminated samples compared to the standard water samples in the same run (the residual and baseline data are also available to all customers as part of our standard data file). For ChemCorrect we have developed and tested criteria so that deviation from pure water data is accurately calculated and samples with organic impurities are consistently flagged. For example, a red flag can be triggered by any of the following:

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

If a flag is raised, a number of things can be done. First, you can utilize Picarro's Micro-Combustion Module (MCM) to remove those artifacts. Second, try some offline sample treatment methods, such as the use of activated charcoal.

FIGURE 1

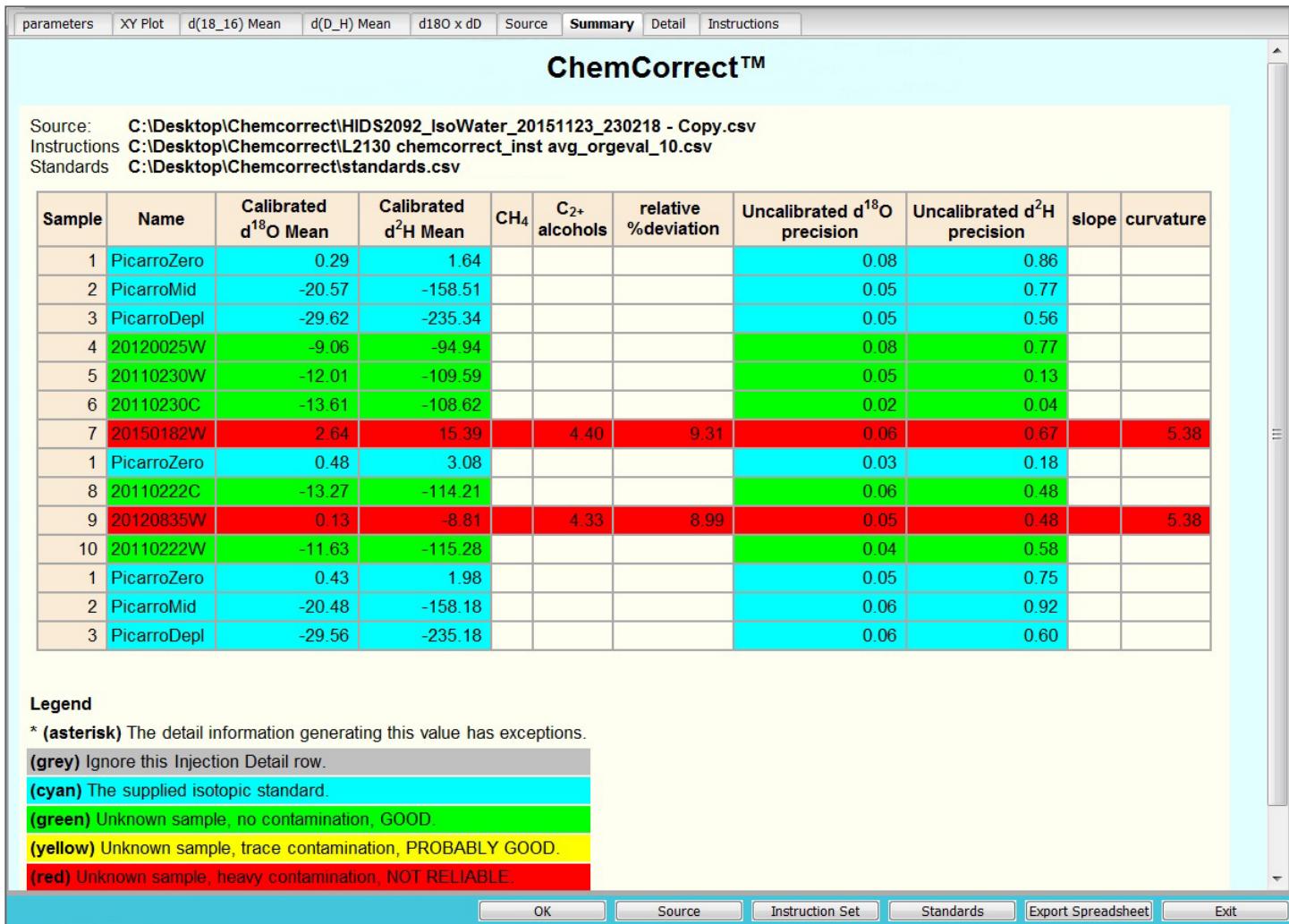


Figure 1. ChemCorrect color-coded output summary. Cyan indicates that the sample is a standard as specified by the user, Green indicates that the sample analysis is valid and does not present any signs of organics contamination, Yellow indicates that the sample contains trace amounts of organics and isotope values are slightly shifted, and Red indicates that the sample analysis is highly compromised by organic contamination.

Micro-Combustion Module

The Micro-Combustion Module (MCM) is Picarro's breakthrough technology that, for the first time, allows scientists to eliminate organic interferences to water isotope analysis in a fully in-line process integrated with sample vaporization and isotope ratio measurements. Installed between the water vaporizer (Picarro A0211) and any L21x0-i series Picarro water isotope analyzer, the MCM provides seamless operation.

The MCM forces all the gaseous phase sample from the vaporizer over an enclosed heated element with air as a carrier gas. The resulting oxidation process efficiently converts the organics into minute quantities of carbon dioxide and nascent water. The element is a self-contained micro-reactor element which can be easily replaced by the customer. The unique design operates with very low-power requirements making it suitable for field deployments.

The MCM has shown to effectively remove spectral interference for commonly occurring alcohols and plant products including multicomponent mixtures of alcohols, terpenes, and green leaf volatiles. It has optimal efficacy for samples containing total organics in concentrations typical for many plant extracts (< 0.35%) due to the

production of nascent water. Higher concentrations of alcohols, such as those found in certain beverages, will not be completely broken down in the MCM. However, the process is highly reproducible and can create high-precision fingerprint data.

FIGURE 2

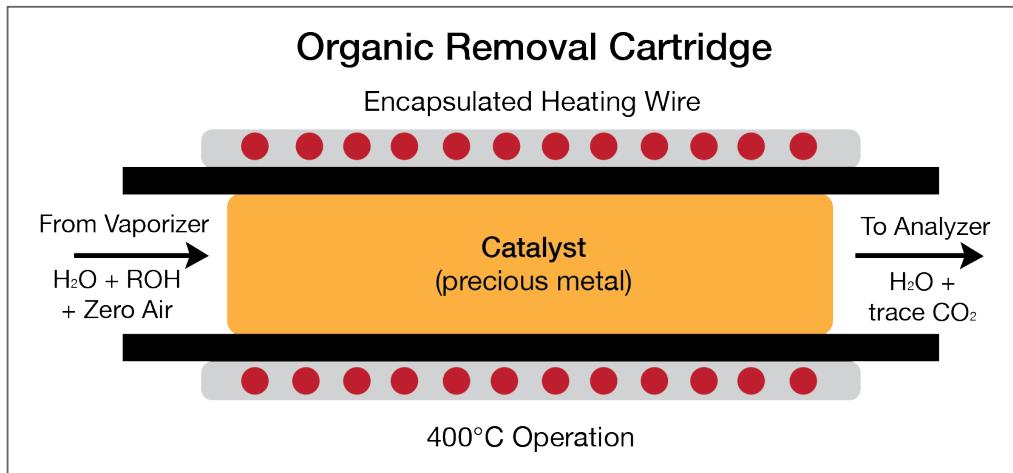


Figure 2. Schematic of the organic oxidation process that occurs within the oxidation cartridge consisting of a quartz tube wrapped with a heating element and filled with the catalytic material. The oxidation reaction converts entrained organic present in the water vapor into H_2O and CO_2 .

1. Experimental Validation

A synthetic plant solution containing a total of 0.348% by volume of organic content was mixed with the following ratios in DI water of unknown isotopic composition (see table 1):

TABLE 1

Components	% in Plant Simulant Solution
Methanol	0.047
Ethanol	0.281
N-hexanol	0.006
Cis-3-hexen-1-ol	0.003
Acetaldehyde	0.011

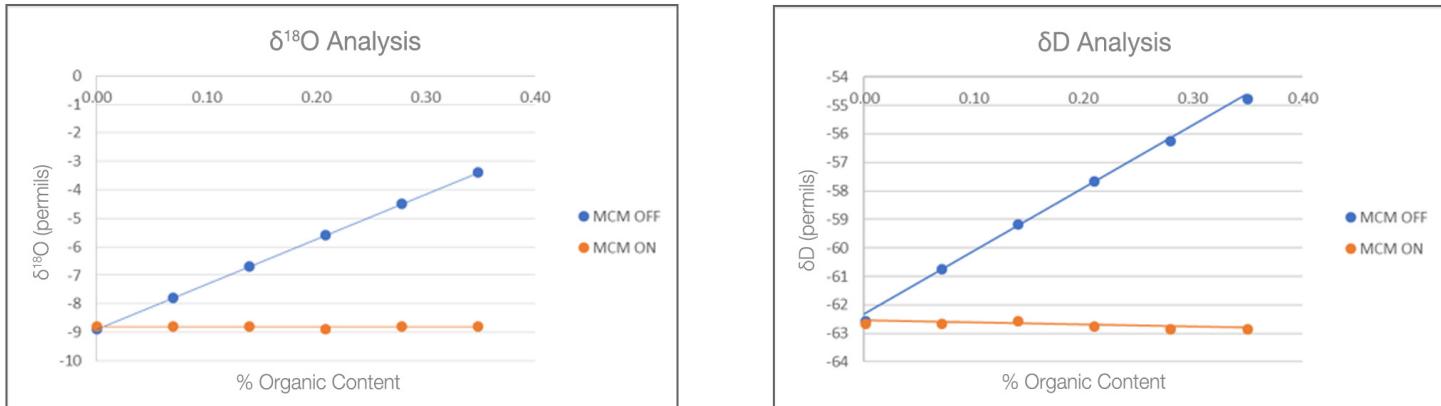
Table 1. List of organic components used in the synthetic plant solution and their volumetric ratios.

Six samples were prepared by diluting further the synthetic plant solution with the same DI water creating organic solutions ranging from 0% to 0.348%.

2. Analysis and Results

The six samples were analyzed on the Picarro water analyzer that included the MCM. The samples were analyzed with the MCM ON to oxidize the organic contaminants and with the MCM OFF (no oxidation).

FIGURE 3



With the MCM turned off, deviations from the isotopic values of the organic-free water increases linearly with the increase of the organic concentration for both $\delta^{18}\text{O}$ and δD . The deviations are as high as 5.5‰ and 7.5‰ for $\delta^{18}\text{O}$ and δD respectively.

With the MCM turned on, the deviations from the true isotopic values do not exceed 0.1‰ and 0.2‰ for $\delta^{18}\text{O}$ and δD . These deviations are well within the maximum acceptable deviations of 0.2‰ and 1.5‰ for $\delta^{18}\text{O}$ and δD set forward for hydrological applications by the IAEA in their 2016 WICO proficiency test¹.

Using ChemCorrect and the MCM to Develop Methods For Water

If the Picarro user does not know whether his/her water samples are contaminated with organics or does not know the level of organic contamination, we recommend the following methodology:

Equip an L2130 ($\delta^{18}\text{O}$ and δD) or L2140 ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$ or δD) with both ChemCorrect and the MCM. In the autosampler tray use two standards to be run before a set of samples. Use the autosampler method software to set up a run that uses one injection each for all standards and samples. Turn the MCM on. This is a time efficient way to run through a complete set of samples and test the results through ChemCorrect before committing to a full analytical method.

Post-processing the results in ChemCorrect would yield the following information:

For samples where the results are highlighted in Green and Yellow, the user can proceed with the full sample analysis by running multiple injections per sample to obtain the most precise measurement. For samples highlighted in Red, the organic level is too high for the MCM to be efficient. We would suggest further organics removal steps, or using an alternative isotope measurement technique. Although dual inlet IRMS is not susceptible to spectral interference from alcohols and other hydrocarbons, continuous flow systems can have similar deviations from accuracy as the laser optical devices.

Conclusion

Interferences from organic contaminated water samples are a well-known concern for LAS instruments. However, Picarro has offered a fully-integrated and seamless solution for their water isotope system to remove organics and to provide reliable isotopic analysis.

¹ L. Wassenaar et al, Seeking excellence: An evaluation of 235 international laboratories conducting water stable isotope analyses by isotope-ratio and laser-absorption spectrometry, *Rapid Commun Mass Spectrom.* 2018;32:393–406.