MINERAL WATER ANALYSIS
WITH RAMAN SPECTROSCOPY

Abstract

This application note documents the spectra of dissolved carbon species in mineral waters with a TSI ChemLogix™ EZRaman-I system. Bicarbonate detection limit is about 150 mg/L.

Background and Motivation

Hardness is a quality of natural and drinking water based on its mineral content. Minerals, predominantly calcium and magnesium, are dissolved in the water as it percolates through chalk and limestone deposits. The hardness of water is calculated from the concentration of multivalent cations in the water. Hard water forms deposits that reduce the lifetime of equipment, raises the cost of heating the water and precipitated scale is known to clog pipes. The scale is principally composed of $CaCO_3$, $Mg(OH)_2$ and $CaSO_4$ and can either occur because of thermal decomposition of HCO_3^- or in cases where the carbonate ion concentration is higher than the solubility limit. The formation of scale from hard water is therefore contingent on both pH and temperature. Many places in the US and abroad have appreciably hard water, and residents in these regions deal with issues of both poor soap use and scale deposits.

On the other hand, calcium and magnesium are essential to a healthy human diet. There are many ways to fulfill this requirement, but water with a high mineral content has been documented to be helpful. High magnesium levels in drinking water have been correlated to lower risk of death due to coronary heart disease.[1] High calcium and bicarbonate water may increase serum and urinary pH, creating optimal conditions for bone mineralization. Because of high bio-availability, it has been proposed to recognize high-calcium mineral waters as good low-calorie nutritional calcium supplements.[2]

The US Food and Drug Administration regulates the definition of mineral water. In order to be labeled thusly, the water must contain at least 250 mg/l total dissolved solids originating from "a geologically and physically protected underground source."[3]

As complicated as the equilibrium chemistry of hard water is, the bicarbonate-carbonate equilibrium of carbonated mineral water is still more interesting. This is due to the presence of the CO_2 in the headspace. CO_2 is soluble in water, forming carbonic acid, which subsequently equilibrates to form the bicarbonate and carbonate anions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+$$

The first thing that is clear from this reaction mechanism is that CO_2 uptake in water is a function of pH. The more acidic the water, the further to the left is the set of reactions, and the lower the amount of CO_2 that will be dissolved in the water. All of the dissolved carbon components in this reaction mechanism have Raman features, presenting an interesting and complex spectrum for each mineral water sample.

CO_2 is a linear molecule with $D_{\infty h}$ symmetry and should therefore have four fundamental modes of vibration. Three normal modes are $\nu_1(\Sigma_g^+)$ the symmetrical stretch at 1339.5 cm^{-1}; $\nu_2(\Sigma_u)$, the doubly degenerate deformation mode at 667.3 cm^{-1}; and $\nu_3(\Sigma_u^+)$, the antisymmetric stretch at 2349.1 cm^{-1}. Both modes ν_2 and ν_3 are infrared active and ν_1 is only Raman active.

In spite of this prediction, instead of a single symmetrical stretching mode, there are two strong Raman features observed in CO_2 at 1289 cm^{-1} and 1389 cm^{-1}. This doublet is due to a Fermi resonance (in fact, it was the system used by Fermi to explain the phenomenon) which is an anharmonic mixing of the overtone of the deformation mode with the symmetrical stretch mode. In water, these features are appreciably broadened, as seen in the spectra of the mineral waters.[4]

Also present in the spectra of the mineral waters are features that can be assigned to HCO_3^- and CO_3^{2-}. CO_3^{2-} can be observed at 1066 cm^{-1} (ν_2) and 1385 cm^{-1} (ν_3). The first feature is documented to be much more intense than the latter, so because the 1066 cm^{-1} feature is in most cases nearly swamped by noise, any contribution to the broad, messy feature around 1390 cm^{-1} is most likely not CO_3^{2-}.

HCO_3^- is also observed in this spectral region. There is a very strong feature at 1016 cm^{-1} which is assigned to be the νC-OH stretch – especially visible in the Gerolsteiner spectrum. There are less intense (half the expected intensity of the C-OH stretch) at 1312 and 1364 cm^{-1}. These are assigned to be δCO-H and $\nu_{as}CO_2$, and are likely components of the broad feature present near 1390 cm^{-1}.[5]

SO_4^{2-} is also present in the San Pellegrino sample. The feature present in the spectra collected is the ν_1 symmetric stretch, at 980 cm^{-1}. Using longer acquisition times than present in this work, we have generated calibration plots of this feature with a limit of detection of about 30 ppm.

Measurements and Results

Table 1 documents the bottler-provided composition of three commercially available mineral waters. The fourth sample used in this data set, La Croix, does not list composition on its website. Instead of representing the range of mineral waters available in the US, this table documents the ones easily available in the Twin Cities area of Minnesota, USA.

Table 1. Bottler-provided Analysis of Mineral Waters

	Gerolsteiner	San Pellegrino	Perrier	Units
TDS	2527	1109	475	mg/L
pH	5.9	7.7	5.5	pH units
Hardness	1299	744	380	mg/L
NO$_3^-$	5.1	2.2	5	mg/L
Ca^{2+}	347	208	147	mg/L
Mg^{2+}	108	56	3	mg/L
Na$^+$	119	44	9	mg/L
K$^+$	10.8	3	1	mg/L
"silica"	40.2	9	12	mg/L
HCO$_3^-$	1817	136	390	mg/L
SO$_4^{2-}$	36.3	549	33	mg/L
Cl$^-$	39.7	74	22	mg/L
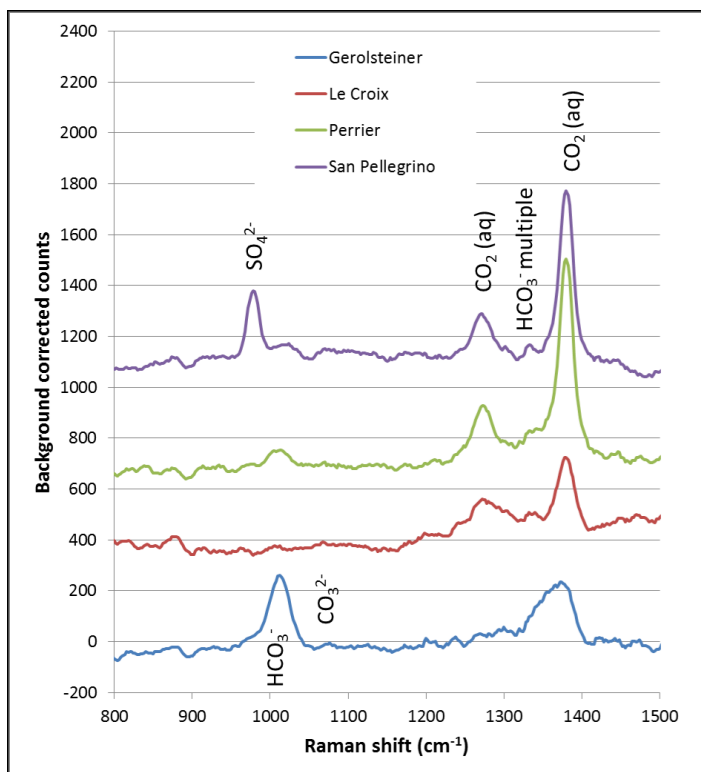
Figure 1. Raman spectra of four mineral water samples, offset for ease of viewing.

1.5 ml samples of mineral water were transferred into glass vials and presented to a TSI ChemLogix EZRaman-I portable instrument in the vial/cuvette holder. This instrument has a 785 nm excitation laser that delivers about 250 mW to the sample at the maximum setting, used for this analysis. 50 second acquisition periods were used to collect the spectra, shown in Figure 1.

The spectral window in this figure shows all the dissolved carbon features previously discussed, as well as a sulfate feature in one of the samples (matching the sulfate concentrations reported by the bottler, in this case San Pellegrino). The aqueous CO_2 present in the sample is likely a complex function of the amount of carbonation initially present, the time the bottle was open prior to sampling and the amount of handling stress on the samples prior to analysis.

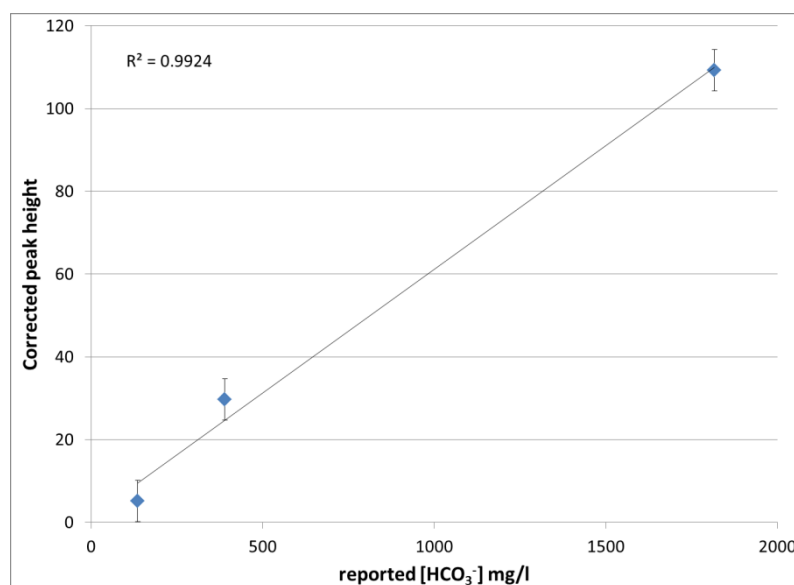These spectra can be used to create a preliminary calibration curve for the bicarbonate anion in the samples, shown in Figure 2. This fairly linear calibration curve shows the corrected peak height for the bicarbonate ion at 1006 cm^{-1} vs. the concentration provided by the bottlers. Although more data should be obtained and the uncertainty on bottler-reported concentrations discovered, it would appear that the detection limit of the system is near 150 mg/L.

Summary

A method for routine analysis of mineral water has been developed using a TSI ChemLogix EZRaman-I instrument and ordinary glass vials. This measurement demonstrates the stability of the instrument well, as it delivers small, but consistent bicarbonate peaks that can be used to create a linear calibration curve sensitive to about 150 mg/L.

Figure 2. Preliminary bicarbonate calibration curve.

References

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