H₂S interference on CO₂ isotopic measurements using a Picarro G1101-i cavity ring-down spectrometer

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Abstract. Cavity ring-down spectrometers (CRDSs) have the capacity to make isotopic measurements of CO₂ where concentrations range from atmospheric (~400 ppm) to 6000 ppm. Following field trials, it has come to light that the spectrographic lines used for CO₂ have an interference with elevated (higher than ambient) amounts of hydrogen sulfide (H₂S), which causes significant depletions in the δ¹³C measurement by the CRDSs. In order to deploy this instrument in environments with elevated H₂S concentrations (i.e., active volcanoes), we require a robust method for eliminating this interference. Controlled experiments using a Picarro G1101-i optical spectrometer were done to characterize the H₂S interference at varying CO₂ and H₂S concentrations. The addition of H₂S to a CO₂ standard gas reveals an increase in the ¹²CO₂ concentration and a more significant decrease in the ¹³CO₂ concentration, resulting in a depleted δ¹³C value. Reacting gas samples containing H₂S with copper prior to analysis can eliminate this effect. Models post-dating the G1101-i carbon isotope analyzer have maintained the same spectral lines for CO₂ and are likely to have a similar H₂S response at elevated H₂S concentrations. It is important for future work with CRDS, particularly in volcanic regions where H₂S is abundant, to be aware of the H₂S interference on the CO₂ spectroscopic lines and to remove all H₂S prior to analysis. We suggest employing a scrub composed of copper to remove H₂S from all gas samples that have concentrations in excess of 1 ppb.

1 Introduction

Cavity ring-down spectroscopy is a relatively new method for making isotopic measurements of carbon dioxide, methane and water vapor at atmospheric concentrations (O’Keefe and Deacon, 1988). Applications for instruments using cavity ring-down spectroscopy include monitoring of greenhouse gas emissions (Chen et al., 2010; Crosson, 2008), monitoring carbon storage and sequestration (Krevor et al., 2010), studying plant respiration (Cassar et al., 2011; Munksgaard et al., 2013), and process monitoring in the automotive and pharmaceutical industries (Gupta et al., 2009). Recent attempts to apply this technique to monitoring of active volcanic centers have been successful (Lucic et al., 2014, 2015; Malowany et al., 2014), but in some instances there have been anomalous responses from the Picarro G1101-i cavity ring-down spectrometers (CRDSs). Volcanoes emit a range of gases whose concentrations can be much higher than their concentrations in the ambient atmosphere. In particular, hydrogen sulfide gas is abundant in certain volcanic centers and can produce interference in the near-infrared spectrum in which the instrument operates. Our goal was to characterize and quantify this interference for future applications of the CRDS in volcanic environments.

Carbon isotopes are powerful tracers of volcanic gases and degassing processes (Gerlach and Taylor, 1990; Taylor, 1986) and are currently analyzed along with a suite of other geochemical tracers to monitor activity at active volcanoes (Carapezza et al., 2004). CRDS has a promising future monitoring activity at volcanic centers and tracking real-time changes in the isotopic composition of volcanic gases. However, interference of H₂S with the isotopes of carbon diox-
Figure 1. Diagram showing the H₂S experimental setup. A sample bag containing a standard gas with known CO₂ concentration and isotopic composition was spiked with various amounts of H₂S. The gas mixture was run directly into the CRDS to observe the interference, and then it was run through a copper tube filled with copper filings to ensure that H₂S was removed and the isotopic value returned to that of the standard. Copper reacts with hydrogen sulfide, precipitating copper sulfide and releasing water. This can be observed by an increase in the water content measured by the CRDS after a sample has been run through the copper apparatus.

ide prevents accurate measurements of the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations, resulting in erroneous δ$^{13}$C measurements. To use CRDS at volcanic centers, the interference of H₂S gas needs to be characterized and removed. This paper reports the results of laboratory tests using carbon dioxide of a known isotopic composition spiked with different amounts of H₂S to assess the nature of the H₂S interference upon the CRDS. These controlled experiments were designed to qualitatively and quantitatively characterize the interference of H₂S from low concentrations (1 ppb) to those observed at volcanic centers (> 10,000 ppb). To use these instruments for in situ measurements, a quick and efficient way of removing H₂S from the sample gas prior to analysis is needed. Metals which have a high affinity for acid species, such as copper and zinc, react rapidly with H₂S to form metal sulfides. If H₂S can be removed from a sample gas without altering the isotopic composition of carbon dioxide, then the successful application of CRDS in H₂S-rich environments will only require application of a simple metal scrub prior to analysis.

2 Methodology

2.1 Experimental setup

Lab experiments were implemented to test the response of a cavity ring-down spectrometer over a range of H₂S concentrations and then to remove all traces of H₂S using a copper scrub. A Picarro G1101-i cavity ring-down spectrometer, S/N CBDS-086, designed for measuring the isotopic concentration of CO₂, was set up in a lab at ambient conditions (25 °C, altitude = 100 m a.s.l., and a summer humidity index of 60–78). The instrument performs continuous measurements while in operation, and samples are run in series, always returning to background values between measurements. This instrument has an intake valve connected to a Tedlar® gas bag containing a mixture of CO₂ and H₂S gas. The internal pump in the CRDS actively pumps the gas at 30 mL min$^{-1}$ into its cavity. Each gas mixture was first run directly into the instrument to observe the H₂S interference at different H₂S and/or CO₂ concentrations, and then it was run through 10 cm of copper tubing containing copper filings before entering the instrument (Fig. 1). Copper readily reacts with the H₂S, removing it from the gaseous phase and leaving the pure CO₂ to be analyzed by the instrument. Copper filings were added to the copper tube to increase the surface area of copper available to react with the H₂S. Both the Tedlar® gas bags and the Tygon® tubing used in these experiments are semi-permeable to CO₂; therefore, samples were prepared immediately prior to analysis to minimize the effects of diffusion. The time between sample preparation and analysis never exceeded 15 min.

2.2 Gas mixture

Gas samples were prepared using mixtures of H₂S, CO₂ and CO₂-free air. A standard CO₂ gas of 995 ppm (±20 ppm), certified according to Fourier transform infrared spectroscopy with reference to the NOAA X2007 CO₂ international standard and having an isotopic composition of $−28.5±0.5\%$ relative to Vienna Pee Dee Belemnite (VPDB), was spiked with different volumes of a 100 ppm H₂S gas to give H₂S concentrations ranging from 1 ppb to 20000 ppb (20 ppm). H₂S concentrations were diluted from a gas cylinder containing 100 ppm H₂S mixed with air by adding an aliquot of the 100 ppm gas of up to 125 mL to 1 L of 995 ppm CO₂ in a Tedlar® gas bag using a syringe. Dilutions were performed such that the CO₂ standard was not diluted to less than 900 ppm and yielded at least 1 L of gas mixture. CO₂ volumes were controlled by a flow meter at a rate of 500 ± 10 mL min$^{-1}$.

A second suite of gas mixtures comprised varying concentrations of both CO₂ and H₂S to illustrate the effect of H₂S upon different CO₂ concentrations. A 100% CO₂ standard gas with an isotopic value of $−16.0±0.5\%$ relative to VPDB was diluted to 500, 1000, 2000 and 3000 ppm by adding air that had been scrubbed using ascarite (NaOH) to remove background CO₂; 1 L of CO₂-free air was added to the gas bag using a flow meter, while the CO₂ gas was added in different volumes using a syringe. The flow meter ran at a rate of 500 ± 10 mL min$^{-1}$ and the syringe was accurate to ±0.05 mL. Uncertainties associated with preparing the CO₂ ranged from ±30 ppm at 3000 ppm CO₂ to ±45 ppm at 500 ppm CO₂. The diluted CO₂ gas was subsequently spiked with the 100 ppm H₂S gas to concentrations of 100, 200 or 300 ppb H₂S using the same technique as described above. The addition of H₂S to the prepared CO₂ gas caused additional dilution of the intended CO₂ concentration of up to 100 ppm. Final CO₂ concentrations were calculated based on the effective dilution from the added volume of CO₂-free air and the H₂S, and were then compared to the CO₂ concentrations.
measured by the CRDS following the application of the H$_2$S scrub. Uncertainties associated with the dilution of CO$_2$ upon the addition of H$_2$S to the prepared sample gas ranged from ±28 ppm at 500 ppm CO$_2$ to ±119 ppm at 3000 ppm CO$_2$. CO$_2$ concentrations were maintained at concentrations less than 3000 ppm because the instrument is not designed for CO$_2$ concentrations higher than this. H$_2$S can generate interferences at concentrations less than 20 ppb; hence, samples were run at H$_2$S concentrations of 1–20 000 ppb (0.001–20 ppm).

2.3 Procedure

Prior to the start of every set of analyses, the 995 ppm CO$_2$ standard gas was analyzed to monitor instrumental drift and to use as a baseline for the subsequent analyses. A sample was run on the instrument by attaching a gas bag using Tygon® tubing and allowing the CRDS to pump gas into the intake. Between measurements the instrument measured the background air in the lab (~500 ppm), but when a sample bag was attached, there was an increase in the CO$_2$ concentration to 995 ppm. At this concentration level, the samples have lower instrumental noise than the background measurements. In order to obtain a reliable measurement, the gas bag was measured for 10–15 min. Using the statistical tools of the spectrometer’s interface, the δ$^{13}$C value of the gas sample was averaged using the raw delta value for the duration of the sample analysis. This yielded a time-averaged measurement of the isotopic composition, as well as the $^{12}$CO$_2$ and $^{13}$CO$_2$ concentrations. Slight variations in the background air were due to the respiration of one or more people in the lab during the analysis; however, this did not affect the outcome of the experiments as the instrument flushes the cavity with new gas every 1–3 s.

After a CO$_2$ gas sample spiked with H$_2$S was analyzed, the sample bag was removed, and the instrument was allowed to return to background values. High H$_2$S concentrations can cause large interferences with the isotopic measurements, and it sometimes took several minutes to return to background δ$^{13}$C values, even after CO$_2$ concentrations had stabilized at ambient levels. After returning to background, the same sample was again connected to the instrument using Tygon® tubing, then run through a copper tube filled with copper filings before entering the instrument. This procedure removed all H$_2$S and allowed the instrument to measure the CO$_2$ gas without any interference from H$_2$S. We used a 10 cm long utility grade copper tube with an outer diameter of 9.6 mm and an inner diameter of 7.5 mm filled with CHEM.57B copper filings which contain up to 10% metal impurities. These materials are easily acquired, and the copper grade appears to be sufficient for scrubbing large H$_2$S concentrations. The filings are necessary to provide a large surface area for reaction with H$_2$S. Trials with only the copper tube did not remove all H$_2$S.

With the attached copper scrub, data collection was similar to the previous run; the sample bag was analyzed for 10–15 min, and then the instrument was brought back to background values. With H$_2$S removed, the instrument was able to visibly return to background levels of δ$^{13}$C and CO$_2$. A single 10 cm tube of copper filled with copper filings was used for all analyses and was effective for all H$_2$S concentrations. Other trials (not included here) have shown that repeated measurements at H$_2$S concentrations in excess of 1 ppm should use more copper (i.e., a longer tube and more filings) than used for these experiments. The deposition of copper sulfide on the filings is a good indication of the efficiency of the scrub; once a large portion of the copper is visibly reacted, the scrub should be changed.

The instrument also measures H$_2$O and CH$_4$ concentrations continuously because of reported cross sensitivities with CO$_2$ for both water vapor (Rella et al., 2013) and methane gas (Vogel et al., 2013). We used the built-in water vapor correction to correct for variable water concentrations in each sample (Rella et al., 2013). Water concentrations were below 2% H$_2$O by volume in all samples; thus, the instrument correction factor remained valid at these concentrations such that the dry mole fraction of CO$_2$ was maintained within the Global Atmospheric Watch limits of ±0.1 ppm. The reaction of H$_2$S produced water vapor, but the concentrations were not significant to the overall correction factor. Methane concentrations were monitored during each run for concentrations which would cause significant changes to the isotopic value using the sensitivity value of 0.42 ±0.024 ‰ ppm$^{-1}$ of methane (Vogel et al., 2013). CRDS-reported CH$_4$ levels were constant at 3.86 ±0.21 ppm for all runs with the 995 ppm CO$_2$ standard and were much lower for samples run with the 100% CO$_2$ standard (1.65 ±0.1 ppm CH$_4$). Overall, variability in the methane concentration is negligible during all runs with a given standard, allowing for comparison of results; however, comparison of the runs using different CO$_2$ standard gases is not advised due to the different methane levels contained therein.

3 Results

Interference was first observed with the addition of 20 ppb H$_2$S, causing a change in δ$^{13}$C of −0.5 ‰ from the 995 ppm CO$_2$ standard (δ$^{13}$C = −28.5 ‰). As H$_2$S concentrations increased, the δ$^{13}$C decreased proportionally (Fig. 2). A sample without H$_2$S returned a stable δ$^{13}$C value, but with increasing amounts of H$_2$S the δ$^{13}$C value started to decrease over the course of a single run. This resulted in an increasingly negative slope in the raw δ$^{13}$C signal with the addition of greater amounts of H$_2$S.

The decrease in the measured δ$^{13}$C resulted from changes in the $^{12}$CO$_2$ and $^{13}$CO$_2$ concentration measurements in the presence of H$_2$S. Figure 3 shows an increase in the $^{12}$CO$_2$...
There is an apparent decrease of nearly 50 % in the $^{13}$CO$_2$ concentration reported by the CRDS with the addition of 20 000 ppb H$_2$S, whereas the $^{12}$CO$_2$ concentration has an apparent increase of only 3.5 % for the same amount of H$_2$S. The end result is that H$_2$S causes a large negative interference on the $\delta^{13}$C value measured by the instrument, predominantly governed by a negative interference with the $^{13}$CO$_2$ concentration. This apparent decrease is a result of instrument interference between the H$_2$S molecule and the $^{13}$CO$_2$ and $^{12}$CO$_2$ molecules in the absorption spectra. The gas samples prepared with the H$_2$S and CO$_2$ mixture had elevated $^{12}$CO$_2$ and depleted $^{13}$CO$_2$ with respect to the same sample after the H$_2$S had been removed with the copper scrub.

Furthermore, the addition of H$_2$S to the CO$_2$ standard gas to create our gas mixture resulted in a decrease in the true
chemical concentration of both $^{12}$CO$_2$ and $^{13}$CO$_2$. The real changes in CO$_2$ concentration are known by the large difference between the predicted dilution of CO$_2$, and that measured after H$_2$S had been removed. Figure 4 shows this decrease in both the $^{12}$CO$_2$ and $^{13}$CO$_2$ concentrations when H$_2$S is added compared to the pure CO$_2$ standard gas. Dilution of the standard occurs by addition of 3 mL of H$_2$S via syringe to 1000 mL of the 995 ppm CO$_2$ standard in a gas bag. This should result in a decrease of $^{12}$CO$_2$ and $^{13}$CO$_2$ concentrations of only 2.9 ppm and 0.032 ppm, respectively. However, the observed decreases in the $^{12}$CO$_2$ and $^{13}$CO$_2$ concentrations are much greater than the predicted dilution, 45 ppm for $^{12}$CO$_2$ and 0.6 ppm for $^{13}$CO$_2$. This is on the order of 15 times greater than the predicted dilution. Since the decrease in CO$_2$ concentration cannot be explained by dilution when H$_2$S is added, we propose that there is a compound reaction which consumes CO$_2$ with the addition of H$_2$S to the gas mixture.

Sample analyses with H$_2$S concentrations from 1 to 500 ppb show a linear interference of $-1\%$ for every 23 ppb H$_2$S added (Fig. 5). The interference was successfully eliminated by reacting samples with copper. Figure 6 shows a larger range of samples from 1 ppb to 20 000 ppb. The higher H$_2$S concentrations still show a linear interference, but the interference is smaller at $-1\%$ for every 37 ppb H$_2$S. We believe that this discrepancy is a result of diluting the CO$_2$ standard gas with larger volumes of H$_2$S during sample preparation. The suite of samples from 1 to 500 ppb H$_2$S had larger volumes of diluted H$_2$S (1 ppm) added than the sample suite from 500 to 20 000 ppb. The larger dilutions resulted in lower CO$_2$ concentrations, suggesting that the H$_2$S interference also depends on CO$_2$ concentration. Hence, we ran a further series of experiments to examine this effect.

The set of experiments performed at a range of CO$_2$ concentrations (500 to 3000 ppm CO$_2$) revealed that the H$_2$S interference also depends strongly on the CO$_2$ concentration (Fig. 7). The interference from H$_2$S is much smaller at high CO$_2$ concentrations and is quite large at atmospheric concentrations. For example, an interference of $-1\%$ resulted from the addition of 21 ppb H$_2$S at 500 ppm CO$_2$, whereas at 3000 ppm CO$_2$ an interference of $-1\%$ required the addition of 154 ppb H$_2$S. Thus, the H$_2$S interference is also dependent on the CO$_2$ concentration of the sample. During experiments performed at a fixed H$_2$S concentration, it was found that the H$_2$S interference with $^{13}$C was inversely proportional to the CO$_2$ concentration of the sample. Figure 8 illustrates

Figure 4. The addition of 3 mL of 100 ppm H$_2$S to 1 L of the 1000 ppm standard gas resulted in a large drop in $^{12}$CO$_2$ and $^{13}$CO$_2$ concentrations. The observed concentrations are significantly lower than those predicted to result from dilution of the standard gas with the addition of 3 mL of H$_2$S. When the copper scrub removed H$_2$S, the CO$_2$ concentration remained anomalously low. It is likely that a reaction between H$_2$S and CO$_2$ removes a portion of the CO$_2$ from the mixture before it is analyzed.
4 Discussion

Carbon isotopic measurements of CO₂ using cavity ring-down spectroscopy have a clear interference in the presence of H₂S that is dependent on both the H₂S and CO₂ concentrations. At lower CO₂ concentrations, the H₂S interference was more pronounced due to the relatively higher proportions of H₂S contained within the sample. This may explain the discrepancy between the slopes of Figs. 5 and 6, where there was more dilution of the CO₂ standard gas at lower H₂S concentration (Fig. 5) than at higher H₂S concentration (Fig. 6), resulting in a larger H₂S/CO₂ ratio in samples with lower CO₂ concentrations.

The H₂S interference with the G1101-i CRDS is an inherent property of the spectral lines that are fitted to determine the ¹²CO₂ and ¹³CO₂ concentrations (Fig. 9). The specific spectral lines used in the Picarro G1101-i were chosen to avoid overlapping ambient levels of common gas species encountered in atmospheric air (i.e., H₂O, CH₄, NH₃, etc.). In the case of water vapor for example, where it is not possible to choose CO₂ lines that are free from overlap, the system measures and corrects for such species to the extent that they interfere with either the ¹²CO₂ or ¹³CO₂ spectral features. For H₂S specifically, the chosen spectral lines avoid the strongly absorbing H₂S spectral lines, but there are weaker
weak lines have no measurable effect on the reported CO
2
. Since the isotope ratio measurements in CRDS use ra-
3
allel to H2S concentration. This interference should be accounted for by dilution and not by any significant exchange reaction between CO2 and H2S in the system.

Since the isotope ratio measurements in CRDS use ratios of the absorption peaks of the two spectral lines of the CO2 isotopologues, it is the relative concentration of H2S to CO2 that determines the effect of the H2S on the isotope ratio (Fig. 9). The more pronounced effect of H2S on the isotope ratio at lower CO2 concentrations is due to a weak H2S spectral line slightly overlapping the 13CO2 line such that when the ratio of CO2 to H2S concentration is low, the measured 13CO2 line will be more affected by the H2S since it makes up a larger proportion of the overall measured line shape. There is a similar overlapping H2S line near the 12CO2 peak that has a similar (but opposite sign) concentration-dependent effect on the reported 12CO2 concentration as compared to the 13CO2 concentration. The reason for the sign difference of these two H2S concentration-dependent effects is related to how the independent spectroscopic fitting algorithms used for each peak to calculate the isotopologue concentrations interpret the change in line shape imparted by the interfering H2S signal.

In addition to the H2S interference, there was an unanticipated decrease in both the 13CO2 and 12CO2 concentrations with the addition of H2S to the standard gas that could not be accounted for solely by dilution (Fig. 4). We propose that a reaction between CO2 and H2S is occurring to consume CO2 upon combination in the Tedlar® bags. However, we have not directly measured any products; hence we are uncertain as to what reaction will be consuming these reactants at atmospheric conditions. Isotopic readings of our gas mixture indicate that the effects of any reactions are small compared to the effects of H2S, so the major concern for these and future experiments is the removal of H2S from all samples prior to analysis.

Although all H2S experiments conducted in this study use an older model (G1101-i) of the carbon isotope analyzer from Picarro, all subsequent models have maintained the same spectral lines for CO2, and their H2S performance is presumed to be equivalent. We have verified that no spectroscopic corrections for H2S have been applied to any model of the carbon isotopic analyzer, and as such the copper scrub proposed here is a simple and effective solution to the H2S interference for all current models. The operating lines of the instrument were chosen to minimize strong overlap of spectral lines from ambient levels of small molecules found in ambient air such as ammonia, water vapor, H2S etc., and as such the H2S interference only occurs at concentrations > 1 ppb. Normal atmospheric concentrations are much less than this amount, and no correction for the H2S overlap has

![Figure 8](image_url)

**Figure 8.** The H2S interference is inversely related to the CO2 concentration. (a) The isotopic signal from the CRDS varies with changing CO2 concentration when the H2S concentration is held constant at 300 ppb. (b) Isotopic value vs. 1/CO2 illustrating the change in δ13C with the addition of H2S to a standard gas (−16.0‰) at different concentrations.

![Figure 9](image_url)

**Figure 9.** HITRAN model for 400 ppm CO2 and 1 ppm H2S (45 °C, 140 Torr) illustrates the overlapping of H2S lines with CO2 lines. The relative magnitude of H2S interference is much larger for 13CO2 than for 12CO2. Note the logarithmic scale.
previously been warranted. In non-atmospheric conditions, such as those on active volcanoes or sour gas plants, these concentrations are more common and H$_2$S should be considered as an interferent.

5 Concluding remarks

Isotopic measurements using this particular implementation of CO$_2$ spectroscopy in cavity ring-down spectrometers have a clear and quantifiable interference resulting from the presence of H$_2$S in excess of a few parts per billion. Laboratory experiments using controlled amounts of H$_2$S mixed with a CO$_2$ gas of known concentration and isotopic composition show that the interference is linear and dependent on both the H$_2$S and CO$_2$ concentrations of the sample. The H$_2$S interference arises as a result of the line choice for this type of spectrometer (Picarro$^\circledR$ G1101-i), which avoids interference with other common atmospheric species such as H$_2$O, CH$_4$, NH$_3$, etc., but it has some small lines remaining in the range of H$_2$S that causes the interference observed at high H$_2$S concentrations. All models of the carbon analyzer from Picarro$^\circledR$ use the same spectral lines and, thus, are susceptible to the same type and magnitude of interference with H$_2$S.

The most practical approach to eliminating H$_2$S interference when measuring the $\delta^{13}$C value is the use of a metal scrub, for example copper, to remove all H$_2$S before the sample is run through the CRDS. Removing this interference is an important step to making real-time measurements of $\delta^{13}$C of CO$_2$ with cavity ring-down spectrometers in environments with high sulfur concentrations, such as actively degassing volcanoes. Volcanoes have a range of CO$_2$ concentrations (400–1 000 000 ppm), and the H$_2$S interference is significant in the operational range of the CRDS (0–3000 ppm). Therefore, the most practical approach to eliminating the interference is with a simple scrub for all samples containing H$_2$S in excess of 1 ppb.

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References


