



**H₂S interference on
CO₂ isotopic
measurements**

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This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

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

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Received: 28 April 2015 – Accepted: 12 May 2015 – Published: 5 June 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Cavity ring-down spectrometers (CRDS) 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 CRDS. 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. However, experiments also revealed that the addition of H₂S to CO₂ results in the formation of carbonyl sulfide (OCS) and carbon disulfide (CS₂), causing a decrease in the overall CO₂ concentration without affecting the δ¹³C value. 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 (CRDS) 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 CRDS include monitoring of greenhouse gas emissions (Chen et al., 2010; Crosson, 2008),

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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., 2015, 2014; Malowany et al., 2014), but in some instances there have been anomalous responses from the Picarro G1101-i CRDS. 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 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 dioxide prevents accurate measurements of the ¹²CO₂ and ¹³CO₂ concentrations, resulting in erroneous $\delta^{13}\text{C}$ 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

5 Lab experiments were implemented to test the response of a cavity ring-down spectrometer over a range of H₂S concentrations, and then 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
10 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
15 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
20 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.

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2.2 Gas mixture

Gas samples were prepared using mixtures of H₂S, CO₂ and CO₂ – free air. A standard CO₂ gas of 995 ppm and isotopic composition of –28.5‰ was spiked with different volumes of a 100 ppm H₂S gas to give H₂S concentrations ranging from 1 to 20 000 ppb (20 ppm). Dilutions were performed such that the CO₂ standard was not diluted to less than 900 ppm and yielded at least one litre of gas mixture. 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‰ was diluted to 500, 1000, 2000 and 3000 ppm by adding air that had been scrubbed using ascarite (NaOH) to remove background CO₂. The diluted gas was then spiked with 100, 200 or 300 ppb H₂S. CO₂ concentrations were maintained at concentrations less than 3000 ppm because the instrument is not designed for CO₂ concentrations higher than this. H₂S can generate interferences at concentrations less than 20 ppb, hence samples were run at H₂S concentrations of 1–20 000 ppb (20 ppm).

2.3 Procedure

Prior to the start of every set of analyses, the CO₂ 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 atmosphere composition (~ 500 ppm), but when a sample bag was attached, there was an increase in the CO₂ 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 $\delta^{13}\text{C}$ 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

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well as the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations. The instrument also measures H_2O and CH_4 concentrations continuously.

After a CO_2 gas sample spiked with H_2S was analyzed, the sample bag was removed, and the instrument was allowed to return to background values. High H_2S concentrations can cause large interferences with the isotopic measurements, and it sometimes took time to return to background $\delta^{13}\text{C}$ 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_2S and allowed the instrument to measure the CO_2 gas without any interference from H_2S . Data collection was similar to the previous run; the sample bag was analyzed for 10–15 min, and then the instrument was brought to background values. With H_2S removed, the instrument was able to return to background levels of $\delta^{13}\text{C}$ and CO_2 quickly. A single 10 cm tube of copper filled with copper filings was used for all analyses, and was effective for all H_2S concentrations. Other trials (not included here) have shown that repeated measurements at H_2S concentrations in excess of 1 ppm should use more copper (i.e. 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.

3 Results

Interference was first observed with the addition of 20 ppb H_2S , causing a change in $\delta^{13}\text{C}$ of -0.5‰ from the 995 ppm CO_2 standard ($\delta^{13}\text{C} = -28.5\text{‰}$). As H_2S concentrations increased, the $\delta^{13}\text{C}$ decreased proportionally (Fig. 2). A sample without H_2S returned a stable $\delta^{13}\text{C}$ value, but with increasing amounts of H_2S the $\delta^{13}\text{C}$ value

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started to decrease over the course of a single run. This resulted in an increasingly negative slope in the raw $\delta^{13}\text{C}$ signal with the addition of greater amounts of H_2S .

The decrease in the measured $\delta^{13}\text{C}$ resulted from changes in the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentration measurements in the presence of H_2S . Figure 3 shows an increase in the $^{12}\text{CO}_2$ concentration and a significant decrease in the $^{13}\text{CO}_2$ concentration measured by the CRDS when comparing samples diluted with variable amounts of H_2S to the same diluted samples that had been scrubbed of H_2S . The percent change in the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations are represented by Eq. (1), illustrating how the addition of H_2S affects the measurements of the carbon isotopes used to calculate the $\delta^{13}\text{C}$ value:

$$\% \text{ change in } ^{12}\text{CO}_2 \text{ concentration} = \frac{[^{12}\text{CO}_2 \text{ with } \text{H}_2\text{S} - ^{12}\text{CO}_2 \text{ with copper scrub}]}{[^{12}\text{CO}_2 \text{ with copper scrub}]} \times 100, \quad (1a)$$

$$\% \text{ change in } ^{13}\text{CO}_2 \text{ concentration} = \frac{[^{13}\text{CO}_2 \text{ with } \text{H}_2\text{S} - ^{13}\text{CO}_2 \text{ with copper scrub}]}{[^{13}\text{CO}_2 \text{ with copper scrub}]} \times 100. \quad (1b)$$

There is a nearly 50% decrease in the $^{13}\text{CO}_2$ concentration with the addition of 20000 ppb H_2S , whereas the $^{12}\text{CO}_2$ concentration only increases by 3.5% for the same amount of H_2S . The end result is that H_2S causes a large negative interference on the $\delta^{13}\text{C}$ value measured by the instrument, predominantly governed by a negative interference with the $^{13}\text{CO}_2$ concentration.

Furthermore, the addition of H_2S to the CO_2 standard gas to create our gas mixture resulted in an unanticipated decrease in both $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$. Figure 4 shows this decrease in both the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations when H_2S is added compared to the pure CO_2 standard gas. Dilution of the standard occurs by addition of 3 mL of

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H₂S to 1000 mL of the 995 ppm CO₂ standard. This should result in a decrease of ¹²CO₂ and ¹³CO₂ concentrations of only 2.9 and 0.032 ppm respectively. However, the observed decreases in the ¹²CO₂ and ¹³CO₂ concentrations are much greater than the predicted dilution, 45 ppm for ¹²CO₂ and 0.6 ppm for ¹³CO₂. This is on the order of 15 times greater than the predicted dilution. Since the decrease in CO₂ concentration cannot be explained by dilution when H₂S is added, we propose that H₂S and CO₂ reacted in the gas mixture, removing some CO₂ before the analysis.

Sample analyses with H₂S concentrations from 1 to 500 ppb show a linear interference of −1‰ for every 23 ppb H₂S added (Fig. 5). The interference was successfully eliminated by reacting samples with copper. Figure 6 shows a larger range of samples from 1 to 20 000 ppb. The higher H₂S concentrations still show a linear interference, but the interference is smaller at −1‰ for every 37 ppb H₂S. We believe that this discrepancy is a result of diluting the CO₂ standard gas with larger volumes of H₂S. The suite of samples from 1–500 ppb H₂S had larger quantities of dilute H₂S added than the sample suite from 500–20 000 ppb. The larger dilutions resulted in lower CO₂ concentrations, suggesting that the H₂S interference also depends on CO₂ concentration. Hence, we ran a further series of experiments to examine this effect.

The set of experiments performed at a range of CO₂ concentrations (500 to 3000 ppm CO₂) revealed that the H₂S interference also depends strongly on the CO₂ concentration (Fig. 7). The interference from H₂S is much smaller at high CO₂ concentrations, and is quite large at atmospheric concentrations. For example, an interference of −1‰ resulted from the addition of 21 ppb H₂S at 500 ppm CO₂, whereas at 3000 ppm CO₂ an interference of −1‰ required the addition of 154 ppb H₂S. Thus, the H₂S interference is also dependent on the CO₂ concentration of the sample. During experiments performed at a fixed H₂S concentration, it was found that the H₂S interference with δ¹³C was inversely proportional to the CO₂ concentration of the sample. Figure 8 illustrates the variation of the H₂S interference at different CO₂ concentrations and shows this inverse relationship between CO₂ concentration and H₂S interference.

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 vapour 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 lines that partially overlap with both spectral features of the CO₂ used in the system. At typical ambient levels of H₂S for which the spectroscopy of the G1101-i was designed, these weak lines have no measurable effect on the reported CO₂ concentrations or carbon isotope ratio. However, at elevated levels, they begin to cause the observed measurement bias.

Since the isotope ratio measurements in CRDS uses ratios of the absorption peaks of the two spectral lines of the CO₂ isotopologues, it is the relative concentration of H₂S to the 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

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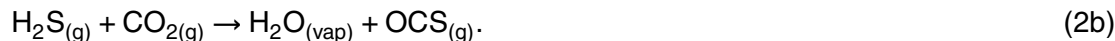
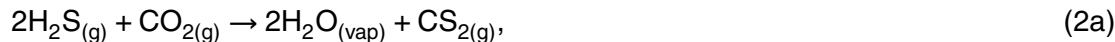
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H₂S since it makes up a larger proportion of the overall measured line shape. There is a similar overlapping H₂S line near the ¹²CO₂ peak that has a similar (but opposite sign) concentration-dependent effect on the reported ¹²CO₂ concentration as compared 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 ¹²CO₂ and ¹³CO₂ concentrations with the addition of H₂S to the standard gas that could not be accounted for solely by dilution (Fig. 4). It is possible that when the two gas species are combined, they react to form either carbon disulfide (CS₂) or carbonyl sulfide (OCS), both of which can be stable at atmospheric conditions. The suggested reactions for both species are:



Carbon disulfide and carbonyl sulfide are also present in small amounts at actively degassing volcanoes, but relatively little effort has been put forth to characterize their concentrations (Watts, 2000). If indeed the formation of these compounds is affecting the CO₂ concentration of our gas samples, it does not appear to significantly affect the $\delta^{13}\text{C}$ composition of the standard gas. Isotopic readings of our gas mixture indicate that the effects of the above compounds are small compared to the effects of H₂S.

5 Concluding remarks

Isotopic measurements using this particular implementation of the CO₂ spectroscopy in cavity ring-down spectrometers have a clear and quantifiable interference resulting from the presence of H₂S in excess of a few ppb. Laboratory experiments using

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controlled amounts of H₂S mixed with a CO₂ standard gas of known concentration and isotopic composition show that the interference is linear and dependent on both the H₂S and CO₂ concentrations of the sample. The H₂S interference arises as a result of the line choice for this type of spectrometer (Picarro[®] G1101-i), which avoids interference with other common atmospheric species such as H₂O, CH₄, NH₃, etc., but has some small lines remaining in the range of H₂S that causes the interference observed at high H₂S concentrations. The most practical approach to eliminating H₂S interference when measuring the $\delta^{13}\text{C}$ value is the use of a metal scrub, for example copper, to remove all H₂S before the sample is run through the CRDS. Removing this interference is an important step to making real-time measurements of $\delta^{13}\text{C}$ of CO₂ with cavity ring-down spectrometers in environments with high H₂S concentrations, such as actively degassing volcanoes. Volcanoes have a range of CO₂ concentrations (400–1 000 000 ppm) and the H₂S 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 H₂S in excess of 1 ppb.

Acknowledgements. The authors would like to thank the technical staff at Picarro Inc. for their continual support during our effort to characterize and understand the interferences inherent within the G1101-i cavity ring-down spectrometer. This work was funded by the Discovery grant and CREATE grant to John Stix from the Natural Sciences and Engineering Research Council of Canada.

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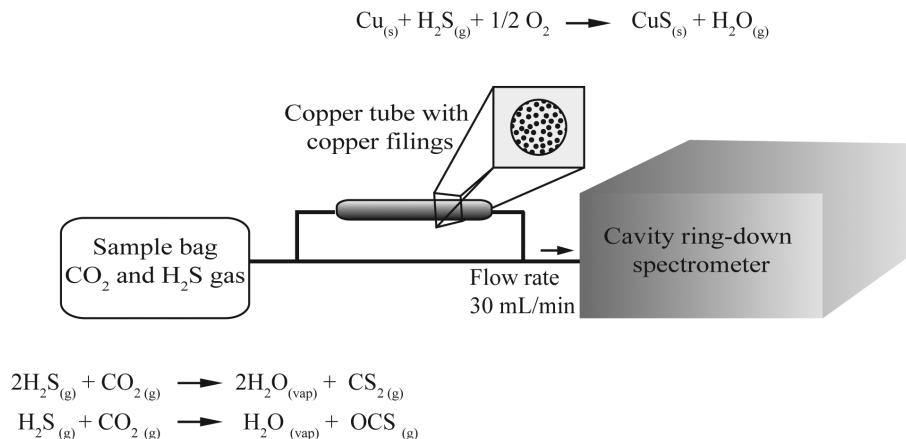


Figure 1. Diagram showing the H₂S experimental setup. A sample bag containing a standard gas with known CO₂ concentration and isotopic composition was spiked with various amounts of H₂S. The gas mixture was run directly into the CRDS to observe the interference, and then it was run through a copper tube 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. A small decrease in the ¹²CO₂ and ¹³CO₂ concentrations is thought to result from the formation of small amounts of carbon disulfide and carbonyl sulfide resulting from the reaction of H₂S with CO₂ in the sample bag.

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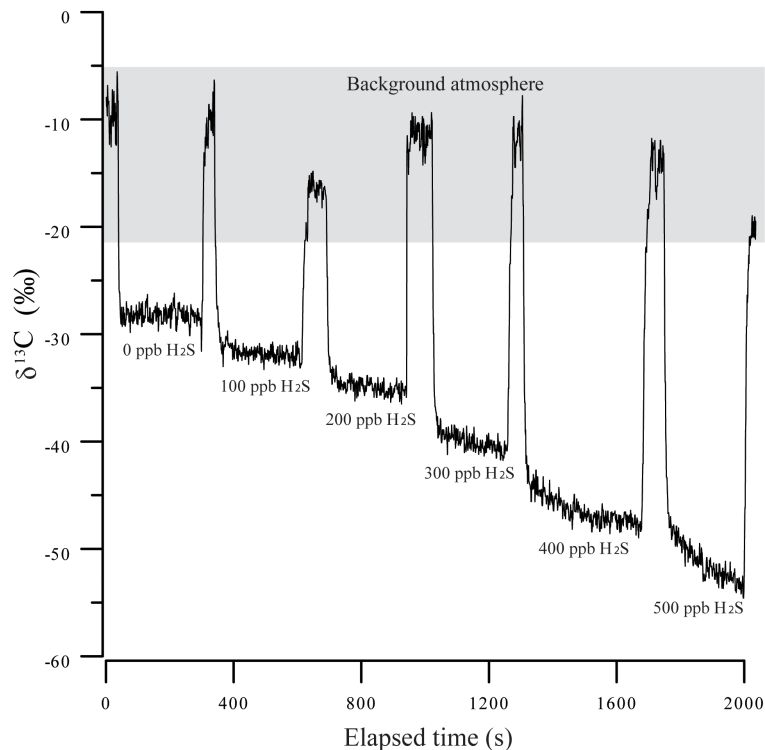
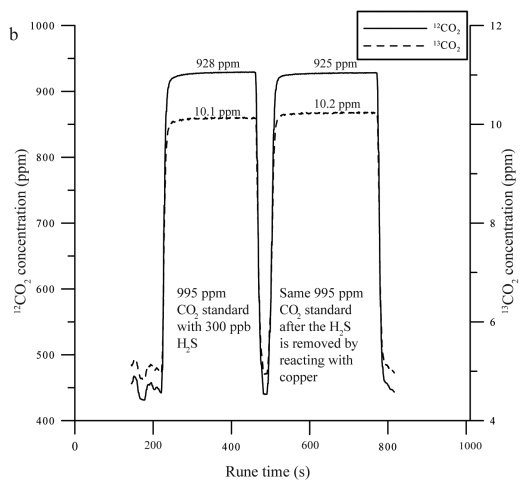
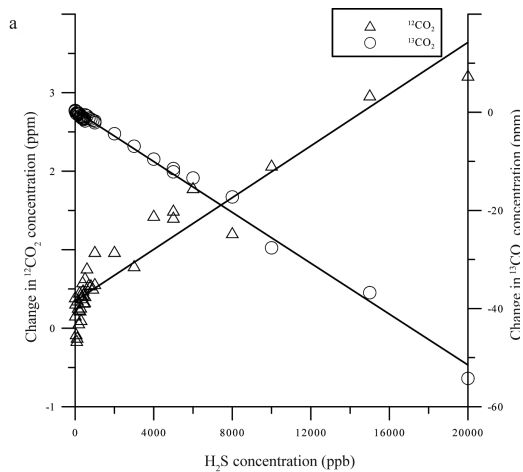


Figure 2. Raw carbon isotope signal from the Picarro G1101-i CRDS with varying amounts of H₂S. Addition of H₂S causes an increasingly negative response for the isotopic value. The raw isotopic signal at each H₂S concentration does not stabilize, but instead starts to slowly decrease resulting in a “sloped” response. Variations in background levels can be attributed to variations in laboratory conditions (i.e., respiration).

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Figure 3. Change in the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ concentrations with addition of H_2S to the standard gas. **(a)** Plot showing the percentage change in CO_2 concentration between gas with H_2S and gas scrubbed of H_2S . There is a visible increase in the $^{12}\text{CO}_2$ concentration and a decrease in the $^{13}\text{CO}_2$ concentration with addition of H_2S . The percentage decrease for $^{13}\text{CO}_2$ is significantly greater than the percentage increase for $^{12}\text{CO}_2$. **(b)** Plot showing the 1000 ppm standard CO_2 gas with the addition of 3 mL of 100 ppm H_2S and the subsequent response after the H_2S was removed with the copper scrub. There is a small, yet visible, increase in the $^{13}\text{CO}_2$ concentration and decrease in the $^{12}\text{CO}_2$ concentration when H_2S is removed.

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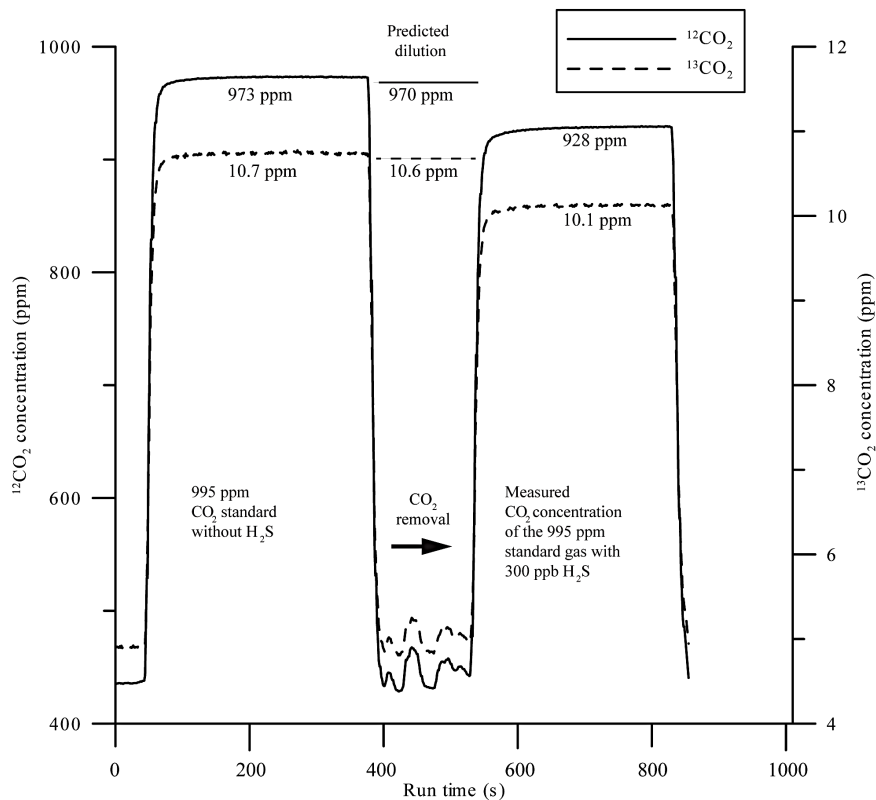


Figure 4. The addition of 3 mL of 100 ppm H₂S to 1 L of the 1000 ppm standard gas resulted in a large drop in ¹²CO₂ and ¹³CO₂ concentrations. The observed concentrations are significantly lower than those predicted to result from dilution of the standard gas with the addition of 3 mL of H₂S. When the copper scrub removed H₂S, the CO₂ concentration remains anomalously low. It is likely that a reaction between H₂S and CO₂ removes a portion of the CO₂ from the mixture before it is analyzed.

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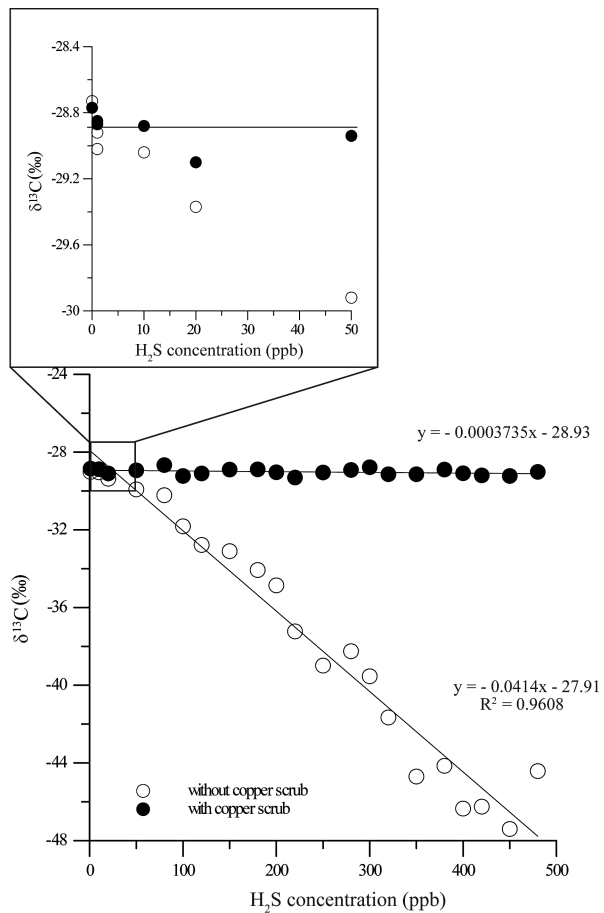
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Figure 5. Isotopic signal from the Picarro G1101-i CRDS for 995 ppm CO₂ with H₂S concentrations ranging from 0 to 500 ppb. Black dots represent isotopic measurements after H₂S has been removed with copper; here the isotopic composition is maintained at the standard value (−28.5‰).

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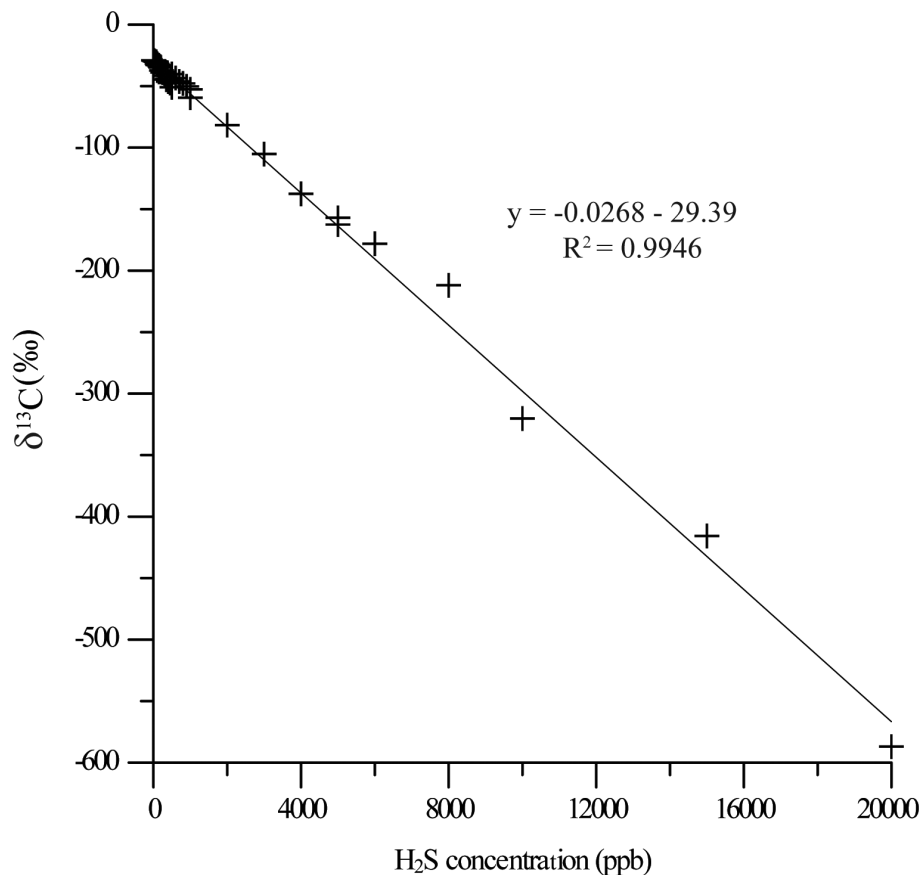


Figure 6. Isotopic signal from the Picarro G1101-i CRDS for 995 ppm CO₂ with H₂S concentrations ranging from 0 to 20 000 ppb (0–20 ppm).

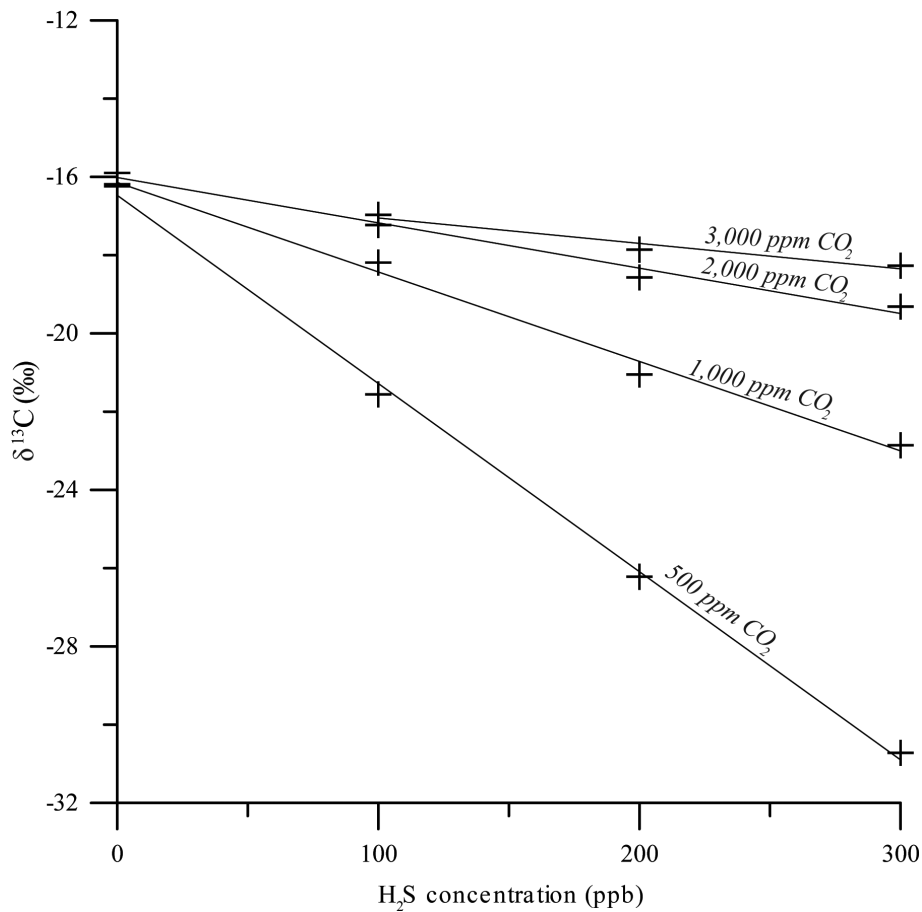


Figure 7. Changes in $\delta^{13}\text{C}$ when H_2S is added to a standard CO_2 gas (-16.0‰) at varying CO_2 concentrations. The H_2S interference is strongly dependent on the CO_2 concentration of the sample.

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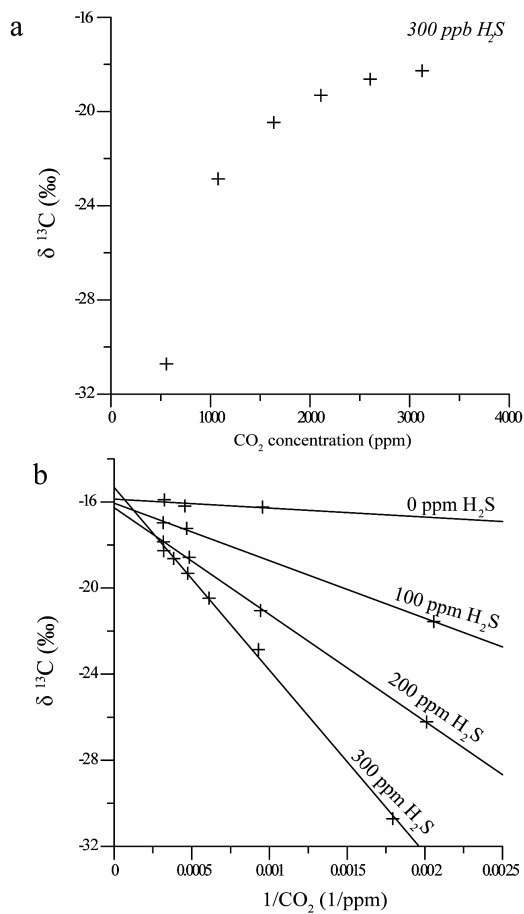
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Figure 8. The H₂S interference is inversely related to the CO₂ concentration. **(a)** The isotopic signal from the CRDS varies with changing CO₂ concentration when the H₂S concentration is held constant at 300 ppb. **(b)** Isotopic value vs. 1/CO₂ illustrating the change in $\delta^{13}\text{C}$ with the addition of H₂S to a standard gas (−16.0‰) at different concentrations.

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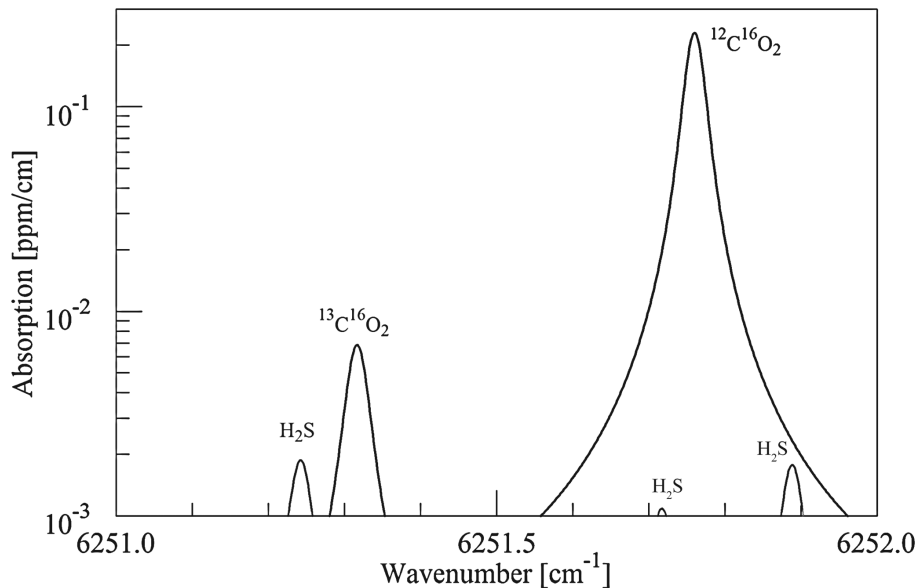


Figure 9. Hitran model for 400 ppm CO₂ and 1 ppm H₂S (45°C, 140 Torr) illustrates the overlapping of H₂S lines with CO₂ lines. The relative magnitude of H₂S interference is much larger for ¹³CO₂ than for ¹²CO₂. Note the logarithmic scale.

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