

# SRS Tech Note

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## BGA244 Binary Gas Analyzer

### Carbon dioxide and the relaxation correction

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#### Introduction

The BGA244 Binary Gas Analyzer can be used to assess the purity of a single gas or determine the composition of a binary gas mixture. To do so, the instrument must be able to accurately measure the speed of sound in a gas and be able to accurately compute the speed of sound in pure gases or gas mixtures.

The speed of sound in the ideal gas approximation is independent of pressure and is given by:

$$W = \sqrt{\frac{\gamma R T}{M}}$$

Here,  $W$  is the speed of sound,  $\gamma = C_p/C_v$  the ratio of heat capacities in the ideal gas limit,  $M$  the molar mass,  $T$  the absolute temperature in kelvin, and  $R$  the ideal gas constant. ( $R = 8.314462 \text{ J/K} \cdot \text{mol}$ ).

Real gases depart from ideal gas behavior in many ways: The compressibility,  $Z = PV/RT$ , is not constant creating a pressure dependence to the speed of sound, and the heat capacities change with temperature and frequency. For accurate results, the BGA244 includes all of these factors into its calculation of the speed of sound.

#### Carbon Dioxide

CO<sub>2</sub> provides a “typical worst case” for an acoustic gas analyzer: The gas has large 2<sup>nd</sup> and 3<sup>rd</sup> acoustic virial coefficients, a large temperature dependence of its heat capacity, and significant relaxation effects which cause dispersion and degrade the cavity Q.

The relaxation correction to the speed of sound, which is particularly large for CO<sub>2</sub> and increases as the pressure is reduced, may be thought of as a frequency correction to the heat capacity of the gas: If the relaxation time,  $\tau_d$ , is comparable to the period of an acoustic cycle, then the vibrational degrees of freedom are partially frozen out, the heat capacity is lower, and so  $\gamma$  and the speed of sound will be higher. (Relaxation computational details are provided in the Appendix.)

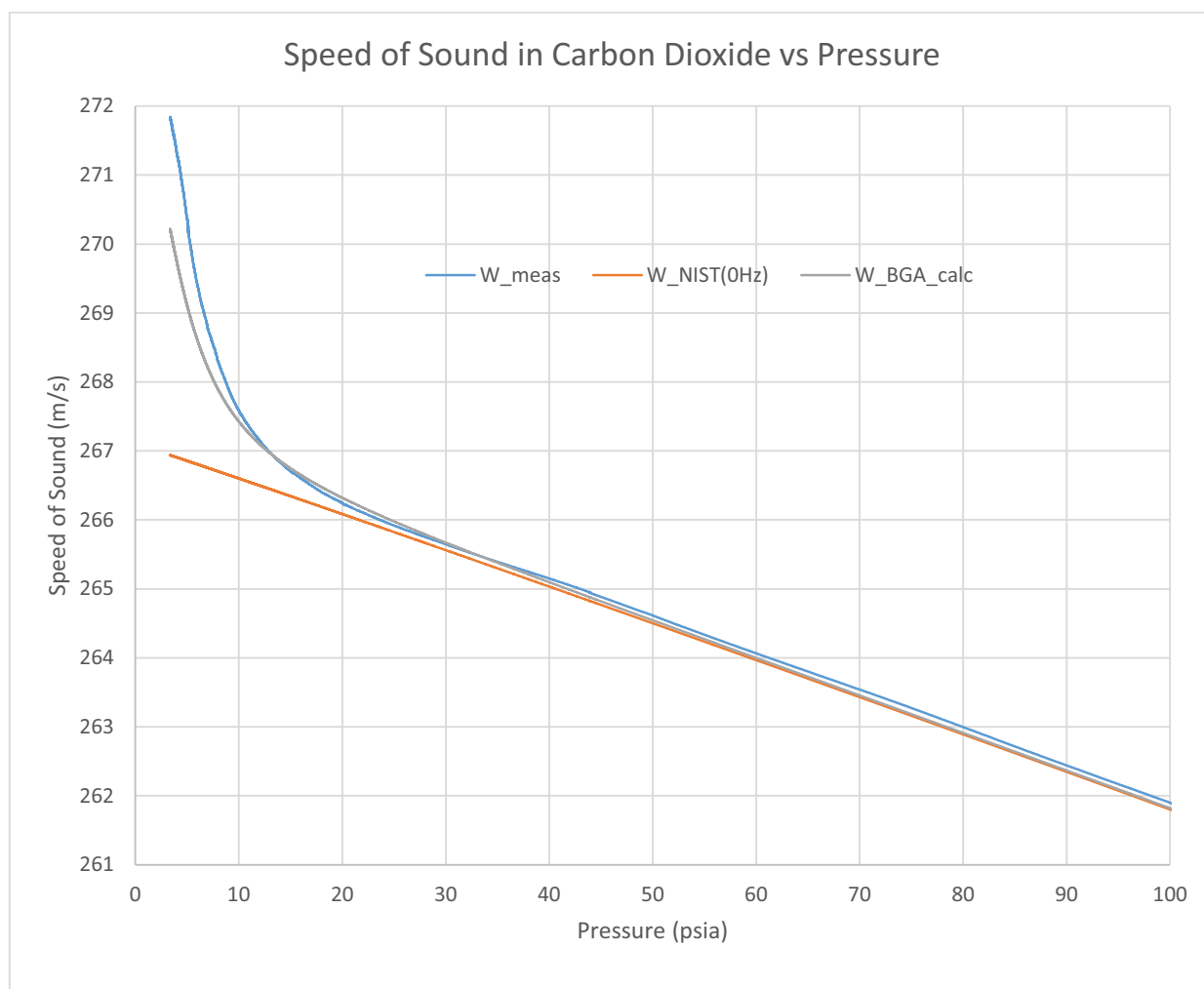
#### Experiment

A BGA244 was evacuated, out gassed, and back-filled with 150 psia of high purity carbon dioxide. After settling, the contents were evacuated via a pin hole into vacuum, allowing the pressure to ramp down exponentially from 150 psia to about 4 psia over two hours. The BGA244's Windows® program, BGA-Mon, was used to record data from the BGA244 during the pressure ramp. Data included the time, temperature, pressure, computed speed of sound, and the measured speed of sound.

The cell was operated at about 25 C, the frequency of the <101> eigenmode was about 6,500 Hz, and the pressure was read by an absolute pressure gauge calibrated in psia, with an accuracy of about ±1 psi.

## Results

The graph below shows the speed of sound for CO<sub>2</sub> vs pressure. There are three lines: The orange line is the speed of sound computed by NIST's REFPROP program. The REFPROP result does not include relaxation effects and so does not turn upward at low pressures. (It reports the speed of sound in the low frequency limit.) The grey line is the speed of sound computed by the BGA244, inclusive of the 2<sup>nd</sup> and 3<sup>rd</sup> virials corrections, the temperature dependence of the heat capacity and relaxation effects. The blue line is speed of sound measured by the BGA244, inclusive of the transducer resonance, transducer effective mass, and thermal and viscous boundary layer effects.



## Conclusion

The measured speed of sound is within  $\pm 300$  ppm of the computed speed of sound for all pressures above 12 psia. Hence the BGA244 is capable of making speed of sound measurements in dispersive gases, and capable of computing the correct speed of sound in those gases, enabling the accurate estimation of the composition of gas mixtures even when dispersive species are present.

## Appendix: The relaxation correction in BGA244 firmware

We followed Zuckerwar's approach for the relaxation correction, recasting his correction to the speed of sound as a frequency dependent heat capacity. Algorithmically, the BGA244 computes the heat capacity,  $C_p(T)/R \approx 4.44$  for  $CO_2$  at 293.15 K, from the polynomial coefficients in the Gas Table (which describe its temperature dependence), then corrects for the frequency dependence using:

$$\frac{C_p(T, f)}{R} = \frac{C_p(T)}{R} \left\{ 1 - \left[ \frac{\varepsilon}{1 - \varepsilon} \cdot \frac{(\omega \tau_d)^2}{1 + (\omega \tau_d)^2} \right] \cdot \left[ \frac{C_p(T)}{R} - 1 \right] \right\}$$

Here,  $\varepsilon$  is the relaxation strength,  $\tau_d$  is the relaxation time,  $\omega = 2\pi \cdot f_{101}$  where  $f_{101}$  is the acoustic frequency of the <101> eigenmode,  $R$  is the ideal gas constant (8.3144 K/K-mol) and  $T$  the absolute temperature. The heat capacity of the lowest lying vibrational state depends on the level's occupancy via thermal collisions and is given by:

$$\frac{C_i}{R} = \left( \frac{\theta_{vib}}{T} \right)^2 \cdot \frac{\exp\left(\frac{-\theta_{vib}}{T}\right)}{\left[ 1 - \exp\left(\frac{-\theta_{vib}}{T}\right) \right]^2} \approx 0.432 \text{ for } CO_2 \text{ at } 293.15 \text{ K} \quad \text{Zuckerwar's Eq. 5.43c}$$

Here  $\theta_{vib}$  is the vibrational temperature for the state (959.7 K for  $CO_2$ ) which is tabulated in Zuckerwar's Table 5.4 and the BGA244 Gas Tables. The relaxation strength is given by:

$$\varepsilon = \frac{RC_i}{(C_p^o - C_i) \cdot (C_p^o - R)} \approx 0.031 \text{ for } CO_2 \text{ at } 293.15 \text{ K} \quad \text{Zuckerwar's Eq. 5.45}$$

Molecular models of relaxation, which track the transfer of translational energy to the internal energy of a molecule, provide a correlation for the relaxation-time pressure  $\tau \cdot P$  product (in units of  $\mu\text{s} \cdot \text{atm}$ ):

$$\log(\tau_d \cdot P) = a_r^{(1)} + a_r^{(2)} \cdot T^{-1/3} + a_r^{(3)} \cdot T^{-1} \quad \text{Zuckerwar's Eq. 5.108}$$

Where the coefficients  $a_r^{(1)} = -2.3143$ ,  $a_r^{(2)} = 21.437$  and  $a_r^{(3)} = 0$  have been tabulated in Zuckerwar's Table 5.5 and the BGA244 Gas Tables allowing the computation of the relaxation time:

$$\tau_d(\mu\text{s}) = \frac{10 \left[ a_r^{(1)} + a_r^{(2)} \cdot T^{-1/3} + a_r^{(3)} \cdot T^{-1} \right]}{P(\text{atm})} \approx 7.8 \mu\text{s} \text{ for } CO_2 \text{ at NTP}$$

The approach detailed here gives excellent results in the pure gas limit, however it is known that the relaxation times can be shortened by the presence of other species. See, for example, Zuckerwar Figure 5.5 (Pg. 205), which shows that 0.5% mole fraction of  $H_2O$  reduces the relaxation time in  $CO_2$  by about 15x. For these cases the BGA244 allows the user to disable the relaxation correction.

Primary reference: Speed of Sound in Real Gases, Vol 1, A. J. Zuckerwar, Academic Press (2002)