¹³C and ¹⁸O Isotope Effects Resulting from High Pressure Regulation and CO₂ Cylinder Depletion

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Stable Isotopes for Environmental Monitoring

- Significant component of environmental research
 - Used for monitoring of landfill contamination, determining source stray gas in soils, and deciphering the origin and fate of nitrate in surface ground water
 - Isotopes in precipitation, combustion, volcanic activity, etc...
 - Concentrations for greenhouse gas determination, natural air monitoring
- \succ FOCUS: Development of new ambient concentration isotopically characterized CO₂ standards that meet WMO **DQO** objectives

Validate Pressure Reduction from the Cylinder to IRMS Doesn't Cause Fractionation

C isotopic composition as a function of delivery pressure

Experimental configuration Gas expansion into After equilibration, ~ 0.5 bar transferred expanded into 2L 2mL tubing segment to sample cylinder flask -⊳-IRMS 10⁻³ torr (1.3X10⁻¹⁰ bar) 830psi CO₂ IRMS (57 bar)

CO₂ flowing at 2L/min: Analysis by FTIR



Low dead volume, 2 stage / piston regulator reaches steady state faster





O isotopic composition as a function of delivery pressure



C isotopic composition as a function of delivery pressure



Δ % is the difference between regulated & unregulated flow



- 21 Kg LCO₂ cylinder
- Withdrawal at \sim 500 mL/min to eliminate possibility of droplet formation in the gas stream
- If the withdrawal rate is too high to prevent equilibration, droplets of LCO_2 will alter the data

Summary

- Careful regulator selection eliminates possibility of fractionation
- Enriched C comes off first leaving the reservoir depleted in ¹³C as the product bleeds off
- Depleted O comes off first leaving the reservoir enriched in ¹⁸O as the product bleeds off
- For precise measurements meeting the WMO DQO, gaseous sources must be used and verified for each use



