



Trace Sulfur and Hydrocarbon Contaminants in Beverage Grade Carbon Dioxide

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Introduction

Beverage grade carbon dioxide is used in large quantities in the manufacture of carbonated beverages, mostly soft drinks. Earlier this year the purity of carbon dioxide used in the production of soft drinks by a major manufacturer in Belgium and France was questioned when a number of people became sick after consuming the beverage. While no particular chemical or biological cause has been determined, the importance of carbon dioxide purity has been highlighted.

Sulfur gases and certain hydrocarbons have been targeted for determination at very low levels in the carbon dioxide. The sulfur gases include hydrogen sulfide, carbonyl sulfide, and sulfur dioxide. The hydrocarbons include acetaldehyde, benzene, and light hydrocarbons.

A two tasking GC system capable of analyzing the target compounds has been developed: 1) a pulsed flame photometric detector (PFPD) is used for the analysis of the sulfur gases down to about 0.1 ppm levels, and 2) trace hydrocarbons (<100 ppbv) in carbon dioxide are determined by preconcentration using the sample preconcentration trap (SPT).

Experimental

A schematic of the system is shown in Figure 1. For Sulfur gas analysis a 100 uL sample is introduced directly onto the capillary column. Permeation tubes were used to generate the sulfur gas standards with carbon dioxide as diluent gas. For the determination of the trace organics, approximately 100 mL of the sample is drawn through the SPT trap. The trapped organics are then thermally desorbed to the capillary column where they are chromatographed. Dynamic dilutions of bottled gas standards served as the sources of hydrocarbon standards in carbon dioxide. Chromatographic parameters for these two applications are shown in Tables 1 and 2:

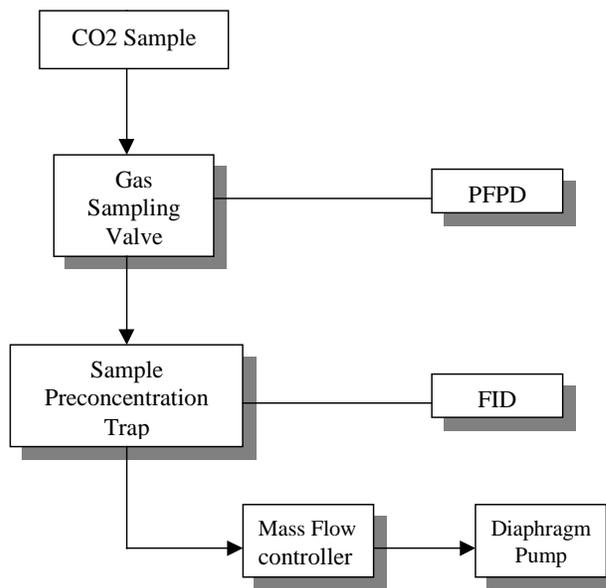


Figure 1: Schematic of beverage grade CO2 system

Table 1: Sulfur Gases

Sample:	100 uL
Column:	30M x 0.32mm CP-SilicaPLOT
Carrier:	Helium, 2ml/min; 15 psi (T-4 EFC)
Column oven	30/10 min, 20°C/min to 200°/10min
PFPD	200°, S filter, R647 PMT H2: 13ml/min Air 1: 17 ml/min Air 2: 10 ml/min

Table 2: Hydrocarbons

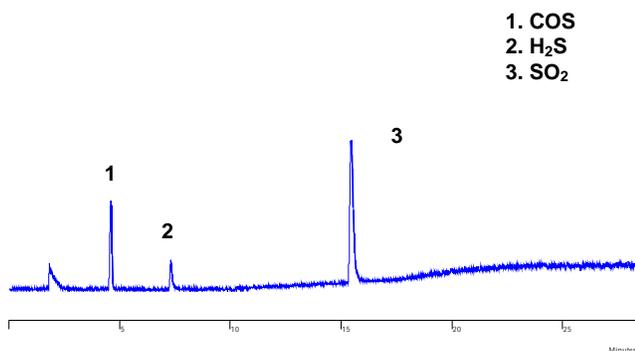
Sample:	100mL
Column:	25M x 0.53mm CP-PoraPLOT Q
Carrier:	Helium, 6ml/min; 5 psi (T-4 EFC)
Column Oven	50°/6 min, 20°/min to 200°/20min
SPT	Trap: Tenax TA (60/80) Trap: 30°; Desorb: 190°
FID	250°, Range 12

Results

Sulfur Gases

All tubing exposed to sample was constructed of Silcosteel® to prevent adsorption of sulfur components, particularly H₂S, on tubing walls.

Sample volumes greater than 100 uL were found to overload the PLOT Silica column resulting in split, broadened, or non-Gaussian peaks, therefore a sample volume of 100 uL was used. Figure 2 shows a chromatogram of approximately 0.2 ppm of COS, H₂S, and SO₂ in CO₂.

**Figure 2: Sulfur Gases in Carbon Dioxide at 0.2ppm**

The peak area and retention time precision at 1.0 ppm were measured and are shown in Table 3.

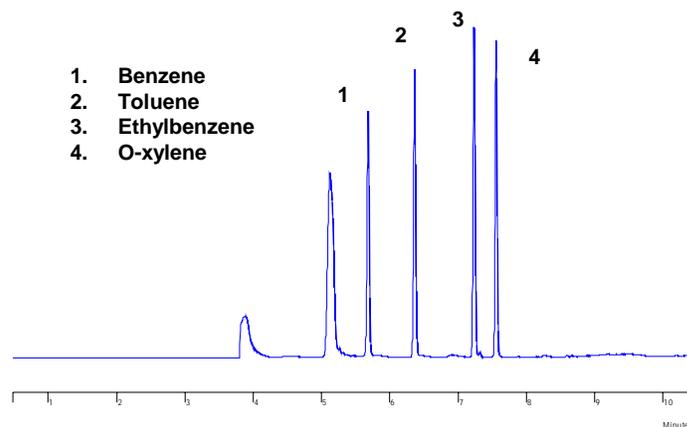
Table 3: Measurement precision for Sulfur Gases, 1.0 ppm

Compound	Precision (n=6)	
	Area Counts %RSD	Retention Time %RSD
COS	1.4	0.3
H ₂ S	5.2	0.1
SO ₂	6.5	0.03

Hydrocarbons

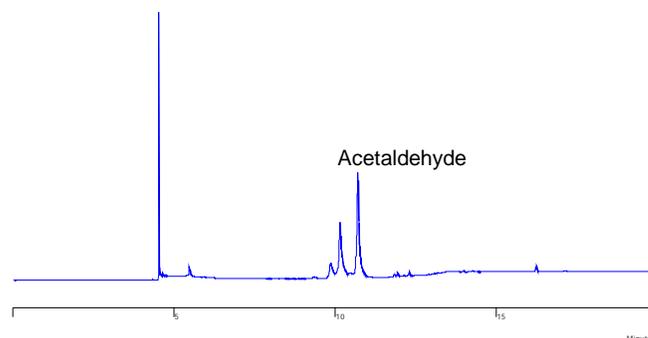
Measuring low levels of hydrocarbons in carbon dioxide is accomplished with the Sample Preconcentration Trap. The molecular weight of the target hydrocarbon dictates what trapping adsorbent is required. If acetaldehyde and simple aromatics are to be determined (shown in this note), then a Tenax TA adsorbent is adequate. If lower molecular weight components down to C₂ hydrocarbons need to be monitored, then a multiphase trap such as the three phase trap, Tenax TA/Carbotrap B®/Carbonsieve S-III® may be used. Ambient temperature is sufficient to trap all components.

Preconcentration of a 100ml sample was used to obtain the required sensitivity. Figure 3 is a chromatogram of four aromatics from a 50 ppbv standard.

**Figure 3: Preconcentration of 50 ppbv aromatics from CO₂. Column: 30M x 0.53 mm VA-1, 1.5uM.**

Measurement precision for the aromatics for six runs averaged 1.2% for area and 0.02% for retention time.

Acetaldehyde is another target analyte in beverage grade CO₂. It is trapped by the Tenax TA and injected as shown in Figure 4.

**Figure 4: Preconcentration of 0.5 ppmv Acetaldehyde from CO₂. Column: 30M x 0.53mm Poraplot Q.**

Conclusions

Trace sulfur and hydrocarbon contaminants may be measured in beverage grade CO₂ with a single gas chromatograph. Sulfur compounds are measured at levels down to approximately 0.05 to 0.1 ppm by introducing a small sample directly to a PLOT Silica column and PFPD via Silcosteel® coated tubing.

Trace level hydrocarbons, in this case aromatics and acetaldehyde, are determined by preconcentrating a 100 mL sample on a preconcentrating trap followed by thermal desorption to a capillary column. Detection levels down to less than 1 ppbv are possible.