

Trace sulfur and hydrocarbon contaminants in beverage grade carbon dioxide

Application Note

Food Testing & Agriculture

Authors

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Introduction

Beverage grade carbon dioxide is used in large quantities in the manufacture of carbonated beverages, mostly soft drinks. 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 was determined, the importance of carbon dioxide purity was highlighted.

Sulfur gases and certain hydrocarbons have been targeted for determination at very low levels in 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 were developed: 1) a pulsed flame photometric detector (PFPD) used for the analysis of the sulfur gases down to about 0.1 ppm levels, and 2) trace hydrocarbons (<100 ppbv) in carbon dioxide determined by preconcentration using the sample preconcentration trap (SPT).



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Experimental

A schematic of the system is shown in Figure 1. For sulfur gas analysis a 100 μ L 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:

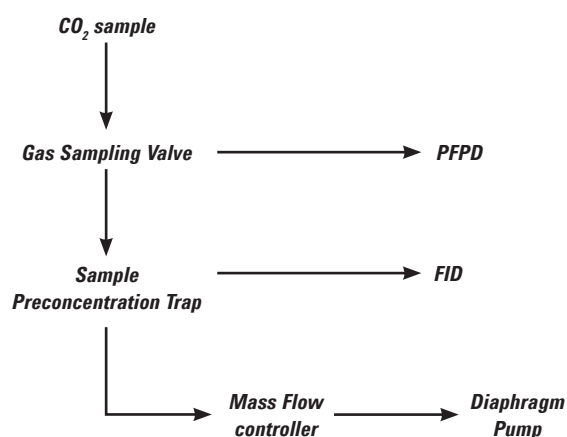


Figure 1: Schematic of beverage grade CO₂ system

Sample	100 μ L
Column 1	Agilent CP-SilicaPLOT, 0.32 mm x 30 m, Part no. CP8567
Carrier	Helium, 2 mL/min; 15 psi (T-4 EFC)
Column Oven	30/10 min, 20 $^{\circ}$ C/min to 200 $^{\circ}$ C/10 min 200 $^{\circ}$ C, S filter, R647 PMT
PFPD	H ₂ : 13 mL/min Air 1: 17 mL/min Air 2: 10 mL/min

Table 1: Sulfur Gases

Sample	100 mL
Column	Agilent PoraPLOT Q, 0.53 mm x 25 m, Part no. CP7554
Carrier	Helium, 2 mL/min; 15 psi (T-4 EFC)
Column Oven	50 $^{\circ}$ C/6 min, 20 $^{\circ}$ C/min to 200 $^{\circ}$ C/20 min
SPT	Trap: Tenax TA (60/80) Trap: 30 $^{\circ}$ C; Desorb: 190 $^{\circ}$ C
FID	250 $^{\circ}$ C, Range 12

Table 1: Hydrocarbons

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 μ L were found to overload the Agilent CP-SilicaPLOT column resulting in split, broadened, or non-Gaussian peaks, therefore a sample volume of 100 μ L was used. Figure 2 shows a chromatogram of approximately 0.2 ppm of COS, H₂S, and SO₂ in CO₂.

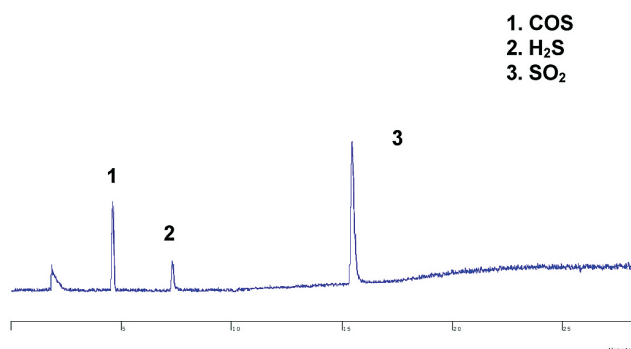


Figure 2: Sulfur Gases in Carbon Dioxide at 0.2 ppm

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

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

Table 3: Measurement precision for Sulfur Gases, 1.0 ppm

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

1. benzene
2. toluene
3. ethylbenzene
4. o-xylene

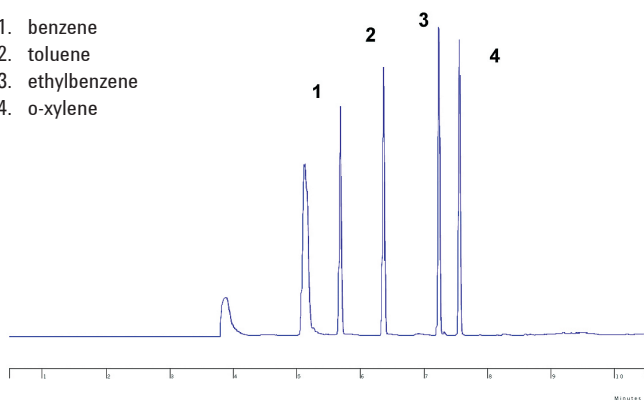


Figure 3: Preconcentration of 50 ppbv aromatics from CO₂.
Column: Agilent CP-Sil 5 CB, 0.53 mm x 30 m, 1.5 µm, Part no. CP8735.

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.

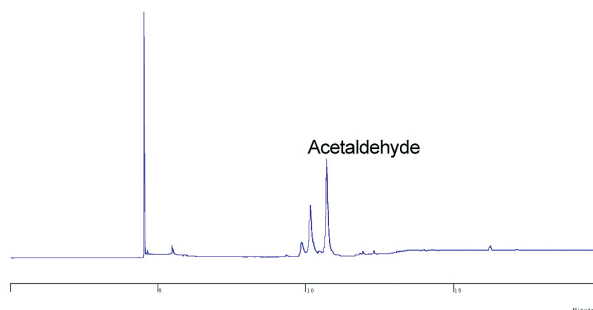


Figure 4: Preconcentration of 0.5 ppmv acetaldehyde from CO₂.
Column: Agilent PorapLOT Q, 0.53 mm x 30 m, Part no. CP7554.

Conclusion

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 UltiMetal deactivated or 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.

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