

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 was questioned when a number of people became ill after consuming the beverage. While no particular chemical or biological cause was discovered, 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.



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Instrumentation

A twotasking GC system capable of analyzing the target compounds was developed: 1) a pulsed flame photometric detector (PFPD) for the analysis of the sulfur gases down to about 0.1 mg/L, and 2) trace hydrocarbons (<100 µg/L) in carbon dioxide determined by preconcentration using a Agilent Sample Preconcentration Trap (SPT). A schematic of the system is shown in Figure 1. Data handling was carried out using Agilent chromatography software.

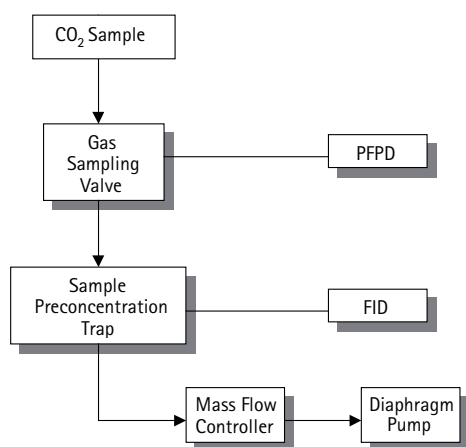


Figure 1. Schematic of beverage grade CO₂ system

Materials and Reagents

For sulfur gas analysis, the sample was introduced directly onto the capillary column. Permeation tubes generated the sulfur gas standards with carbon dioxide as diluent gas. For the determination of the trace organics, approximately 100 mL of the sample was drawn through the SPT trap. The trapped organics were then thermally desorbed to the capillary column where they were chromatographed.

Dynamic dilutions of bottled gas standards served as the sources of hydrocarbon standards in carbon dioxide.

Conditions

Sulfur Gases

Sample: 100 µL
 Column: Agilent J&W CP-SilicaPLOT, 30 m x 0.32 mm (part number CP8567)
 Carrier Gas: Helium, 2 mL/min, 15 psi (T-4 EFC)
 Column Oven: 30 °C /10 min, 20 °C/min to 200 °C/10min
 Detection: Agilent PFPD, 200 °C, S filter, R647 PMT
 H₂, 13 mL/min
 Air 1, 17 mL/min
 Air 2, 10 mL/min

Hydrocarbons

Sample: 100 mL
 Columns: Agilent J&W PoraPLOT Q, 25 m x 0.53 mm, df = 20 µm (part number CP7554) Agilent CP-Sil 5 CB, 30 m x 0.53 mm, df = 1.5 µm (pn: CP8735)
 Carrier Gas: Helium, 6 mL/min, 5 psi (T-4 EFC)
 Column Oven: 50 °C/6 min, 20 °C/min to 200 °C/20min
 SPT Trap: Tenax TA (60/80) (Agilent special order)
 Trap: 30 °C
 Desorb: 190 °C
 Detection: Agilent FID, 250 °C, Range 12

Results and Discussion

Sulfur Gases

All tubing exposed to sample was constructed of UltiMetal to prevent adsorption of sulfur components, particularly H₂S, on tubing walls. Sample volumes greater than 100 µL overloaded the PLOT column, resulting in split, broadened or non-Gaussian peaks. Figure 2 shows a chromatogram of approximately 0.2 mg/L of COS, H₂S and SO₂ in CO₂.

The peak area and retention time precision at 1.0 mg/L were measured and are shown in Table 1.

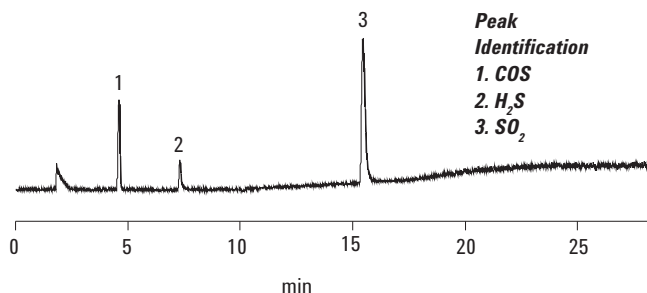


Figure 2. Sulfur gases in carbon dioxide at 0.2 mg/L

Table 1. Measurement precision for sulfur gases, 1.0 mg/L

Compound	Precision (n=6)	
	Area Counts (% RSD)	Retention Time (% RSD)
COS	1.4	0.30
H ₂ S	5.2	0.10
SO ₂	6.5	0.03

Hydrocarbons

Measuring low levels of hydrocarbons in carbon dioxide was accomplished with the Sample Preconcentration Trap. The molecular weight of the target hydrocarbon dictated the choice of trapping adsorbent. If acetaldehyde and simple aromatics are to be determined (shown in this note), then a Tenax TA adsorbent was 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/Carbosieve S-III, may be used. Ambient temperature was 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 µg/L standard.

Peak Identification

1. Benzene
2. Toluene
3. Ethylbenzene
4. *o*-Xylene

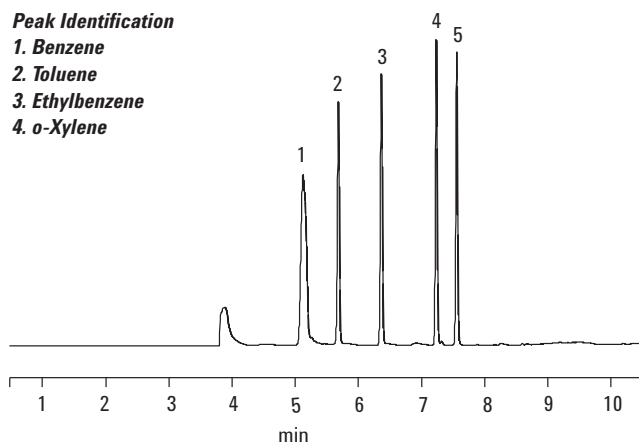


Figure 3. Preconcentration of 50 µg/L aromatics from CO₂
(Column: Agilent CP-Sil 5 CB, 30 m x 0.53 mm, df = 1.5 µm)

Measurement precision for the aromatics for six runs averaged 1.2% for area and 0.02% for retention time. Acetaldehyde was another target analyte in beverage grade CO₂. It was trapped by the Tenax TA and injected as shown in Figure 4.

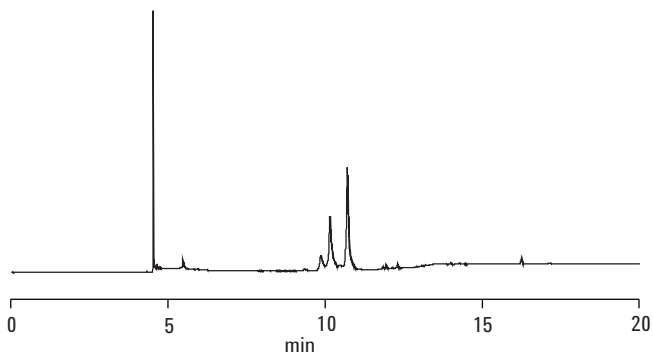


Figure 4. Preconcentration of 0.5 mg/L acetaldehyde from CO₂
(Column: Agilent PoraPLOT Q, 25 m x 0.53 mm, df = 20 µm)

Conclusion

Trace sulfur and hydrocarbon contaminants can be measured in beverage grade CO₂ with a single gas chromatograph. Sulfur compounds were assessed down to approximately 0.05 to 0.1 mg/L by introducing a small sample directly to a CP-SilicaPLOT column with pulsed flame photometric detection. Trace level hydrocarbons, in this case aromatics and acetaldehyde, were determined by preconcentrating a 100 mL sample on a preconcentration trap followed by thermal desorption to a capillary column. Detection levels below 1 µg/L were possible.

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