

# Trace Impurities in Beverage-Grade CO<sub>2</sub> Incorporating the Amperometric Sulfur Detector

## Introduction

PerkinElmer-Arnel has developed a new family of analyzers for measuring trace sulfur and other impurities in beverage-grade carbon dioxide (CO<sub>2</sub>). The unique amperometric sulfur detector\* (ASD) is incorporated in this suite of analyzers.

Each guaranteed turnkey solution has a different feature set that addresses the interests of the CO<sub>2</sub> manufacturers, deliverers and beverage producers or users. Table 1 shows compounds detected with measured minimum detection limits (MDLs) attainable for each analyzer.

There are 16 different models, 8 with manual pneumatic control and 8 with programmable pneumatic control (PPC). Many of the models include multi-detector configurations to address non-sulfur requirements. The analyzers support the “purity analysis” required by the International Society of Beverage Technologists (ISBT). This specification requires hydrocarbons, oxygenates and aromatics (i.e. benzene) to be measured at sub-ppm levels.

Table 1. Compounds Measured and MDLs for Each Analyzer

Compounds Analyzed	Models Performing Analysis	Minimum Detection Limit (MDL)
Benzene	6030, 6430, 6038, 6438	5 ppb
Acetaldehyde	6031, 6431, 6038, 6438	50 ppb
Speciated Sulfur Components	6025, 6425, 6030, 6430 6031, 6431, 6038, 6438	10 ppb
Alcohols, Ketones and Hydrocarbon Components	6031, 6431, 6038, 6438	5 to 15 ppb
Other Aromatic Components	6030, 6430, 6038, 6438	5 ppb

## ASD components

The ASD (Figure 1) consists of three main components. A high-temperature micro reactor with quartz pyrolysis zone is mounted on the top of the Clarus® GC main oven, allowing combustion

Table 2. GC/ASD Model Matrix

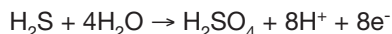
Model No.	Description	Detectors	Permeation Chamber	On-Line Capability
6025 and 6025PPC	Trace sulfur in beverage-grade CO <sub>2</sub>	ASD	No	Yes
6425 and 6425PPC	Trace sulfur in beverage-grade CO <sub>2</sub>	ASD	Yes	Yes
6030 and 6030PPC	Trace sulfur and aromatics in beverage-grade CO <sub>2</sub>	ASD/PID	No	Yes
6430 and 6430PPC	Trace sulfur and aromatics in beverage-grade CO <sub>2</sub>	ASD/PID	Yes	Yes
6031 and 6031PPC	Trace sulfur and hydrocarbons in beverage-grade CO <sub>2</sub>	ASD/FID	No	Yes
6431 and 6431PPC	Trace sulfur and hydrocarbons in beverage-grade CO <sub>2</sub>	ASD/FID	Yes	Yes
6038 and 6038PPC	Trace sulfur, aromatics, and hydrocarbons in beverage-grade CO <sub>2</sub>	ASD/PID/FID	No	Yes
6438 and 6438PPC	Trace sulfur, aromatics, and hydrocarbons in beverage-grade CO <sub>2</sub>	ASD/PID/FID	Yes	Yes

\* Patents pending or granted.

of samples containing high concentrations of carbon. The sample containing sulfur impurities mixes with reaction gas (either hydrogen-air or hydrogen) in the micro reactor in a reductive atmosphere to form hydrogen sulfide (H<sub>2</sub>S). The H<sub>2</sub>S formed in the reactor is then swept into the electrochemical cell for measurement. The electrochemical sensor consists of 3 electrodes (sensing, counter and reference) with an electrolyte in a sealed housing.

In amperometric mode, the electrochemical sensor operates by oxidizing the H<sub>2</sub>S from the sample components

at the sensing electrode, which is maintained at a fixed potential with respect to the reference electrode. The measured current in the sensor is proportional to the concentration of H<sub>2</sub>S present in the sample component. The electrochemical reaction scheme at the sensing electrode is given below:



The electrochemical sensor has high sensitivity to sulfur ( $\leq 1$  ppb H<sub>2</sub>S) and a fast response time (< 1 sec). The sensor is mounted on the top of the Clarus GC at the rear detector port.

A compact electronics module is situated alongside the GC (Figure 1) and provides reaction-gas control. The electronics module is connected via a cable to the sensor for data acquisition.

### ASD precision and stability

The ASD system provides excellent precision and long-term stability (Figure 2). The peak-height stability shows a relative standard deviation (RSD) of 1.2% determined for a period in excess of 24 hours.

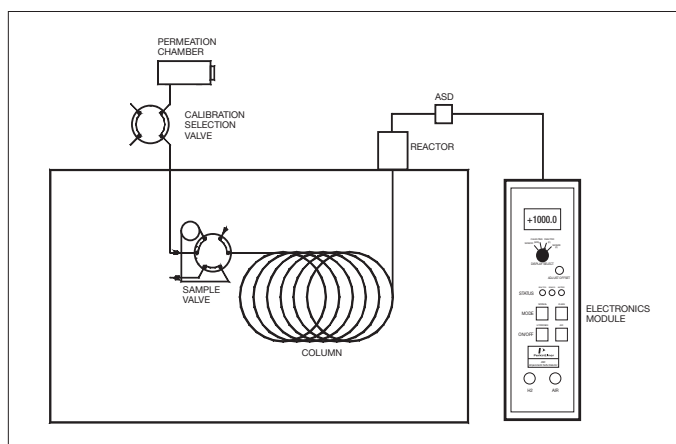


Figure 1. Schematic of GC-ASD PerkinElmer-Arnel engineered system.

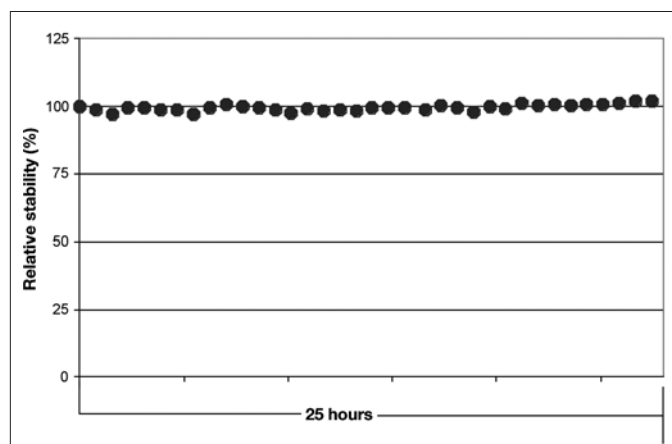


Figure 2. ASD long-term stability – 280 ppb dimethyl sulfide (DMS) standard in beverage-grade CO<sub>2</sub>.

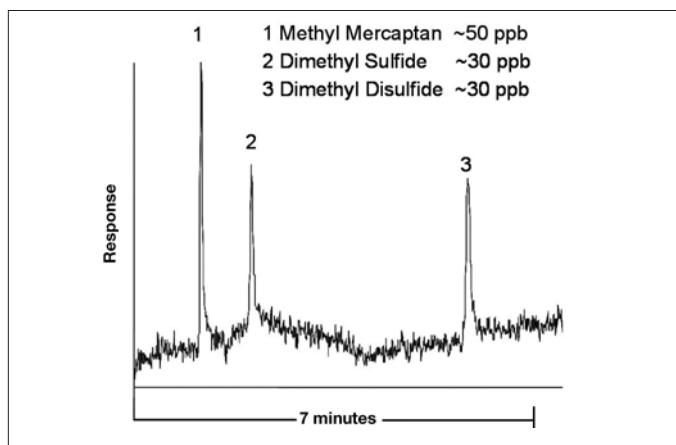


Figure 3. Low-level response for three sulfur compounds using the ASD.

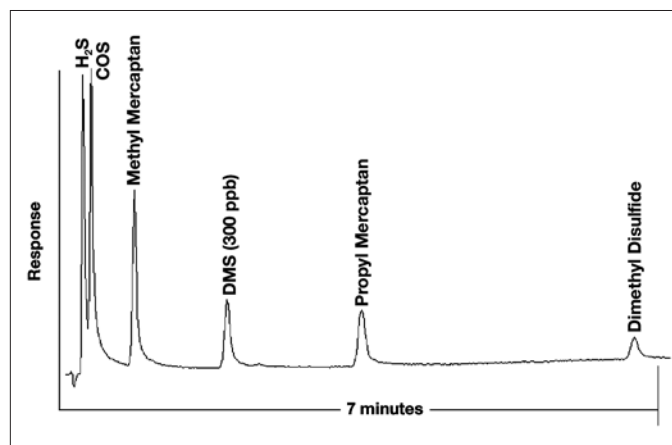


Figure 4. Chromatogram showing sulfur standards spiked in a CO<sub>2</sub> sample matrix.

## Minimum detection limits for sulfur compounds

The MDL for speciated sulfur compounds is 10 parts per billion (ppb) S with equimolar response equivalent to 20 ppb dimethyl sulfide (DMS), as shown in Figure 3.

## Chromatography of trace-sulfur impurities in beverage-grade CO<sub>2</sub>

Trace-sulfur compound measurement at low ppb levels is easily attainable. Figure 4 provides a chromatogram of beverage-grade CO<sub>2</sub> analysis using the ASD system.

## Chromatography obtained from the PID and FID channels

The PID channel has great sensitivity to benzene. It also exhibits a small response to CO<sub>2</sub>, which means that the benzene must be separated from the CO<sub>2</sub>. A polar column is used to delay benzene until CO<sub>2</sub> has eluted. Other aromatics such as toluene and the xylenes are also analyzed on this channel (Figure 5).

The FID channel uses a polar column to separate the alcohols. An additional benefit of this

column is the fact that the light, non-polar hydrocarbons are less retained. They pass through as a single peak and are detected by the FID (Figure 6). Benzene can also be separated and measured on this channel. The benzene detection limit on the FID is not as sensitive as on the PID channel.

## Plumbing design features

Generally, the analyzer models are one, two and three analytical channels, depending upon the model – see Figure 7 for a plumbing diagram of Model 6430. The feature set of all of the models is consistent and designed to eliminate system activity:

- Sampling valve(s) are plumbed directly to columns to minimize peak broadening, maximize reproducibility and eliminate injection port selectivity for lighter compounds.
- All surfaces exposed to samples are constructed out of sulfur-inert materials to eliminate activity to the sulfur compounds.
- Recommended use of an on-board permeation tube chamber for calibration – eliminates calibration-cylinder internal surface activity with concomitant inaccuracies.

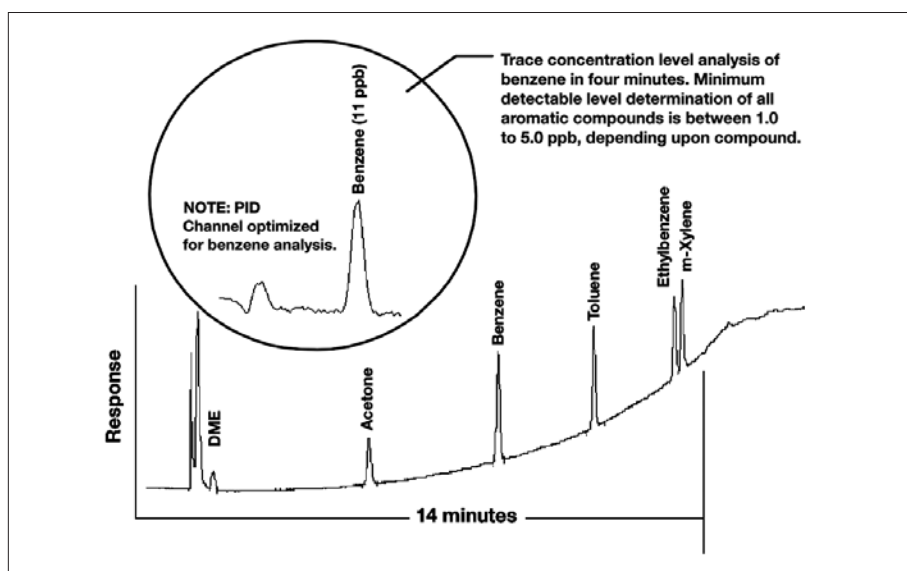


Figure 5. Chromatogram of PID channel.

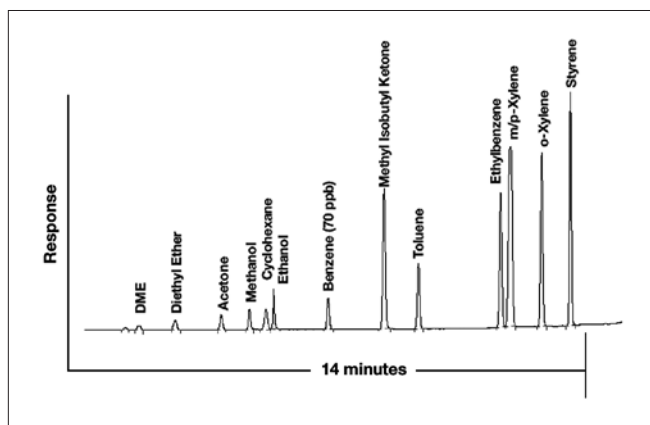


Figure 6. Chromatogram of FID channel (ethylene glycol elutes in about 11 minutes).

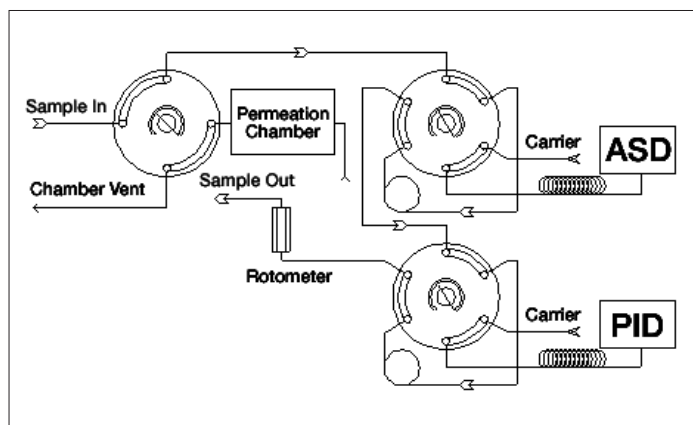


Figure 7. Plumbing diagram of two-channel Model 6430 analyzer.

## Permeation-tube calibration chamber option

The on-board, heated permeation-tube calibration chamber is an added feature to Models 6425, 6430, 6431 and 6438. The option saves both space and cost, plus eliminates the possibility of calibration cylinder activity, as stated previously.

The permeation chamber is mounted on the top of the GC (Figure 8) and can hold up to four different permeation tubes. All models that contain the permeation-chamber option are shipped with a certified DMS permeation tube. The Model 6430 is shipped with an additional certified benzene permeation tube; the Model 6431 is shipped with an additional certified ethanol permeation tube; and the Model 6438 is shipped with all three certified permeation tubes. The permeation tubes shipped with the analyzers are tested in the analyzer and in an NBS traceable permeation-tube calibrator. The difference between the two calibration methods at 50 °C and 100 mL per minute flow is typically less than 5%. The differences in detector response for the

two calibration methods are listed in the manual shipped with the analyzers.

The permeation-tube calibration chamber option also includes a rotometer and a manual four-port stream-selection valve. The four-port valve presents either gas from the permeation chamber or the gas sample to the analyzer. The calibrated rotometer is used to show that the correct dilution gas volume is flowing through the permeation chamber. The rotometer is also used when sample is passing through the gas sample loop as an indicator of sample flow.

## Other options

### Model 4085 liquefied CO<sub>2</sub> expansion apparatus

The Model 4085 liquefied carbon dioxide expansion apparatus is used to vaporize liquefied carbon dioxide. The technological concept is based upon the design of the sampling apparatus described in ASTM Method D-2712, with improvements for handling and expanding liquid carbon dioxide.

The apparatus is used to create gaseous samples from liquid carbon dioxide for accurate trace-impurity analysis. It can also be used to fill containers for shipment to remote laboratories for verification analyses.

A subambient accessory is available for certain applications.

## User interface software and automated multipoint sampling for plant operation

Plant-operation systems can be added to the analyzers and can be designed to individual customer requirements. These options for push-button plant operation include automated, on-line, multipoint stream or truck sampling systems and user interface software for streamlined data handling, monitoring and control (Figure 9).

## Model 3062 reporting software

Model 3062 reporting software can be utilized to provide custom reports and calculations, using the full capabilities of Microsoft® Excel®. It can also be used to translate the resulting report into many languages.



Figure 8. Permeation-tube calibration chamber system.

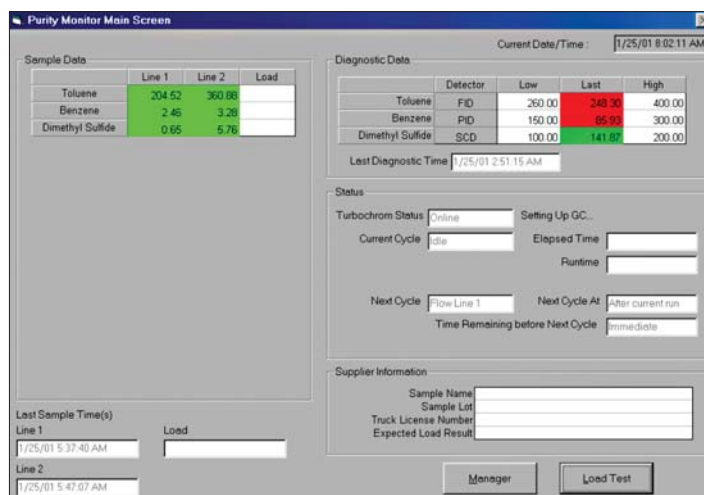


Figure 9. Main screen of user interface software.

Model 3062 reporting software is provided at no charge with multi-channel analyzers.

Model 3062 is an Excel® workbook that must be customized by the user. It requires TotalChrom® data-handling software, Microsoft® Excel® and full knowledge of both applications to use effectively. TotalChrom and Excel® are not included and must be purchased separately.

### ASD Specifications

Detectability:	10 ppb S (equivalent to 20 ppb DMS)
High selectivity:	$\geq 10^6$ gS/gCO <sub>2</sub>
Peak-height precision and stability:	Relative Standard Deviation (RSD) < 5%, 24 hrs
Linear range:	10 <sup>3</sup>
Dynamic range:	10 <sup>5</sup>
Response to S:	Equimolar

PerkinElmer, Inc.  
940 Winter Street  
Waltham, MA 02451 USA  
Phone: (800) 762-4000 or  
(+1) 203-925-4602  
[www.perkinelmer.com](http://www.perkinelmer.com)

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