APPLICATION NOTE

Analyzers For Impurities In Beverage CO_2 Models 4025/4030/4031/4038

Analyzer Descriptions

Overview

Arnel has developed a family of analyzers that measure impurities in beverage grade CO_2. The Model 4025 uses a Sulfur Chemiluminescence Detector (SCD™) to analyze H_2S and other sulfur compounds. The Model 4030 analyzes the sulfur compounds with the SCD plus benzene and other aromatics using a Photoionization Detector (PID). The Model 4031 analyzes the sulfur compounds with the SCD and hydrocarbons using a Flame Ionization Detector (FID). Ethylene glycol, acetaldehyde and alcohols are also analyzed with this model. The Model 4031 can also be used to analyze for total non-polar hydrocarbons as a single number and benzene at higher detection limits than the Model 4030.

Finally, the Model 4038 combines all three analytical channels into a single analyzer. All models can be enhanced by the addition of an integrated permeation chamber for calibration. The Models 4425, 4430, 4431 and 4438 feature the added permeation chamber.

Other Possible Combinations

All of these analyzers include the sulfur analysis channel featuring the SCD. If you are interested in only the aromatics, only the hydrocarbon analysis or the aromatics and hydrocarbon analysis without the sulfur analysis, analyzers can be specially provided in any combination.

It is also possible to order an analyzer that includes a "total hydrocarbons" channel. This analysis channel combines all of the hydrocarbons into a single peak.

SCD Analyzed Sulfur Components

- H_2S, COS, SO_2
- Mercaptans
- Aromatic sulfur compounds
- Sulfides

PID Analyzed Aromatic Components

- Benzene
- Toluene
- Xylenes
- Ethyl benzene

FID Analyzed Hydrocarbons

- Acetaldehyde
- $C_1 - C_4$ alcohols
- Ethylene glycol
- Total non-polar hydrocarbons
- Benzene

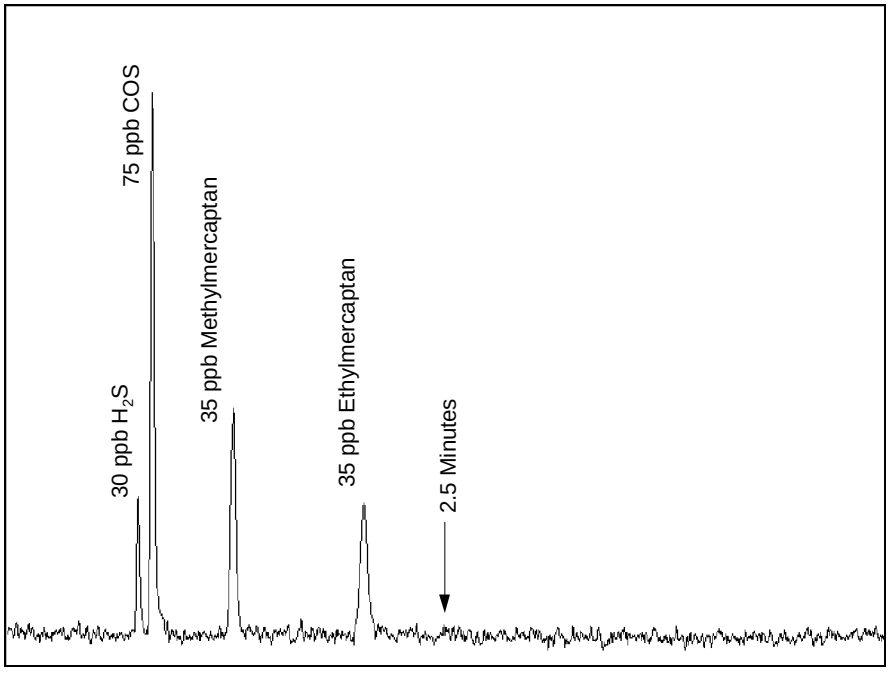

Figure 1. Example chromatogram for trace level light sulfur components.

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Plumbing Diagram

Figure 2 presents the plumbing diagram for the Model 4430. Both analysis channels feature a Gas Sampling Valve (GSV) and a capillary column plumbed to the detector. To minimize peak width spread, improve reproducibility and eliminate any injection port activity for the lightest compounds, the capillary columns are mounted directly onto the gas sampling valves. To minimize activity for the sulfur components such as H_2S, all surfaces that are exposed to the sample are plumbed with nickel valves and specially passivated tubing. Putting the sulfur channel's GSV first in the sample path also helps to minimize the reactivity of the system.

The Model 4038 has the PID and FID mounted normally in the GC. The SCD is added to the GC through the top of the column oven.

Permeation Chamber Calibration Option

Typically, gas sample calibration is accomplished using gas standards from cylinders or external permeation devices. The integrated permeation chamber option (shown in Figure 2) saves both space and cost. The permeation chamber is mounted on the top of the GC in the space that would be taken by the autosampler. This option also includes a rotometer and a manual stream selection valve that selects either the calibration source or the sample input.

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.

The temperature of the permeation chamber is controlled by an unused injection port temperature zone. The chamber can hold up to four permeation devices.

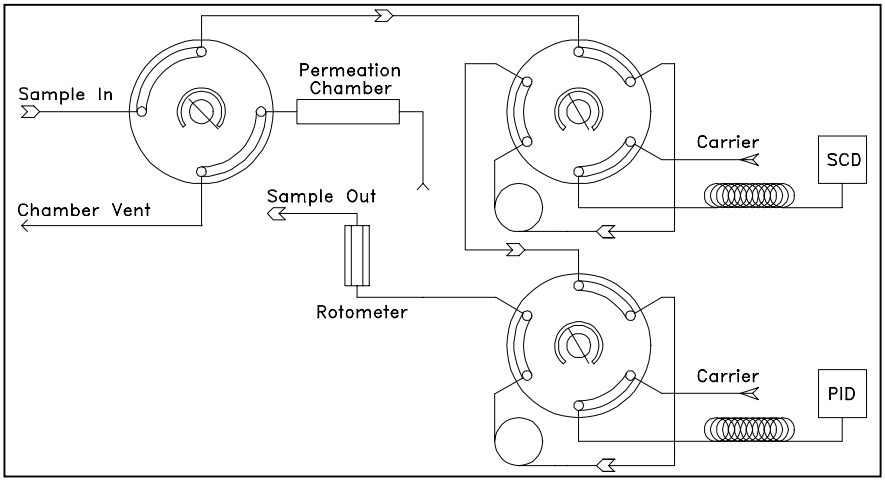

Figure 2. Model 4430 plumbing diagram. All valves are shown in the fill position. The 4431 would have a FID instead of the PID. The Model 4438 adds another valve, column and detector.

All models that contain the permeation chamber option are shipped with a certified dimethylsulfide permeation tube that provides ~250ppb molar at 50°C and 100ml per minute mass flow. Concentrations can be adjusted either higher or lower by using different size permeation tubes, raising the temperature or increasing the dilution flow. The Model 4430 also includes a benzene permeation tube. The benzene concentration is ~250ppb molar. The Model 4431 includes an ethanol permeation tube that provides ~500ppb molar. The Model 4438 is shipped with all three permeation tubes.

Permeation Tube Accuracy

The permeation tubes shipped with the unit are tested in the analyzer and an NBS traceable permeation tube calibrator. The difference between the two calibration methods at 50°C and 100ml per minute flow is typically less than 5%. The differences in detector response for the two calibration methods are listed in the manual.

Blocking the Sample Flow

The permeation chamber option's manually actuated sample selection valve is located on the top of GC outside of the column oven. The primary function of this valve is to present either the calibration gas from the permeation chamber or the CO_2 sample to the GSV's. The selection valve provides another important function during the actual sampling. When the valve is turned half way between the two positions, all flow is blocked. When the sample input is blocked, the pressure in the sample loop drops to atmospheric pressure. Thus, both the calibration stream and the sample can be injected under identical conditions.

Typically, the pressure in the sample loop(s) is further controlled by venting the sample loop through a manometer. When the sample flow is blocked, bubbles stop rising in the manometer. Once the bubbles stop flowing, the GC is started and the GSV turns automatically.

Chromatography Details

The SCD channel uses a methyl silicone capillary column. All components separate on the basis of their boiling points. The SCD has such great carbon rejection that there is no interference from any carbon containing compounds that may be found in this analysis.

The PID has great sensitivity to benzene. It also exhibits a small response to CO_2. This response means that the benzene must be separated from the CO_2. A polar column is used to delay benzene until CO_2 has eluted. Other aromatics such as toluene and the xylenes may also be analyzed on this channel.

The FID channel in the Model 4031 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. Benzene can also be separated and measured on this channel. The benzene detection limit for the FID is worse than the PID channel.

Column Temperature Programs

The GSV's are mounted in the column oven. The upper temperature limit for these valves is 175°C (4030/31/38) or 225°C (4025). This upper limit greatly exceeds the temperature needed for any impurity in beverage CO_2.

If the analysis is started at ambient temperatures, COS and SO_2 coelute. If there is a requirement to separate COS from SO_2, a cryogenic cooling option must be added to the GC. When the cryogenic option is ordered for the GC, all GSV's are placed unheated outside the column oven. This mounting position is used to assure that the GSV's do not leak at low column oven starting temperatures.

The actual starting temperature and temperature program used depend upon the components to be analyzed. To run both channels simultaneously, the identical temperature program is used for the chromatograms in Figure 1 and 3.

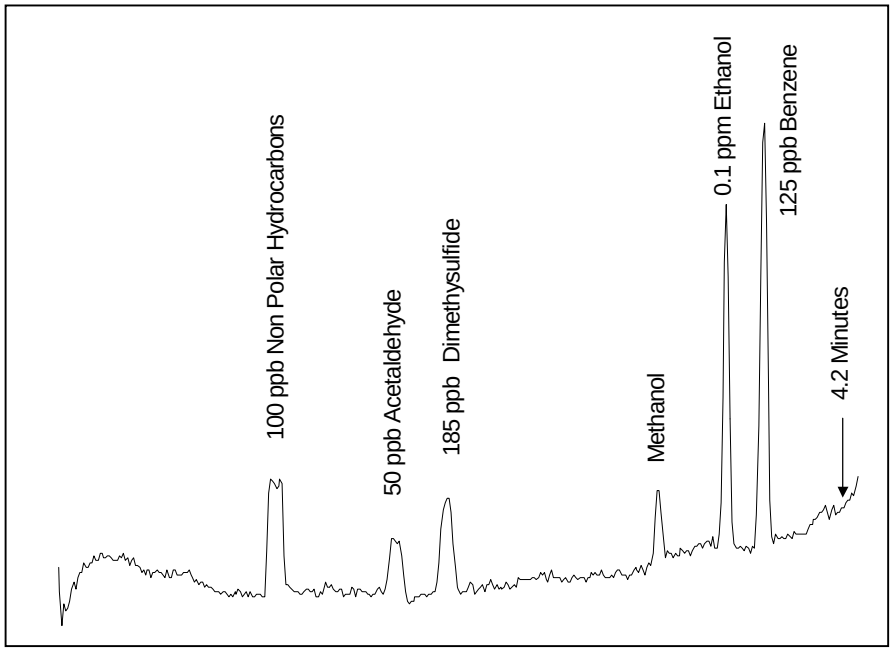

Figure 3. Chromatogram from the FID based hydrocarbon channel. The concentrations are approximate. Ethylene glycol elutes at ~ 11 minutes.

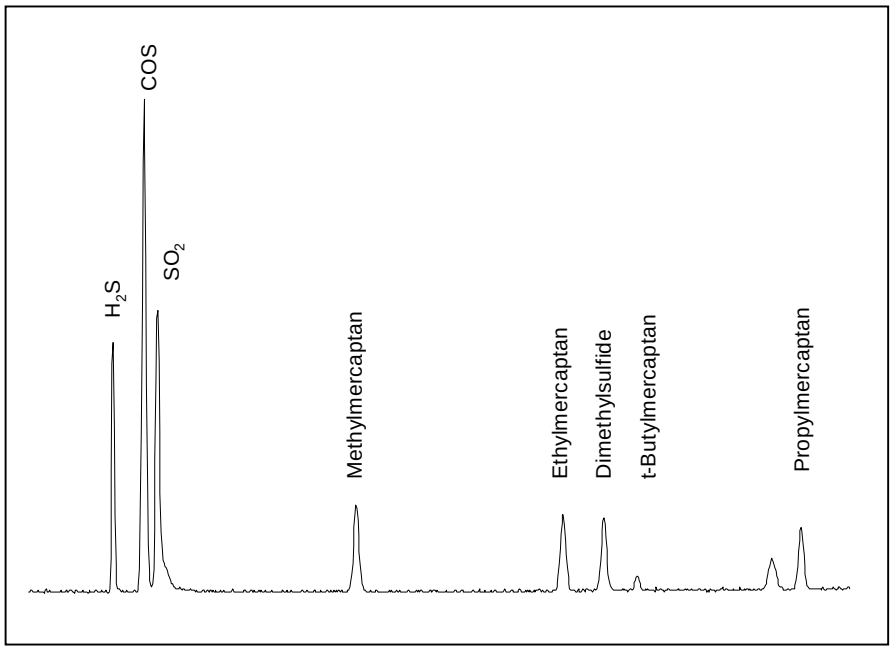

Figure 5. Chromatogram demonstrating the separation of COS and SO_2.

Separating COS and SO_2

Beverage purity specifications allow relatively large concentrations of SO_2 and low concentrations of COS. The ability to separate these two compounds is a key feature of the SCD channel. If total sulfur analysis is used, a load of CO_2 with 100ppb sulfur must be rejected. Even if the sulfur impurity is only SO_2, the load must be rejected. There is no way to be sure that the sulfur impurity is not H_2S.

With complete separation of all of the sulfur compounds, a load of CO_2 containing 150ppb of SO_2 is accepted as completely safe. The financial benefits of this measurement are obvious.

Total Hydrocarbons

Some facilities require a "total hydrocarbons as methane" number. This requirement is met by replacing the FID capillary column with inert

tubing. The sample is injected and detected as a single FID peak. This option can be provided as a custom analyzer. Contact your local PerkinElmer sales engineer for more details.

Detection Limits

The practical detection limit for each of the sulfur compounds is <10ppb molar. Acetaldehyde has a <20ppb molar detection limit. The guaranteed benzene detection limit is 5ppb.

Proper Sampling

The quality of the analysis is only as good as the sample. Detection limits for these analyzers have been achieved by extreme attention to the elimination of system activity. Trace level compounds (especially H_2S and COS) like to "stick" to active surfaces.

These activity issues can affect your reported concentrations in both directions. An example of reported values that are too low is the loss of H_2S in sampling bags. As the sample is transported to the analyzer, the H_2S adsorbs to the walls of the bag. Arnel can help you through the design and implementation of your sampling system.

Activity in the calibration system will cause reported values to be too high. A gas standard stored in a cylinder loses H_2S over time. Also, H_2S is lost in the regulator and connecting tubing. Thus, the actual amount of H_2S that reaches the analyzer is lower than what is stated on the standard's certificate of analysis. A signal of 1mv for 50ppb is really 1mv for 20ppb. This means that properly taken samples will have reported H_2S concentrations that are 150% too high. The use of the integrated permeation chamber eliminates this problem.

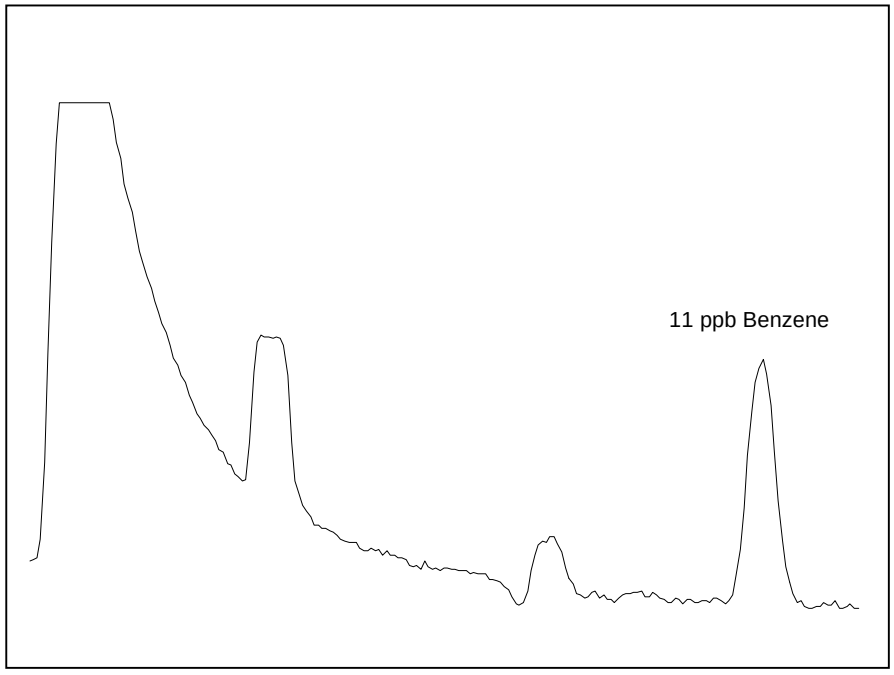

Figure 6. Chromatogram showing an example of a low level benzene peak.

Ordering Options

The SCD is a stand-alone detector with a selectable 10V, 1V or 100mV output. How you input that signal depends upon your data handling choice. If you are using TotalChrom with the Model 4025, 4030 or 4031, include the Integral Link and N612-0060 analog input card options. When ordering the Model 4038 or 4438, eliminate the analog card and add an NCI interface.

When COS and SO_2 must be separated, order the cryogenic cooling option only. Always order a one-year maintenance kit for the SCD.

Each model can be ordered with manual pneumatics or PPC.

Routine Maintenance

The SCD is a trace level analyzer with remarkable characteristics. This performance requires extremely clean gases, a working vacuum pump and a clean, active burner. All of these analyzers are supplied with the sulfur filters needed for one year of continuous use. Filter use depends upon the quality of the supplied gases. The number of filters supplied assumes relatively dirty gases. If you have good quality gases, the supplied filters will last more than one year.

The SCD generates ozone and this gas is pulled to the vacuum pump. The chemical traps supplied in the one-year kit protect the pump by trapping the ozone.

Over long periods of use, SCD burner ceramics can deactivate. The ceramics are also deactivated if exposed to a hydrogen rich atmosphere (due to loss of burner air). Sensitivity is recovered by the replacement of the SCD's ceramics. The best way to assure optimum system performance is to hold to a rigorous preventative maintenance schedule.

The one-year maintenance kit includes everything required to keep the pump (12 chemical traps, four oil mist filters, rebuild kit and pump oil) and burner (two sets of ceramics) running properly for one year.

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