GAS CHROMATOGRAPHY

PRODUCT NOTE

# Sulfur-analyzer Systems using the Amperometric Sulfur Detector

Low-level sulfur detection and determination is an important capability as sulfur compounds have been identified as unwanted impurities in a number of key processes, including the fermentation of beer and in the production of the carbonated beverages we consume. Trace levels (parts per billion) of sulfur impurity compounds are also of importance in the quality control (QC) of bulk gases such as nitrogen, hydrogen and carbon dioxide and in ethylene and propylene monomer used as raw materials for polymer fabrication.

In partnership with Arnel™ Inc., PerkinElmer provides proven turnkey and customized sulfur-measurement solutions specifically for the beverage, bulk gas and petrochemical industries utilizing ethylene and propylene.

The amperometric sulfur detector (ASD) is the latest addition to the PerkinElmer® portfolio of turnkey sulfur analyzers and is a novel detector for the measurement of trace levels of volatile sulfur compounds in gas matrices based on selective, electrochemical cell technology.

With a PerkinElmer-Arnel ASD sulfur-analyzer system, the sample components are separated using gas chromatography and are then combusted in a reducing atmosphere to form hydrogen sulfide ($H_2S$). The hydrogen sulfide is then swept into the electrochemical cell, oxidized in-situ and measured by the sensor. The response from the sensor is then amplified and converted to an output voltage consistent with that of the gas chromatograph used for component separation.

The ASD is fully integrated into PerkinElmer-Arnel's family of analyzers dedicated to trace-volatile sulfur analyses in the parts-per-billion (ppb) range in gas matrices.

## ASD compared to other GC sulfur detectors

Gas chromatography has a wide selection of detectors available to satisfy the ever-increasing requirement for reliable and sensitive sulfur analyses. Some familiar types include the flame photometric (FPD), pulsed flame photometric (PFPD), atomic emission (AED), photoionization (PID), microwave plasma (MIPD), Hall electrolytic conductivity (ELCD) and sulfur chemiluminescence (SCD) detectors.

The FPD became the most commonly used sulfur detector due to its ease-of-use and relatively low cost of operation. It also exhibits moderate sensitivity and selectivity for sulfur. However, the FPD has a number of disadvantages. A key disadvantage is that its response to sulfur is **approximately** proportional to the square of the mass of the sulfur compound.

### Key Benefits

- Available with PerkinElmer-Arnel gas-phase sulfur-analyzer systems
- Sulfur detection in the range of 0.01 to 10.0 ppm
- Equimolar response to sulfur compounds
- Does not require expensive vacuum pumps or ozone generators
- Robust design, easy to use
- Quick, simple maintenance

This requires the purchase of individual calibration standards for each sulfur compound of interest, increasing both costs and complexity, particularly if the exact sulfur compounds are unknown. Other important disadvantages of the FPD include its selectivity which is $10^5$ gC/gS and its detection limit which is about 10 times higher than that of the ASD and the SCD.

In recent years, the SCD has filled the gap between FPD and modern analytical requirements for trace-level sulfur analysis. Although it has demonstrated the requisite sensitivity, selectivity and linearity, it is expensive and notoriously difficult to maintain. All other detectors currently available are cost prohibitive or suffer similar shortcomings as the FPD.

## ASD advantages

The ASD is designed to be a simpler system, providing sulfur selectivity and sensitivity as well as ease-of-use and improved serviceability. The ASD eliminates several high-failure components required in older technologies, drastically improving reliability and performance. The reactor chemistry, thermal dynamics and mass transport variables have also been designed to operate at atmospheric pressure. This eliminates the need for costly vacuum pumps required on other systems. Plus, the chemistry does not require oxidation of the reduced sulfur by the aggressive use of ozone – completely eliminating the need for an ozone generator. Reliability of the ASD sulfur detection system is dramatically improved by the elimination of these costly, short-lived devices.

The ASD is responsive to sulfur on an equimolar basis, requiring only a single calibrant, reducing its overall cost of operation. It is insensitive to hydrocarbon background, thus improving overall sulfur detection. Plus, the ASD is a more cost-effective sulfur detector and provides ease-of-use, while minimizing maintenance requirements.

## ASD components

The ASD 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 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 ($H_2S$). The $H_2S$ 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 $H_2S$ 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 $H_2S$ present in the sample component. The electrochemical reaction scheme at the sensing electrode is given below:

$$H_2S + 4H_2O \rightarrow H_2SO_4 + 8H^+ + 8e^-$$

The electrochemical sensor (patent pending) has high sensitivity to sulfur (≤ 1 ppb $H_2S$) 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 (see Figure 1) and provides reaction-gas control. The electronics module is connected via a cable to the sensor for data acquisition.

## ASD configurations

The ASD is available as part of a preconfigured sulfur solution for the analysis of many types of materials that come under sulfur-impurity scrutiny today.

The ASD complements a family of analyzers that cover a wide range of gas-phase sample matrices:

- All commercial bulk gases such as helium, hydrogen, nitrogen, oxygen, air, carbon dioxide and argon that have sub-parts-per-million (sub-ppm) specifications for sulfur.

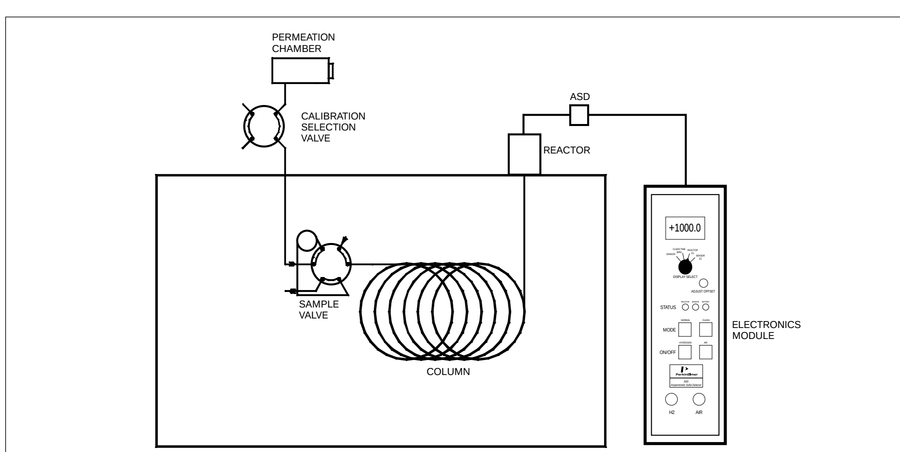


*Figure 1.* Schematic of GC-ASD Arnel-engineered system.

## ASD Quick Glance

**Micro Reactor:**

- Simple reactor design allows easy maintenance
- High temperature for rapid pyrolysis of different sulfur species
- Optimized reactor configuration provides high efficiency
- Inert materials minimize surface activity and carryover

**Electrochemical Sensor:**

- Proprietary, patent-pending design revolutionizes sulfur detection
- High sensitivity for lower detection limits
- Equimolar response eliminates need for multiple calibrants
- Fast response time for high sample throughput
- Large electrolyte capacity with gravity fill minimizes routine maintenance

**Electronics Module:**

- Compact, space-saving
- LCD display of reactor and sensor conditions simplifies operation
- Cleaning mode eliminates coking within the reactor
- Status-indicator lights indicate system readiness

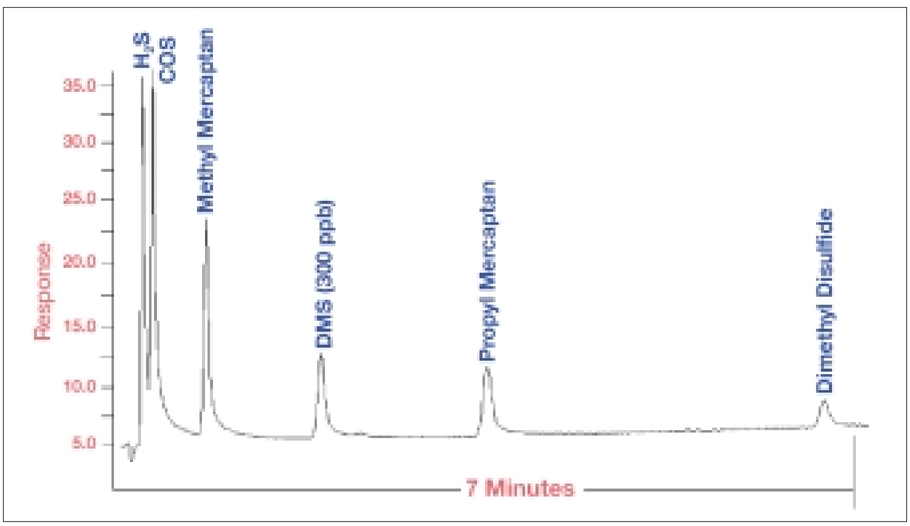


*Figure 2.* Chromatogram of sulfur standards spiked in a $CO_2$ sample matrix, using the ASD system.

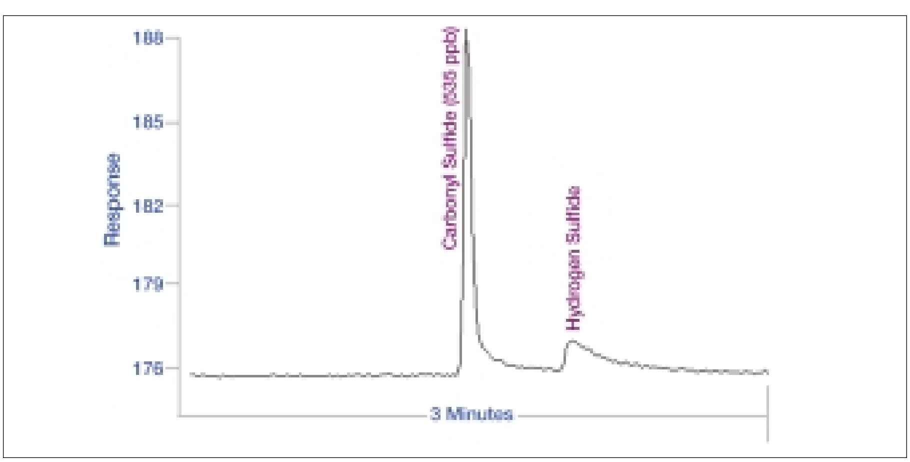


*Figure 3.* Commercial ethylene, off specification product at 535 ppb carbonyl sulfide, using the ASD system configured for ethylene and propylene analysis.

- Beverage-grade carbon dioxide that currently has individual sulfur-compound limits well under 100 ppb
- Petrochemical samples where industry limits for carbonyl sulfide in polymer-grade ethylene and propylene are under 30 ppb

PerkinElmer and Arnel have designed these systems to meet the rigorous requirements of sub-ppm sulfur determinations with reliability and ease-of-use.

## Applications and performance

The ASD product offerings are all built on specific application requirements. Sample type or matrix defines the design, sampling and chromatographic path(s). Many of the models include multi-detector configurations to address non-sulfur requirements. An extremely important sulfur-detection application is the determination of sulfur in beverage-grade carbon dioxide ($CO_2$). The turnkey offering supports 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.

Figure 2 illustrates the chromatogram obtained for sulfur impurities at ppb levels from the integrated beverage-grade $CO_2$ analyzer system. The determination of sulfur impurities in polymer-grade olefins is another important application that requires trace-level sulfur analysis. Figure 3 shows a typical chromatogram obtained from the GC-ASD system for the determination of sulfur impurities in ethylene for the petrochemical industry.

These are just two examples of GC-ASD applications. Table 1 lists the available models based on the application. Each model is designed to provide the sample handling and inertness required to achieve the levels indicated in the industry specification. All are performance guaranteed to the specific matrix type. These turnkey systems require no method development or high operator skill level. Plus, they are provided at a reasonable cost with minimal maintenance requirements!

## GC-ASD systems provide trouble-free sulfur determinations

All of the sulfur analysis applications performed by the 8 systems in Table 1 have distinctly different analytical requirements, but all are driven by a trace-sulfur impurity analysis. The PerkinElmer ASD is the perfect technology to meet these diverse requirements in a cost- and time-effective manner. Plus, the ASD has been engineered to eliminate the disadvantages of traditional sulfur-detection devices. When incorporated into an Arnel-engineered Clarus GC system, the ASD provides a turnkey solution for sulfur analysis that requires minimal training and maintenance and guarantees system performance.

*Table 1.* GC/ASD Model Matrix

| Arnel Part No. (no PPC) | Model No. | Description | Detectors | Permeation Chamber | On-Line Capability | Specification Tests |
|---|---|---|---|---|---|---|
| NARL7001 | 6025 | Trace sulfur in gases | ASD | No | Yes | ISBT and Polymer-grade Olefins |
| NARL7002 | 6425 | Trace sulfur in gases | ASD | Yes | Yes | ISBT and Polymer-grade Olefins |
| NARL7003 | 6030 | Trace sulfur and aromatics in gases | ASD/PID | No | Yes | ISBT and Polymer-grade Olefins |
| NARL7004 | 6430 | Trace sulfur and aromatics in gases | ASD/PID | Yes | Yes | ISBT and Polymer-grade Olefins |
| NARL7005 | 6031 | Trace sulfur and hydrocarbons in gases | ASD/FID | No | Yes | ISBT and Polymer-grade Olefins |
| NARL7006 | 6431 | Trace sulfur and hydrocarbons in gases | ASD/FID | Yes | Yes | ISBT and Polymer-grade Olefins |
| NARL7007 | 6038 | Trace sulfur, aromatics, and hydrocarbons in gases | ASD/PID/FID | No | Yes | ISBT and Polymer-grade Olefins |
| NARL7008 | 6438 | Trace sulfur, aromatics, and hydrocarbons in gases | ASD/PID/FID | Yes | Yes | ISBT and Polymer-grade Olefins |

## ASD Specifications

| | |
|---|---|
| Detectability: | 10 ppb S (equivalent to 20 ppb DMS) |
| High selectivity: | $\geq 10^6$ $gS/gCO_2$ |
| Peak-height precision and stability: | Relative Standard Deviation (RSD) < 5%, 24 hrs |
| Linear range: | $10^3$ |
| Dynamic range: | $10^5$ |
| Response to S: | Equimolar |

**PerkinElmer Life and Analytical Sciences**
710 Bridgeport Avenue
Shelton, CT 06484-4794 USA
Phone: (800) 762-4000 or
(+1) 203-925-4602
**www.perkinelmer.com**

ARNEL

PerkinElmer®
precisely.

**For a complete listing of our global offices, visit www.perkinelmer.com/lasoffices**



007016A_01 KG030405 Printed in the USA