Improve Storage Stability for Sulfur Compounds

Using Sulfinert® Treated Sample Cylinders

By Neil Mosesman, Air Monitoring Product Marketing Manager

- Eliminate sample-surface reactions in sample cylinders, collect and store active compounds.
- Obtain accurate data for active sulfur compounds at ppb levels.
- Many treated system components available from stock.

High-pressure sample cylinders are commonly used for collecting and storing refinery and natural gas samples containing trace amounts of sulfur compounds. These highly active compounds degrade very rapidly in stainless steel sample cylinders, making accurate determination of sulfur compounds virtually impossible. Restek's exclusive Sulfinert® surface treatment eliminates the reactivity of high-pressure sample cylinders and allows collection and stable storage of sulfur compounds, even at ppb levels. Figure 1 shows the recovery of 17ppbv hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, and dimethyl disulfide after 60 hours of storage in a Sulfinert® treated sample cylinder. The data show that these active compounds were unaffected by long-term storage in the Sulfinert® treated cylinder.

In addition to Sulfinert® treated cylinders, we also offer Sulfinert® treated valves, tubing, and sample loops to ensure the entire sample pathway is inert. Custom treatment is available for a wide range of items.

Sulfinert®-Treated Sample Cylinders

- Stable storage of low concentrations of sulfur compounds.
- D.O.T. rated to 1800psi at room temperature.
- 316 stainless steel, 1/4" female NPT threads on both ends.

Size	qty.	cat.#
75cc	ea.	24130
150cc	ea.	24131
300cc	ea.	24132
500cc	ea.	24133
1000cc	ea.	24134
2250cc	ea.	21394

Sulfinert®-Treated Sample Cylinder Valves and Rupture Discs

- All "wetted" valve parts are Sulfinert®-treated.
- Maximum pressure rating, 5000psi.

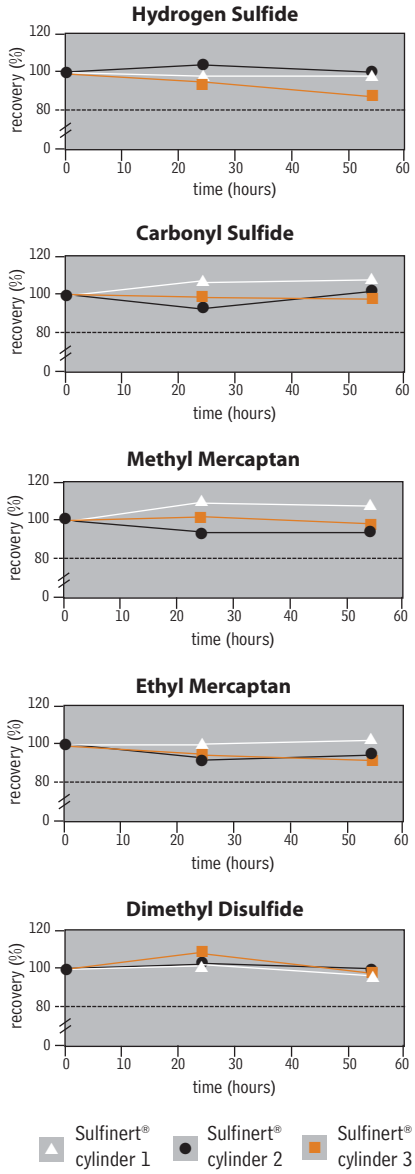
Description	qty.	cat.#
1/4" NPT Exit, Kel-F® Stem Tip	ea.	24127
1/4" Compression Exit, Kel-F® Stem Tip	ea.	24128
1/4" Female NPT Outlet (built-in rupture disc)	ea.	21395

Sulfinert®-Treated Gas Sample Loops

- Ideal for samples containing low concentrations of sulfur compounds.
- Sizes from 5µL to 5cc.; 1/16" fittings, for "W Type" valves.

Size	qty.	cat.#
5µL	ea.	22840
10µL	ea.	22841
20µL	ea.	22842
25µL	ea.	22843
50µL	ea.	22844
100µL	ea.	22845
250µL	ea.	22846
500µL	ea.	22847
1cc	ea.	22848
2cc	ea.	22849
5cc	ea.	22850

Figure 1 Active sulfur compounds are stable in Sulfinert® treated sample cylinders.



17ppbv each compound

for **more** info

Please request Applications Note **#59164B** for more details about storing sulfur compounds in Sulfinert® treated cylinders.

Accurately Monitor Mercury-Sulfur-Nitrogen Compounds

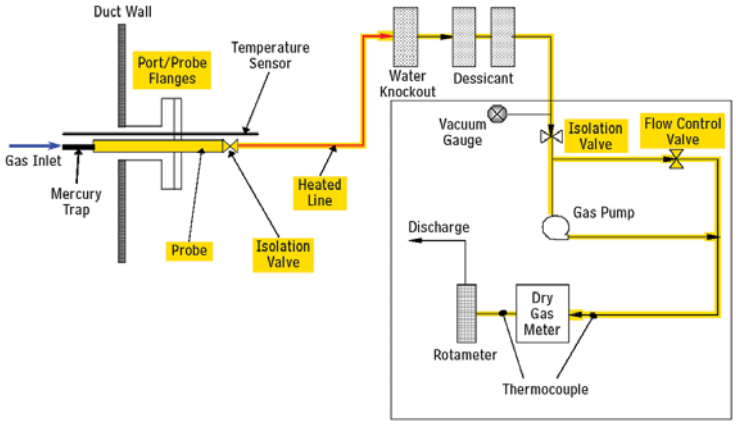
Siltek®/Sulfinert® Treatment Prevents Adsorption of Mercury, Sulfur Oxides, or Nitrous Oxides in Emission Monitoring Equipment

By Gary Barone, Restek Performance Coatings Division Manager, David Smith, RPC Chief Scientist, and Martin Higgins, RPC Chief Engineer

- Improved analytical reliability and sensitivity for mercury, SO_x, or NO_x compounds.
- Protection from corrosion—longer component lifetime.
- Apply to new or existing equipment.

The United States Environmental Protection Agency (US EPA) is actively developing regulations, limits, and control measures for monitoring and controlling mercury emissions from coal-fired power generators—one of the major sources of mercury emissions into the environment.[1] As these regulations and guidelines are developed and implemented, proper equipment will be needed for accurate sampling and analysis. Testing costs for mercury can be substantial (Table 1)[2], so inaccurate analyses can have financial as well as environmental repercussions.

Figure 1 Highlighted components of a mercury sampling train,[4] and all tubing in the system, can be Siltek®/Sulfinert® treated.



In flue streams from coal-fired power generators, mercury exists in three forms: elemental, the +2 oxidation state (Hg^{++}), and attached to particulate matter. Hg^{++} often reacts with sulfur compounds, nitrogen, chlorine, and/or oxygen, to produce sulfurous, nitrous, chloride, and oxide mercury species. Elemental and oxidized mercury can easily be lost to reactions and adsorption on the inner surfaces of monitoring equipment. In order to accurately sample and quantify mercury in all forms, it is important to use inert sample pathways. Laboratory testing and field results have proven that Sulfinert® treated sampling and testing equipment is essentially inert to active molecules[3], including mercury.

Siltek®/Sulfinert® treatment can be applied to many of the components in a mercury sampling stream, including probe tubing, impingers, fittings, filters, housings, and transfer tubing (Figure 1). Treating all of the components of a stack or continuous emission monitoring system will greatly improve analytical reliability and sensitivity, which will be needed as regulations are brought on line and emission quotas are enforced. Fast and accurate testing, without re-work, can save a great deal of time and money.

Similarly, a Siltek®/Sulfinert® treated sampling system will improve the reliability of data for sulfurous oxides and nitrous oxides (SO_x and NO_x). As with mercury, it is difficult to reliably transfer these compounds through untreated sampling equipment.

In addition to preventing adsorption of reactive compounds, Siltek®/Sulfinert® treatment will act as a barrier, protecting and prolonging the lifetime of treated equipment. The durable layer will withstand temperatures to 400°C.

We offer Siltek®/Sulfinert® treated tubing, sample cylinders, and other components from stock; to discuss custom treatment of system components, please contact the Restek Performance Coatings team.

Restek offers treated and untreated tubing, fittings, and valves, passive air sampling kits, air sampling canisters and miniature air canisters, sample loops, and more. For more information, request our catalog or visit us online. **www.restekcoatings.com**

Table I Typical costs of mercury sampling (U.S.).[2]

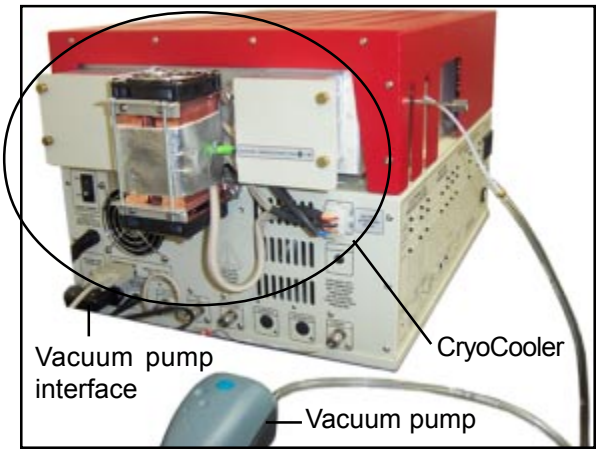
Method	Approx. Cost of Analysis
US EPA 29	$300
US EPA 101A	$100
ASTM D6784-02	$250
US EPA 324	$430
FAMS	$640

References

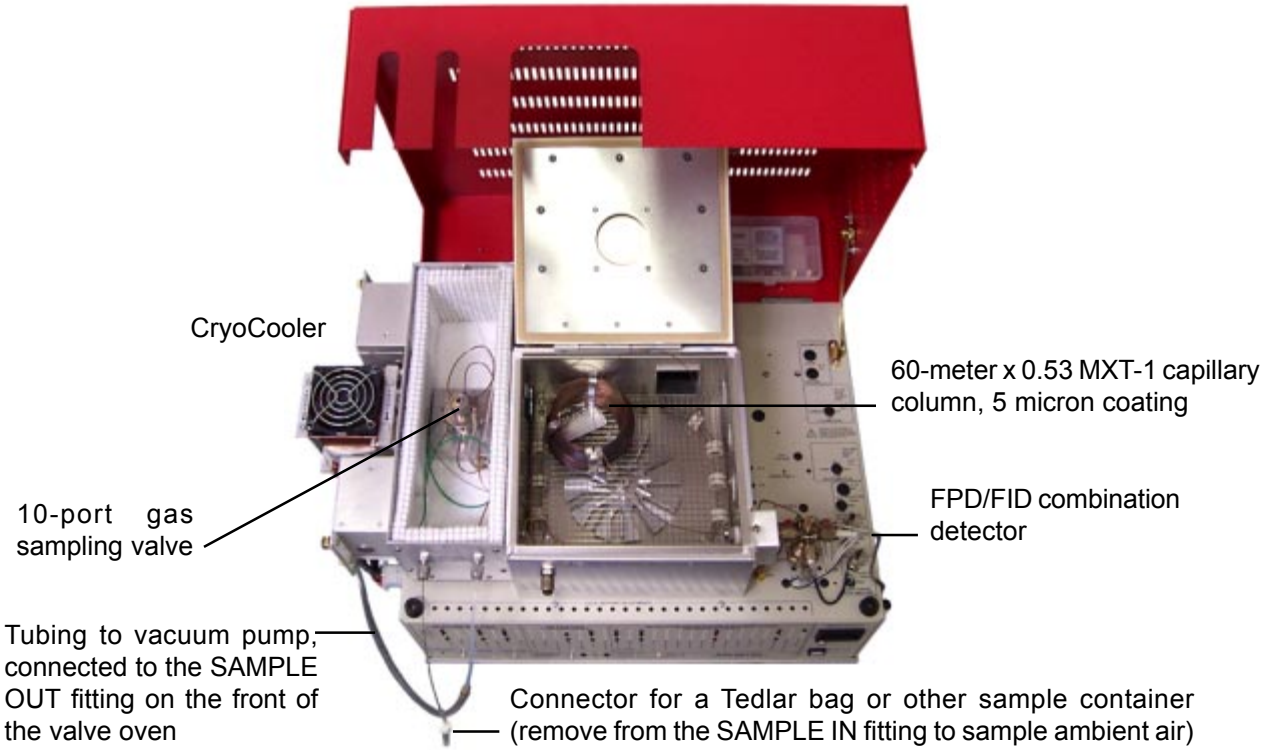
1. Pottinger, M., S. Stecklow, and J.J. Fialka, *Invisible Export, A Hidden Cost of China's Growth: Mercury Migration* The Wall Street Journal Online, Dec. 17, 2004.
2. Serne, J.C., *An Overview and Comparison of Available Mercury Emission Test Methods for Boilers* Symposium on Air Quality Measurement; Methods and Technology 2005, San Francisco, CA; Air & Waste Management Association. paper no. 439, pg. 9.
3. Barone, G., M. Higgins, D. Smith, S. Rowan, W.J. Gross, and P. Harris, *The Surface for Sulfurs* Hydrocarbon Engineering, Dec. 2004, pp 47-50.
4. Proposed Method 324. *Determination of Vapor Phase Flue Gas Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling* United States Environmental Protection Agency. Washington, D.C. p. 5.

System Overview

The SRI CryoSulfur GC comes with everything you need to detect low-level sulfur compounds in gas samples. Since some sulfur compounds do not trap well, the CryoSulfur GC uses the CryoCooler Peltier Trap Accessory to enrich the sample, providing lower detection limits. The CryoSulfur GC uses a vacuum pump (provided) to draw gas or air samples into the CryoCooler. You can sample ambient air, or use the provided adaptor to connect a Tedlar bag. The vacuum pump interface, which is an electrical outlet on the left-hand side of the GC, allows the vacuum pump to be turned ON/OFF by the PeakSimple data system to provide consistent sampling times.



Like all SRI traps, the CryoCooler Peltier Trap Accessory is plumbed as the loop of a 10-port gas sampling valve. It has it's own power cord that must be plugged into a wall outlet, and an interface cord that plugs into the left-hand side of the GC. After enrichment, the valve injects the sample onto the 60-meter capillary column. Once the sample components are separated by the column, they will be detected by the Flame Photometric and Flame Ionization detectors.

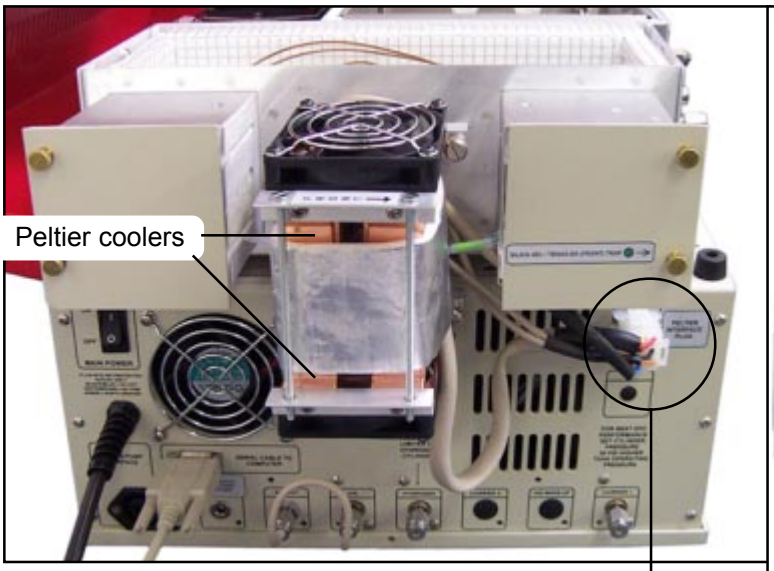


POPULAR CONFIGURATION GCs
Cryosulfur GC

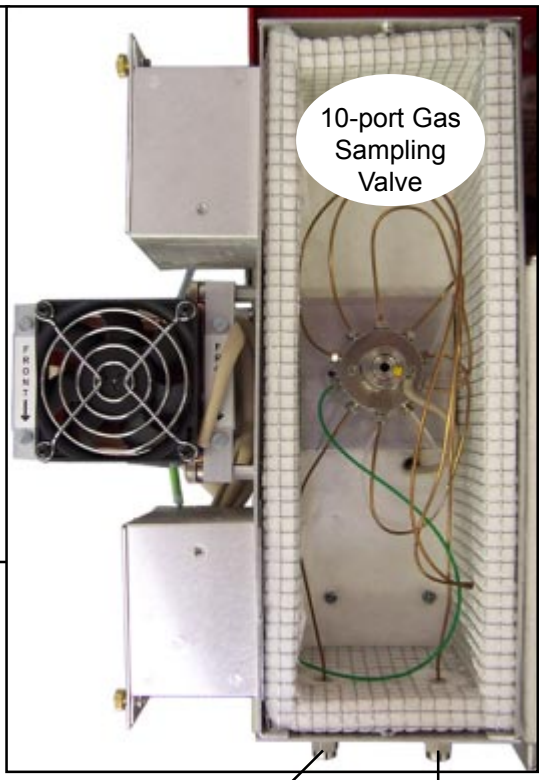
Theory of Operation

Some sulfur compounds do not trap well, but can be enriched for lower detection limits. The CryoCooler Peltier Trap Accessory is basically a heated trap sandwiched between two peltier coolers. The trap is filled with Tenax-GR (about 30%) and Silica Gel (about 70%) adsorbents. The vacuum pump draws sample through the CryoCooler from ambient air, or from a Tedlar bag or other sample container. The peltier coolers can cool the trap down to -15°C to enrich the sample.

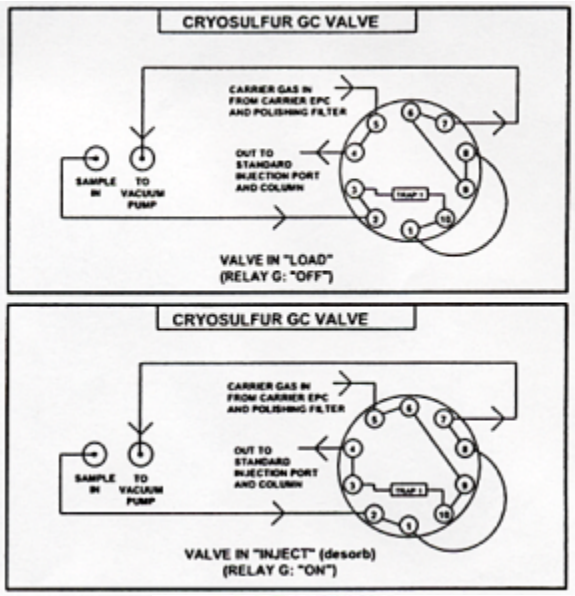
The CryoCooler



CryoCooler - Top View



Valve Diagram Label on Valve Oven Lid:



While the CryoCooler is enriching the sample, the 10-port gas sampling valve is in the LOAD position. At the conclusion of the sampling period, the heater heats the trap to 150-200°C and the valve is actuated to the INJECT position; this places the trap in the carrier gas stream and sweeps the enriched analytes onto the column.

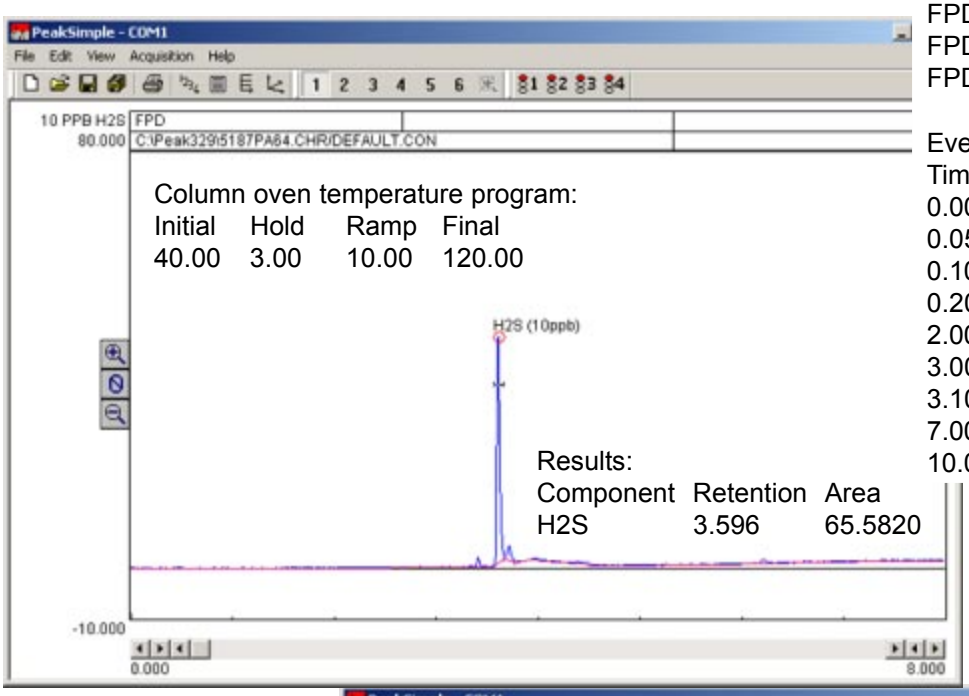
Expected Performance

The following chromatograms were generated by an SRI CryoSulfur GC. The first chromatogram shows the FPD rsponse to 10ppb hydrogen sulfide (H_2S), as enriched by the CryoCooler at -10°C. The second chromatogram shows the FID response to 1000ppm C_1-C_6 hydrocarbons.

Sample: 10ppb H2S
Column: 60-meter MXT-1
Carrier: helium at 10mLs/minute
Vacuum pump: 20mLs/minute
Trap: -10°C
FPD gain: HIGH
FPD temperature: 150°C
FPD volts: 500

Event Table:

Time	Event
0.000	Zero baseline
0.050	D OFF (vacuum pump)
0.100	A OFF (CryoCooler)
0.200	F ON (trap heat)
2.000	G ON (valve INJECT)
3.000	F OFF (trap heat)
3.100	G OFF (valve LOAD)
7.000	A ON (CryoCooler)
10.000	D ON (vacuum pump)



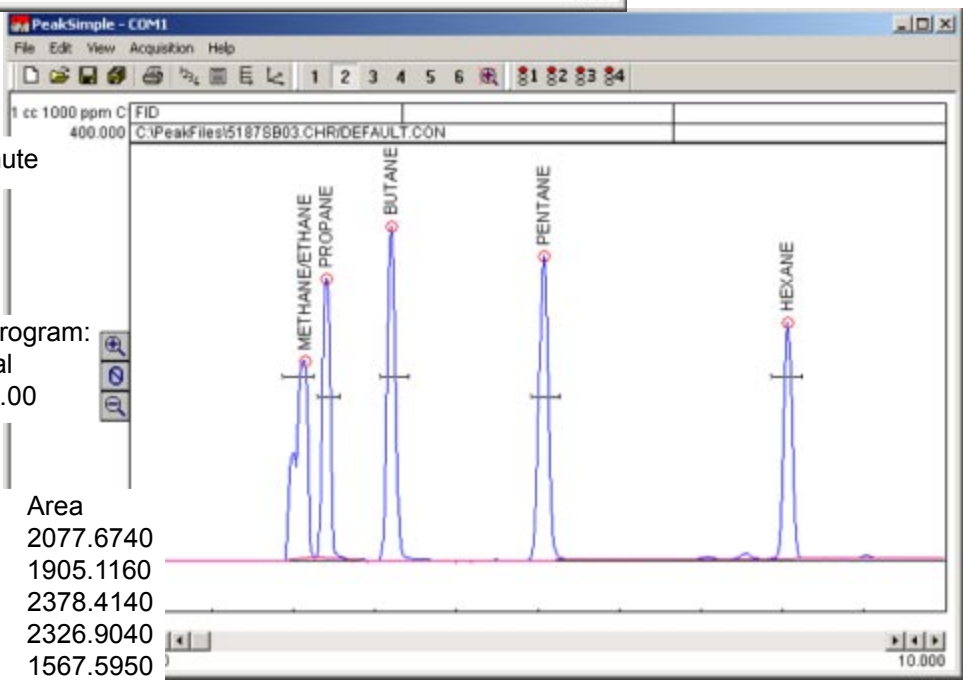
Sample: 1000ppm C1-C6
Column: 60-meter MXT-1
Carrier: helium at 10mLs/minute
FID gain: HIGH
FID temperature: 150°C
FID ignitor: -400

Column oven temperature program:

Initial	Hold	Ramp	Final
40.00	3.00	10.00	140.00

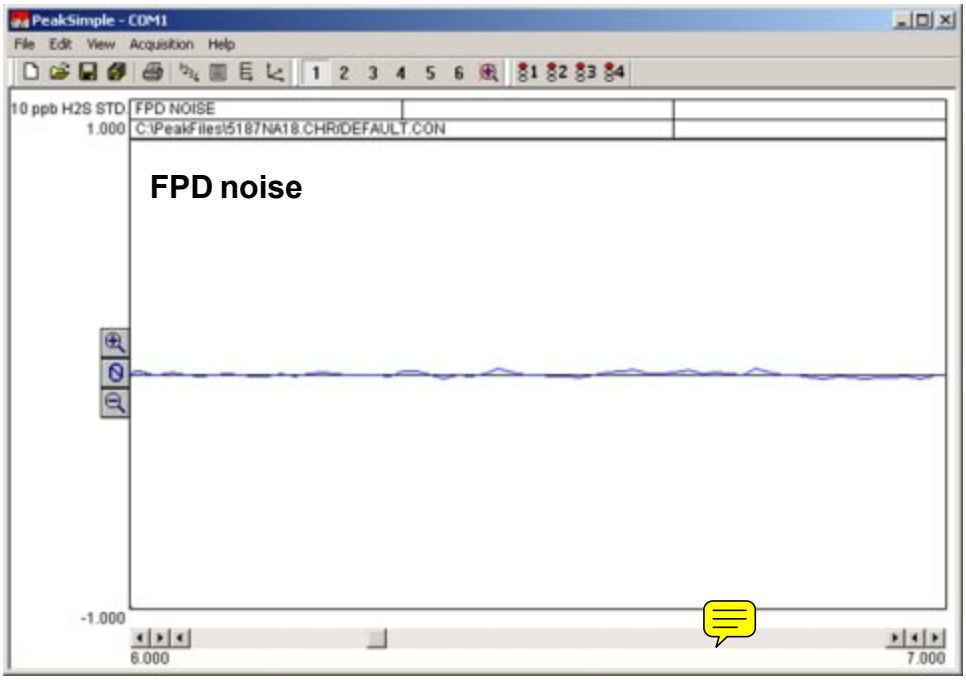
Results:

Component	Retention	Area
Methane/ethane	2.116	2077.6740
Propane	2.383	1905.1160
Butane	3.183	2378.4140
Pentane	5.050	2326.9040
Hexane	8.050	1567.5950
	Total	10255.7030



Expected Performance continued

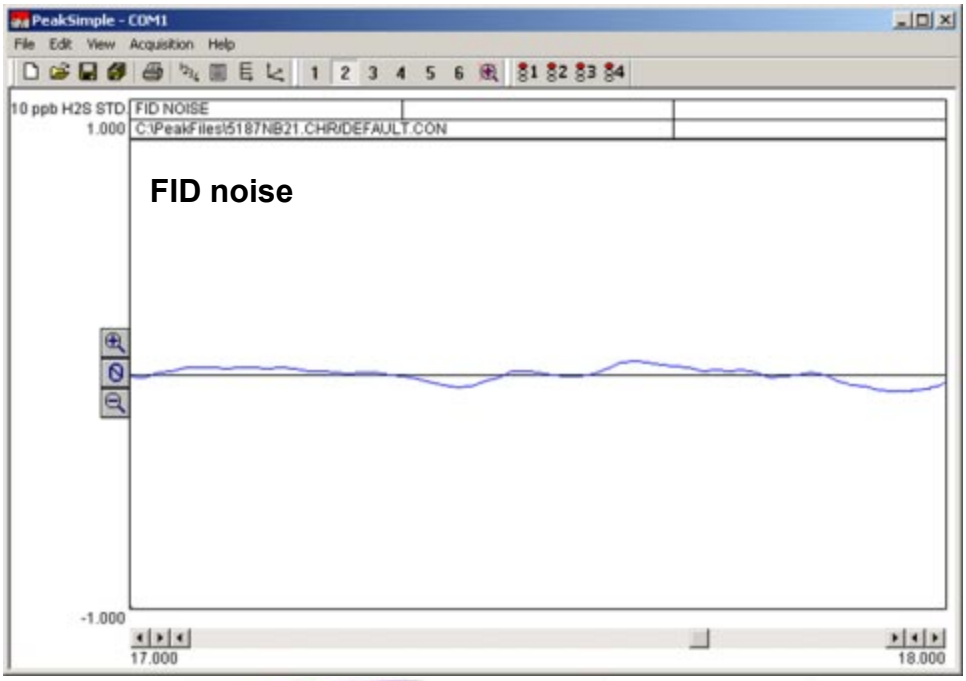
The following two noise runs were generated by a CryoSulfur GC. Both used the same isothermal column oven temperature program, 60-meter MXT-1 column, and helium carrier at 10 milliliters per minute.



FPD gain: HIGH
FPD temperature: 150°C
FPD volts: 500

Column oven temperature program:

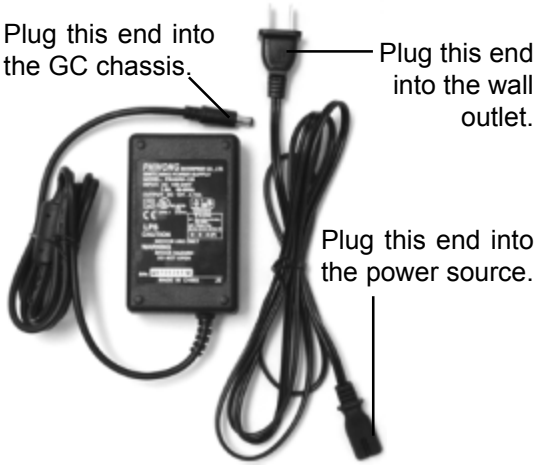
Initial	Hold	Ramp	Final
80.00	24.00	0.00	80.00



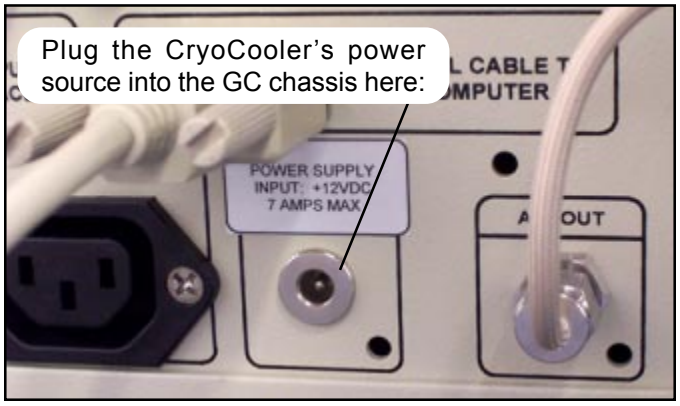
FID gain: HIGH
FID temperature: 150°C
FID ignitor: -400

General Operating Procedure

CryoCooler power source:



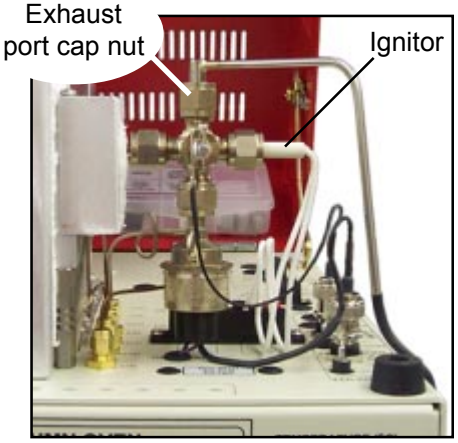
1. Plug the GC power cord into a wall outlet and turn the main power ON. Plug the CryoCooler into it's power source, and plug the power source cord into the wall outlet. The CryoCooler power source plugs into the GC chassis between the vacuum pump interface and the Air Out fitting on the left-hand side of the GC as shown below.



2. Connect your helium source to the carrier gas inlet on the left-hand side of the GC. Connect your hydrogen source to the hydrogen inlet. Leave the jumper in place if you plan to use the built-in air compressor to supply air for the detectors. Otherwise, remove the jumper and connect your air source to the air inlet on the left control panel.

3. Set the hydrogen flow to 60-80mLs/minute; this correlates to a flow of 30-40mLs/minute each for the primary and secondary hydrogen used by the FPD/FID combination detector. Set the air flow to 100mLs/minute. The detector air supply tubing is T'd inside the GC so that 10-30mLs/minute of air flows across the face of the photomultiplier (PMT). The gas pressures required to achieve these specific flows are printed on the right-hand side of the GC.

4. Use the switch on the GC front control panel to light the detector flame (vertically labeled "FLAME IGNITE" under "DETECTOR PARAMETERS"). Often the flame can be difficult to light because of the hydrogen-rich atmosphere inside the detector body. Make sure that the PMT voltage is OFF (that switch is also on the GC front control panel, vertically labeled "PMT VOLTS" under "DETECTOR PARAMETERS"), then remove the cap nut on the detector exhaust port. KEEP YOUR FACE AWAY FROM THE DETECTOR WHILE LIGHTING THE FLAME, and try the ignitor switch again. When the flame lights, there will be a loud noise like the backfiring of a car; this is normal and does not indicate a problem. The noise is accompanied by a flash of flame. Replace the exhaust cap nut after the flame is lit.



5. Switch ON the PMT voltage and set it at 400-500 by adjusting the appropriate trimpot ("PMT VOLTAGE" under "DETECTOR PARAMETERS"). The greater the voltage setting, the higher the FPD sensitivity. The PMT volts were set at 500 for the 10ppb H2S analysis shown on the Expected Performance page.

General Operating Procedure continued

6. Connect the provided vacuum pump to the SAMPLE OUT/VACUUM PUMP fitting on the front of the valve oven. Plug the vacuum pump power cord into the vacuum pump interface outlet on the left-hand side of the GC.

7. Connect your sample source to the SAMPLE IN fitting. It is critical to use as inert a sample pathway as possible to avoid absorption of sulfur compounds. You can also sample ambient air through the SAMPLE IN inlet, just remove the fitting.

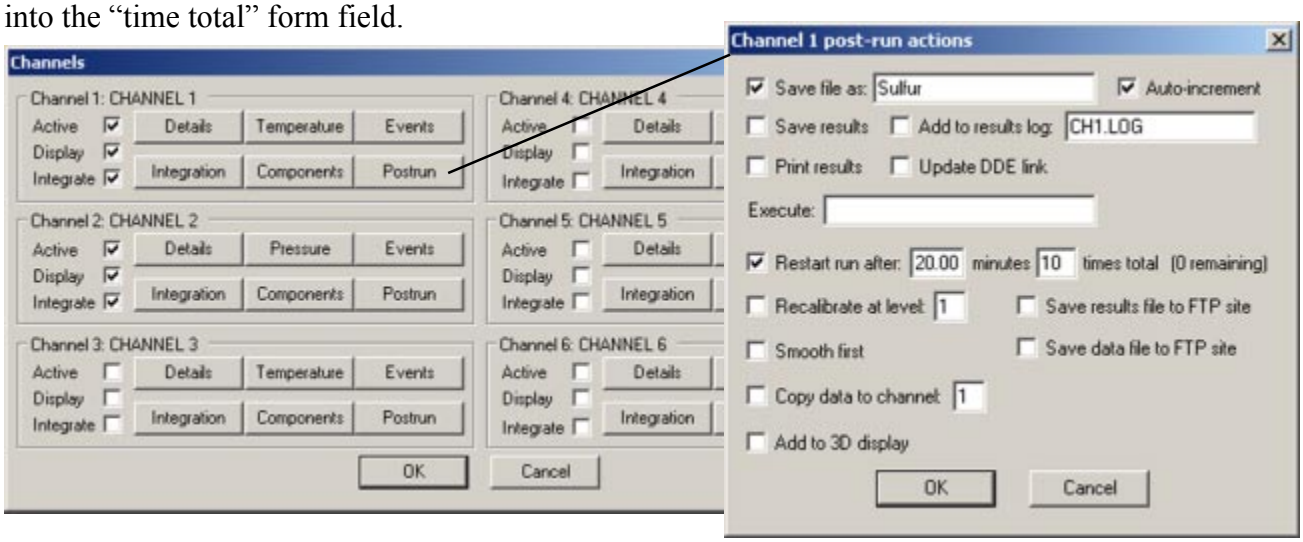
8. In PeakSimple, type in the following event table:

Event Table:

Time	Event
0.000	Zero baseline
0.050	D OFF (vacuum pump)
0.100	A OFF (CryoCooler)
0.200	F ON (trap heat)
2.000	G ON (valve INJECT)
3.000	F OFF (trap heat)
3.100	G OFF (valve LOAD)
7.000	A ON (CryoCooler)
10.000	D ON (vacuum pump)

Then, in the Edit > Overall window, uncheck the box labeled "Reset relays at end of run."

9. The system works best when operated automatically every 20 minutes. The CryoCooler and vacuum pump are left ON between runs for sampling. The first run's results are ignored, as it takes multiple runs to equilibrate the sulfur compounds inside the GC system and achieve reproducibility. In PeakSimple, open the Channels window by clicking Edit > Channels. Click the Postrun button for channel 1. Click the "Save file as" checkbox, type a name for the chromatograms in the form field, and click the "Auto-increment" checkbox. For example, if you type in Sulfur, the second chromatogram will be saved as Sulfur1, followed by Sulfur2, and so on. Click the checkbox labeled "Restart run after" and type 20 minutes in the form field. Type the number of times you want to repeat the analysis into the "time total" form field.



10. Press the START button on the front of the GC, or press your computer keyboard spacebar to start the run.