DEVELOPMENT OF A LOW COST ETHYLENE OXIDE DETECTOR
PHASE II FINAL REPORT

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Dr. David Hyatt
Robin Stewart
James Butz

ADA Technologies, Inc.
304 Inverness Way So., Suite 110
Englewood, CO 80112

(303)792-5615

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SUMMARY OF SIGNIFICANT FINDINGS

A research project was performed to develop an instrument to monitor the concentration of ethylene oxide (EtO) in trace concentrations. EtO is used extensively in medicine to sterilize equipment and supplies that cannot be heat-sterilized. It has been shown to be a mutagen and carcinogen, and exposure is regulated by the Occupational Health and Safety Administration (OSHA).

The design approach for the EtO monitor was to employ a solid-state semiconductor gas sensor to measure the level of EtO in room air. A chromatographic separation column was used to solve the problem of interfering species that could result in false alarms in the instrument. Room air was used as the carrier gas, eliminating the need for gas cylinders and regular maintenance.

The operating cycle of the instrument consisted of four flow configurations. First, clean carrier air flowed through the separation column while a room air sample was acquired in a sample loop. Second, the sample was injected onto the separation column. Third, additional clean carrier air was added to the column to elute the EtO to the solid-state sensor at the column outlet. Finally, the column was backflushed to remove contaminants. The complete cycle was about two minutes in length.

The instrument was controlled by a microprocessor, which was programmed to store acquired data and to drive a display of average exposure levels to EtO in accordance with OSHA regulations. The instrument featured a serial connection to allow data records to be printed or downloaded to a personal computer.

The prototype instrument demonstrated the ability to detect EtO at 0.2 parts per million at a signal to noise ratio greater than 1.5. In the long term test phase, a more efficient operating cycle was conceived, and was used as the basis for a cost estimate for a commercial instrument. It is believed that the monitor could be manufactured and sold profitably at a price of $5,000.

I. EXECUTIVE SUMMARY

The goal of the research and development program was to design, build and test a prototype ethylene oxide (EtO) monitor for use in hospitals and other installations where EtO sterilization is employed. This monitor was designed to be versatile enough to be used as a hand-carried portable monitor or a wall-mounted area monitor.

The prototype EtO monitor developed at ADA operates continuously as a direct-reading instrument, employing a rugged solid state semiconductor sensor. The instrument uses room air as the carrier gas. The prototype instrument consists of a combustibles trap and a Nafion dryer to remove organics and water from the carrier gas (room air), a Teflon gas chromatography column with THEED packing to separate EtO from other constituents in the sample air, a solid-state Taguchi Gas Sensor to determine EtO concentration and a programmable microcontroller to control flow valve positions throughout the flow cycle, monitor sensor output, and operate instrument displays, alarms and data storage. The prototype instrument is capable of detecting EtO at a concentration of 0.2 ppm. The gas chromatography column and combustibles trap provide the specificity for EtO that is lacking in low-cost commercial real-time monitors.

The prototype provides an updated digital concentration reading once every two minutes, and activates appropriate audio and visual alarms when the EtO concentration exceeds programmed threshold and danger levels. The unit also computes and stores the EtO values for the required 15 min excursion level and the 8 hr time weighted average.

The final instrument design incorporates low cost components so that the anticipated price of a commercial version will not exceed $5,000.

II. BACKGROUND

The primary objective of the Phase II research and development effort was to design, assemble and test a prototype EtO monitor and evaluate its performance in a long-term evaluation. The goal of this research program was to produce a simple, reliable EtO detection instrument that would give a reading of the ambient EtO concentration once every two minutes, around the clock. The target commercial price of the instrument was under $7,000.

A. ETHYLENE OXIDE

Ethylene oxide has been used as a sterilant for many years. However, concern about the health effects of EtO exposure for those working with this chemical has been increasing over the past decade. Within the past five years, OSHA has promulgated regulations which have significantly increased the level of surveillance required to protect workers from occupational exposure to EtO. The EtO monitor developed by ADA Technologies, Inc. (ADA) is a response to the sterilization industry's demonstrated need for a monitor which will protect their employees from harmful exposure.

Approximately 0.24 percent of the EtO produced annually in the United States is used in health care industries, primarily for the manufacturing of medical products and secondarily for gas sterilization in hospitals (Landrigan, 1984). Hospitals experience a high incidence of worker exposure to EtO due to the nature of the hospital sterilization process. The National Institute of Occupational Safety and Health (NIOSH) estimates that there are in excess of 10,000 EtO sterilizers in use in U.S. health care facilities and that approximately 62,400 employees are directly exposed to the gas in hospitals (Glaser, 1977). Another 25,000 workers may be exposed occasionally due to improper or inadequate venting of sterilizers and aerators, handling of improperly/incompletely aerated EtO-sterilized items, and the physical arrangement of the sterilization facility or workroom (Grunberg, 1987).

There are three major daily sources of EtO emissions in hospital sterilizer areas (Kercher, 1987). First, employee exposure could occur during the evacuation phase of the sterilization cycle when most of the EtO in the sterilizer is removed by a water-sealed vacuum pump and discharged at the sewer drain. Secondly, exposure to EtO occurs when the employee opens the sterilizer door. A third period of exposure occurs when the EtO-sterilized items are removed from the sterilizer and transferred to the aerator. The greatest potential for worker exposure occurs during the loading or unloading of transport tanks, during product sampling, and during equipment maintenance and repair.

B. CHEMICAL PROPERTIES AND HEALTH EFFECTS

At room temperature and atmospheric pressure, EtO is a colorless gas, although at higher pressures it may be a volatile liquid. It has a characteristic ether-like odor with a widely variable threshold of detection in humans; the mean detectable concentration is about 700 ppm. EtO is highly reactive and potentially explosive in the presence of metal hydroxides and highly active catalytic surfaces, or when heated. However, it is relatively stable in aqueous solutions, or when diluted with carbon dioxide or halocarbons. In order to reduce explosion hazards, when EtO is used as a fumigant or sterilant it is often in mixtures such as 10% EtO and 90% carbon dioxide or 12% EtO and 88% Freon-12 (NIOSH, 1981).

Ethylene oxide is hazardous to workers. Acute exposure may cause irritation of the eyes, nose, and throat; burns to the skin; and allergen sensitization. Animal toxicity studies have shown EtO to be a mutagen and a carcinogen. Some studies of exposed workers have indicated increased mutagenic activity in human cells, an increase in the incidence of leukemia, and adverse reproductive effects such as increased incidence of spontaneous abortion (Schoenborn, 1977). It appears that this is a result of the activity of EtO as an alkylating agent, which allows it to react irreversibly to form covalent bonds to DNA and protein.

In 1988 NIOSH initiated the largest and most comprehensive human epidemiological study on EtO that has been done to date. The study, which will conclude in 1989, is attempting to determine if industrial EtO exposure results in an increased incidence of leukemia or other cancers. If a correlation between EtO exposure and development of cancer is discovered, the consequences for the EtO industry with regard to EtO use and occupational exposure litigation could be significant.

C. REGULATORY ENVIRONMENT

In 1984, OSHA established a Permissible Exposure Level (PEL) for occupational exposure to EtO of one part per million by volume (ppmv) determined as an eight-hour time-weighted average (TWA) concentration (Dept. of Labor, 1984). In addition, an action level of 0.5 ppmv as an 8-hour TWA was established as the level above which employers must monitor employee exposure. On April 6, 1988, OSHA amended the existing EtO standard to add an excursion limit (EL) standard of 5 ppmv measured over a 15-minute period (Dept. of Labor, 1988). These regulations govern the levels of worker exposure to EtO and are very specific with regard to monitoring requirements. Surveillance in both the employee breathing zone and the sterilization area is necessary in order to comply with the regulations.

Although the PEL, action level and EL all refer to airborne concentrations in the employee's breathing zone, the regulation also states: "where there is a possibility of exposure to EtO due to an emergency, means shall be developed to alert potential affected employees of such occurrences promptly....the purpose of this provision is to protect workers from unexpected significant releases of EtO that pose an acute or other health risk" (Dept. of Labor, 1988). Hospitals have been cited by state and federal authorities for violating occupational health laws by not providing a system to promptly alert employees of an EtO emergency. In some cases, citations specifically recommend installation of a continuous monitor, with an alarm level set below the OSHA PEL of 1 ppm. Monitors are also required by OSHA to have a high specificity for EtO.

D. COMPETING TECHNOLOGY

The need for a new EtO monitor is justified by the problems encountered by users of instruments presently on the market. Complaints about commercial monitors include: 1) the instrument is difficult to operate and operating instructions are vague; 2) the instrument is not reliable, and certain parts require frequent replacement, resulting in lengthy down times; 3) the instrument gives false alarms due to steam, perfume, cleaning solvents, or increased noise from the detector. In addition, the Occupational Safety and Health Administration (OSHA) is inspecting hospitals for compliance with OSHA EtO standards. Both area monitoring and personnel monitoring are recommended by OSHA in order to gather data on employee exposure and provide a means for alerting employees to excessive EtO levels due to leaks. Hospitals are required to use a monitor that is specific to EtO and sounds an alarm before the ambient EtO concentration exceeds the PEL of one part per million (ppm).

Hospitals and OSHA have established several performance criteria for an EtO monitor. These criteria include sensitivity, specificity, reliability, low cost, and ease of operation. The following methods or instruments commonly used for EtO measurement are evaluated with regard to these performance criteria.

The personal dosimeter badge is widely used in hospitals. This device is manufactured by several companies and satisfies OSHA requirements for sensitively monitoring exposure levels in the breathing zone. The primary disadvantage of the badges is that they provide no instantaneous EtO measurement and therefore cannot alert employees of accidental leaks or other occurrences of high EtO concentrations. The cost of these badges, including analysis, range from $25 to $40 each.

Infrared monitors are specific for EtO provided the analysis is being performed at the proper wavelength to avoid detecting interfering gases. However, these continuous monitors lack sensitivity, require a high degree of operator skill, and are expensive. Their cost ranges from $5,000 to 15,000.

Solid state detector-based continuous monitors are inexpensive, provide real-time EtO measurements and audible/visual alarms, and usually require little maintenance. A lack of specificity makes this detector susceptible to numerous interferences which can trigger false EtO alarms. The cost of these units range from $625 to $2,000.

Gas chromatographs are sensitive and specific. Many models include alarms and can provide a continuous readout of EtO exposure levels in the sterilization area. The drawbacks of the conventional gas chromatograph include considerable expense and cylinder gas requirements. Most of the commercial EtO gas chromatographs use the photoionization detector (PID), which requires frequent cleaning. A poor quality PID requires frequent replacement as well, and high noise levels can cause false EtO alarms. The cost range for these units is $7,000 to $20,000.

The proposed EtO monitor will combine the low cost and low maintenance characteristics of a solid state detector-based monitor with the specificity and sensitivity of a gas chromatograph. The monitor will alert employees of EtO levels exceeding the PEL, EL and action level. Employees will be aware of their exposure levels at all times from the continuous digital readout on the monitor. Using the built-in printout capability of the new monitor, hospitals will be able to provide OSHA with documentation of long- and short-term exposure levels as proof of compliance with the current regulations.

Based upon industry trends and the opinions of industry experts, the market for the ADA EtO monitor in the health care industry is excellent. The widespread use of EtO as a sterilant in hospitals is likely to continue. Industry experts have predicted that OSHA's surveillance of worker exposure to this toxic gas will increase. Instrumentation which is sensitive, reliable, accurate and inexpensive is necessary to measure EtO in the hospital setting. Although several types of monitoring instruments are available, none can meet the sensitivity and specificity requirements at a price that is acceptable to cost-responsive hospitals. The EtO monitor developed by ADA will satisfy this unmet market need.

III. TASK RESULTS

There were nine tasks defined to reach the goal of building and testing a prototype EtO monitor. These tasks addressed the selection of components for the prototype, the integration of the components into an instrument, design and fabrication of the control electronics and software to operate the instrument, testing of the instrument in the laboratory and a simulated field environment, and reporting of the project results. Details of the activities for each of the nine tasks are presented in this section.

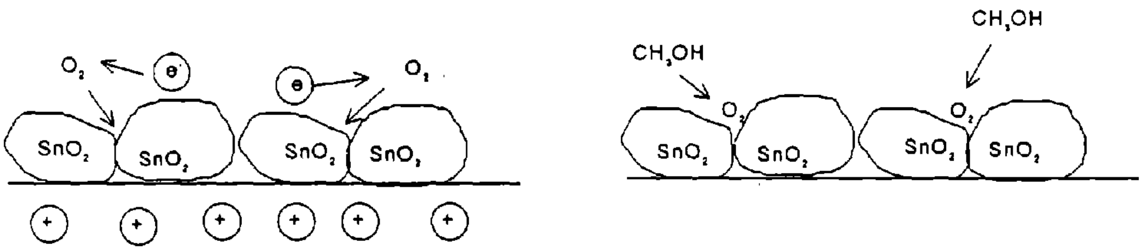
A. TASK 1: OPTIMIZATION OF THE TAGUCHI GAS SENSOR FOR THE MEASUREMENT OF ETO

The major purpose of this Task was to determine variability among sensors of the same type as well as to find the optimum sensor operating conditions for the detection of ethylene oxide. The approach was to assemble a test fixture where six sensors could be simulaneously exposed to the same environment, where known quantities of EtO would be periodically introduced so that the sensor response could be measured and recorded for comparison.

The evaluation of sensor performance required that a number of measurements be made for sensor outputs and operating conditions, as well as physical conditions at other locations in the flow path through the instrument. The data acquisition requirements included the measurement of voltage, current, resistance, temperature, pressure, relative humidity and binary status (on/off). In order to partially automate the experiments, there needed to be a means to control current, voltage and digital inputs to the instrument. There was also a requirement for logic and arithmetic functions in the intelligent control of the experiment. These included the ability to ramp or switch voltages and currents at specified rates, to supply valve actuation capability based on the output of the TGS or flow conditions, and to manipulate raw data before storage by the data acquisition system. A data acquisition add-in board for use in a personal computer was purchased that had the capacity to perform all of these functions.

1. Theory of TGS Operation

The capability of the Taguchi Gas Sensor, or TGS (Figaro Engineering, Inc., Wilmette, IL), to detect EtO at ppm levels was demonstrated in the Phase I technical effort. The TGS is an n-type semiconductor, composed of powdered tin oxide formed by a sintering process which results in a large number of grain boundaries between the crystals. The adsorption of oxygen on the surface of the semiconductor results in the formation of potential barriers at these grain boundaries, and a subsequent decrease in electrical conductivity (Figure III-1a). The TGS maintains this constant low conductivity while it is measuring ambient air, provided the sensor temperature remains constant. If the TGS is exposed to a combustible gas, an increase in conductivity is observed as the gas replaces the electron-accepting oxygen molecules on the sensor surface (Figure III-1b).



a. Low conductivity due to potential barriers at grain boundaries.

b. Conductivity increases due to decreased potential barriers resulting from O_2 removal.

Figure III-1. Illustration of TGS Theory of Operation

One important characteristic of the TGS is its ability to return to the baseline conductivity even after continuous exposure to high concentrations of combustible species (e.g., methane, carbon monoxide, or hydrogen). In addition, the sensitivity of the TGS will not be altered after continuous exposure to oxygen-displacing gases. Other advantages of the TGS include vibration and mechanical shock resistance, long life (at least nine years), and relatively low cost due to the need for few electrical components in support circuitry.

Two sensors, models TGS 812 and TGS 822, were recommended by Figaro Engineering for the measurement of EtO (Figure III-2). These sensors are composed of a sintered tin oxide layer deposited on an alumina ceramic tube. A heater coil passes through the center of the tube, making the TGS 812 and 822 indirectly heated sensors.

Model TGS 812 is highly sensitive to combustible and toxic gases such as propane, butane, and carbon monoxide. TGS 822 is particularly sensitive to organic solvent vapors, such as acetone, ethanol and benzene. Both sensors were evaluated in Task 1.

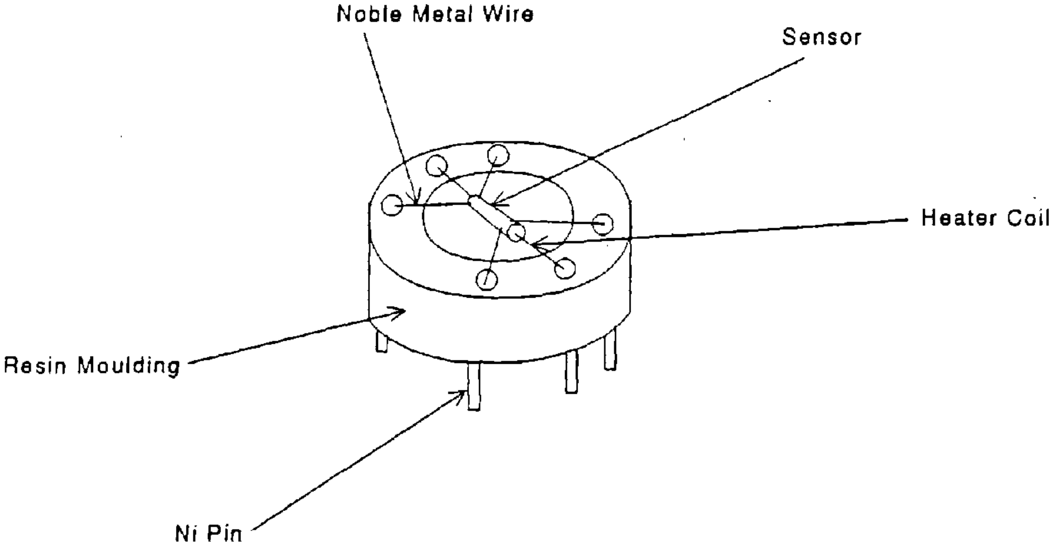


Figure III-2. TGS 812 and 822 Sensor Configuration

The output signal from the TGS is typically measured as electrical resistance. Thus, the detection of a combustible gas such as organic solvent vapors is observed as a decrease in the sensor resistance. The sensitivity of the sensor to the concentration of the contaminant under study is dependent on the heater supply voltage, and the temperature and humidity of the carrier air stream. The three primary types of sensors supplied by Figaro Engineering detect a wide variety of hydrocarbons and their derivatives, halogens, alcohols, ethers, ketones, esters, nitrogen-containing organic compounds, and inorganic gases such as ammonia and carbon monoxide. These sensors have been incorporated in smoke alarms, alcohol detectors, carbon monoxide monitors, and combustible gas detectors. A warm-up period of no more than seven days is required after the sensor has been stored in an unenergized state. Because of the required warm-up period, the sensors used in the EtO studies were constantly energized.

One sensor, TGS 822, was recommended by Figaro Engineering as best suited for the measurement of EtO. The TGS 822 is particularly sensitive to organic solvent vapors, such as acetone, ethanol and benzene. The TGS 822 response is also dependent on the atmospheric temperature and humidity. Figaro Engineering stated that the resistance of a

TGS 822 exposed to 300 ppm ethanol in air was shown to vary by less than a factor of 1.4 over a period of one year.

2. Comparison Test Fixture

The sensor comparison test fixture consisted of sockets for six TGS units mounted such that the heater voltage leads to the sensors were wired as a parallel array. The fixture was placed in an enclosed chamber at ambient temperature. This configuration provided data for each of the sensors in a rigidly controlled environment. A mass flow controller was used in a continuous flow system which allowed flows of up to 100 cc/min through the test enclosures. This system provided precise, continuous concentrations of EtO and interferent gases to the test fixture. A fan was mounted in the interior of the test chamber to uniformly mix the air and to provide circulation of the controlled concentration of EtO over the sensors.

3. Power Supplies and Electronics for Energizing the TGS

A power supply was assembled to control the operating voltage to the heater circuit of the each of the TGS sensors under test. The sockets of the test fixture were wired in parallel for the heater voltage, so that the six sensors under test were subjected to the exact same voltage. An analog output from the data acquisition board in the PC was configured to send a control voltage signal to the heater voltage power supply. With this control circuit it was possible to ramp the heater voltage so that the resistance of the TGS sensors under test could be measured as a function of applied heater voltage. The heater voltage ramp functions were timed in conjunction with the alternating clean air and EtO-doped feed cycles to the chamber so that the sensor performance for both gas conditions at the same heater voltage could be obtained.

Each of the six sensors in the array was controlled and monitored separately for the resistance of the semiconductor element in the TGS sensor and the operating temperature of the TGS sensor. The TGS temperature readings were taken using Type K thermocouples which were wired into the PC data acquisition board and programmed to produce an output in degrees Fahrenheit. The thermocouples were carefully installed to measure the sensor temperature on the underside of the semiconductor surface. The output leads of the individual TGS sensors were routed to separate resistance-to-voltage amplifiers; the resulting sensor output voltages were connected to separate channels in the data acquisition board, displayed on the PC monitor and recorded on a disk data file.

4. Strawberry Tree Software

A PC-based data acquisition system was employed to record data on the performance of the TGS sensors during evaluation in the comparison test fixture. The objective of this test series was to identify the operating point where the signal to noise ration of the sensor was maximized. The approach was to measure signal levels for clean air and compare them to signal levels for an air stream spiked with EtO, both measured as a function of sensor temperature. The difference in these values at a fixed temperature was then the net signal change that would be measured in an operating environment for the prototype instrument. This difference could be plotted as a function of temperature from the data obtained with the data acquisition system, and a maximum value found for the temperature range of interest.

A software package was purchased with the data acquisition hardware for programming of the data acquisition function on the PC. The data acquisition software package was Workbench PC 1.05 (Strawberry Tree Inc., Sunnyvale, CA). This system was icon-based, and provided extreme speed and versatility of programming in the construction of a sophisticated data acquisition, scaling, screening and logging program for the comparison test fixture. The program was completed quickly, and featured on-screen graphs of temperature and sensor resistance histories. All conditions were logged to disc at 0.8 second intervals for later retrieval and analysis with a spreadsheet program. The software also provided a control function by sending a signal to ramp the heater voltage at specified rates.

5. TGS Optimization Experiments

The voltage applied to the TGS heater was varied to identify the values at which the sensor demonstrated maximum sensitivity to ethylene oxide, and minimum sensitivity to interferents such as isopropyl alcohol. The ratio of these two values was used to define the operating point at which the sensors are most sensitive to EtO and least sensitive to interferents; that is, where the sensor demonstrates maximum EtO-to-interferent signal ratio.

Initial experiments were performed by placing the TGS 812 in a 5.4-liter gas test chamber and flowing 4 ppm EtO or clean air through the chamber. The Strawberry Tree software system collected data from the TGS during experiments in which the sensor was exposed to 4 ppm EtO alternately with a "clean air" mixture of nitrogen and oxygen. The data monitored by Strawberry Tree is listed in Table III-1.

Table III-1. Data Monitored by Strawberry Tree Software

Parameter	Range
TGS Heater Voltage	0 - 5.5 VDC
TGS Temperature	70 - 500°F
TGS Output Voltage/Resistance	0 - 10 volts (0 - 1 Mohm)
Humidity	(10 mv/%RH)

Experiments were performed where the TGS heater voltage was ramped up and down while alternating EtO and clean air flow in the chamber. Over a heater voltage range of 1 to 5 volts, the ratio of clean air signal to EtO signal was a maximum at about 3.5 to 3.6 volts. However, later experiments in Tasks 2 and 6 showed that the optimum TGS heater voltage which could be used without risk to the sensor life was 5.6 volts. This apparent discrepancy is due to the sensor response time to an EtO spike. At 3.5 volts the sensor was the most sensitive, but the response time was quite long. The tests showing a optimum voltage of 3.5 volts were done using a steady stream of a gas at a constant composition. When the sensor was monitored in later Tasks where it was subjected to clean carrier gas followed by a spike of EtO, the response was fastest at higher voltages. The manufacturer of the sensors indicated that a voltage less than 5.5-5.6 volts would not seriously effect the life of the sensor.

The time required to fill the chamber and detect changes in the output signals of the six sensors was quite long, so a single sensor was placed in a 1.5-inch-by-1.2-inch aluminum block, which was also used in the Phase I work. This reduced the working volume around the sensor, and provided a fast-response environment for the sensor in the succeeding tasks.

Figure III-3 presents the results from a test of a group of six sensors to exposure to EtO-doped air. The minimum resistance for all sensors is seen to fall into the range of 3.4 to 3.7 volts heater excitation. Based upon this similarity in response, further testing in Task 2 was done to determine the best sensor under other conditions. For comparison, the sensor resistances for all sockets in clean air are over 500 kohms at heater voltages below 4 volts.

The tests completed in Task 1 indicated that the model 812 TGS sensor showed the greatest sensitivity to EtO at the concentrations of interest for the development of an EtO monitor, less than 10 ppm.

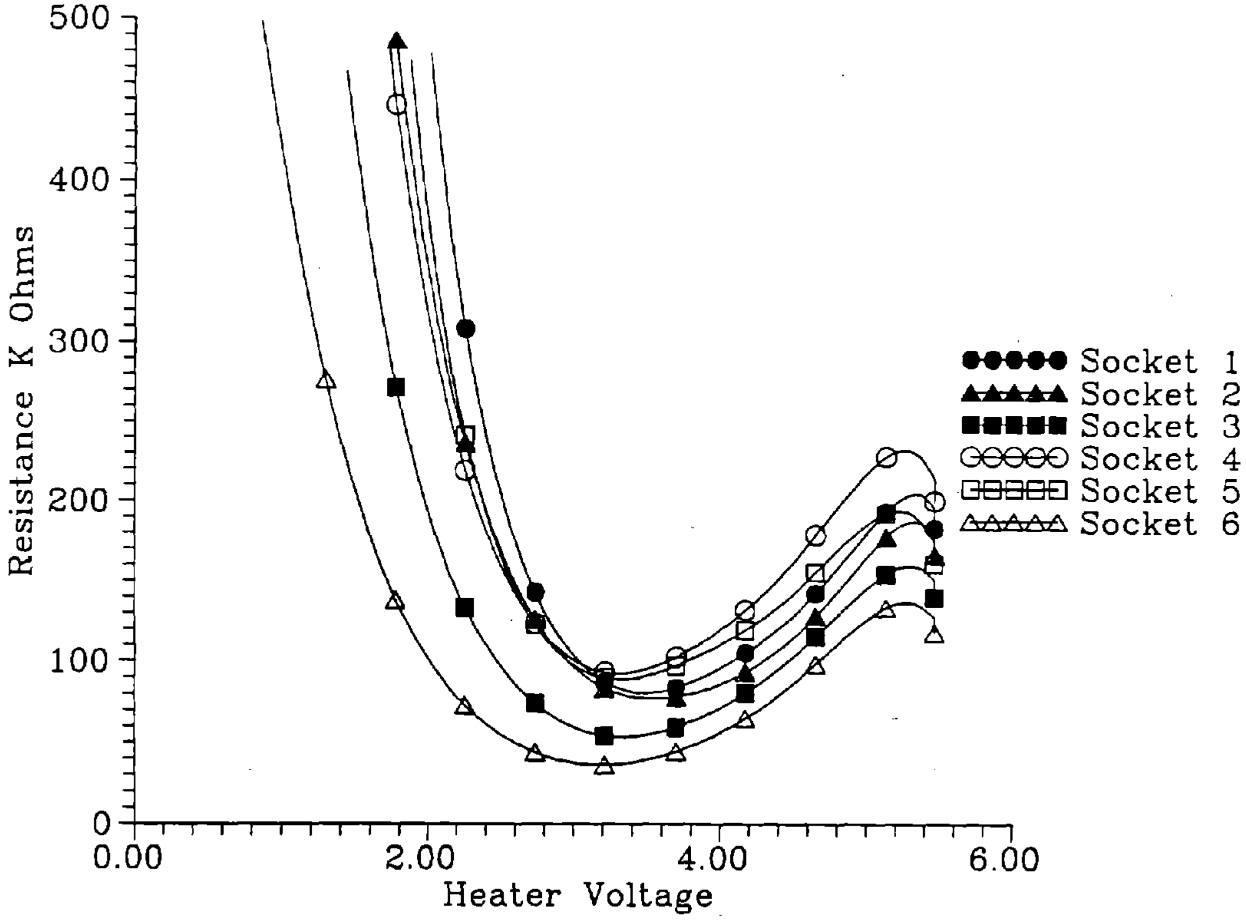


Figure III-3. Responses of a Group of TGS Sensors to Exposure to EtO

B. TASK 2: OPTIMIZATION OF CHROMATOGRAPHIC PARAMETERS

The objective of this Task was to identify column parameters and the proper operating conditions that would result in: (1) fast and repeatable elution of EtO in less than a two minute cycle and (2) baseline separation of EtO from interfering compounds. Considerable testing was performed in this Task due to the importance of identifying optimum chromatographic conditions in the development of a viable EtO monitor.

In order to avoid pressure transient peaks and minimize the pump requirements for the prototype instrument, the target column operating pressure was set at less than 20 psig. It was preferable that the column temperature be as close to ambient as possible to minimize heating requirements, and because higher operating temperature was shown to reduce the separation that could be achieved in the column. Elevated temperatures may also lead to EtO decomposition on the column.

Because of the ease with which EtO sorbs to surfaces, Teflon was selected as the material from which the 3.2-mm (0.125-in) column tubing was fabricated. Some researchers have found that columns made of Teflon or nickel perform better than those made of stainless steel (Allen et al., 1987).

A gas chromatograph, Model SRI-8610 (Buck Scientific, Inc., East Norwalk, CT), was employed to provide the capability to heat columns and to analyze for EtO using the TGS sensor. Gas samples of 0.5-1.0 ml size were injected with a gas sample injection valve (compressed air served as the column carrier gas for these experiments). A TGS was mounted in an aluminum block at the outlet of the test column; this aluminum block was the same configuration used in the Phase I work. The sensor block was mounted outside the GC oven, with the column extending into the sensor cavity, as shown in Figure III-4. All chromatography experiments were conducted isothermally. Data were collected using both a strip chart recorder (Cole-Parmer Instrument Co., Chicago, IL) and the personal computer-based data acquisition system. EtO standards in the range of 0.1 to 10 ppm were prepared by injecting 1% EtO-in-nitrogen gas standard (U.S. Welding, Denver, CO) into a 5 or 45-liter Tedlar bag filled with compressed air. An air sample from the bag was then injected using the flow system shown in Figure III-5. The pump was activated for a minute to flow the sample through the sample loop. The pump was shut off, then a few seconds later the sample in the loop was injected by manually switching the valve.

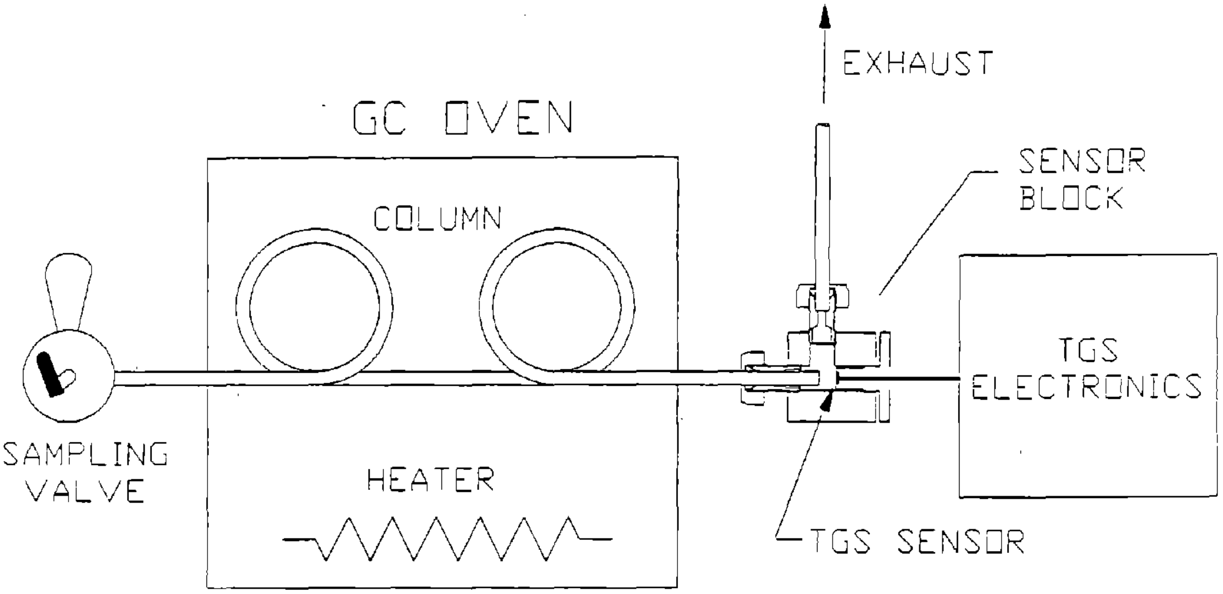


Figure III-4. GC Test Configuration for TGS Sensors

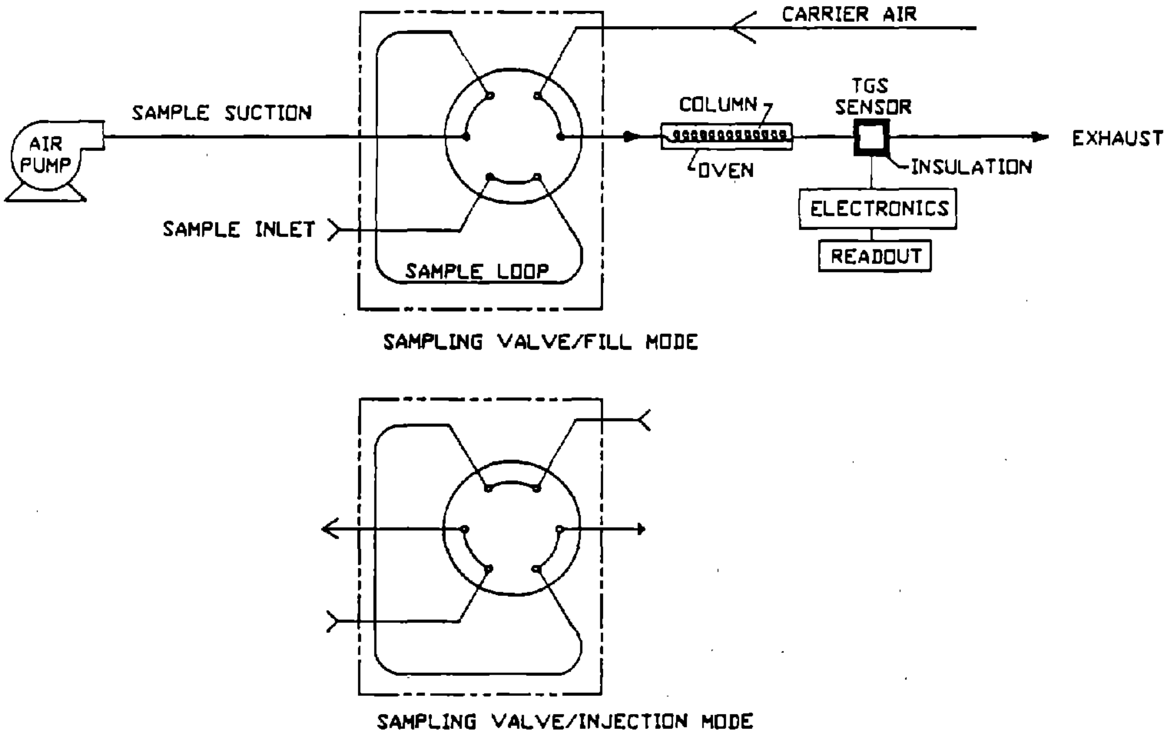


Figure III-5. EtO Injection Schematic for GC Testing

As a continuation of Task 1 experiments to investigate the performance of the TGS sensor, both the TGS 812 and TGS 822 were tested in some of the column experiments. An EtO calibration was performed with both sensors, and the limits of detection (LODs) were compared. EtO peak characteristics as a function of sensor temperature were plotted (recall that there is an internal heating element in the sensor).

A comparison was made of the two data collection methods (strip chart recorder vs. computer data acquisition). The computer software was programmed to integrate the EtO peaks in order to obtain peak areas as well as peak heights. For 1 to 8 ppm EtO, the 2 peak height and 1 peak area calibration curves were very linear (r^2 = 0.995-0.998). The computer program was not successful at measuring peak heights or integrating peaks at EtO concentrations below 1 ppm. However, the results for 1 to 8 ppm EtO demonstrate that peak height measurement is comparable to peak area in linearity of the calibration curve. It was therefore possible to program the prototype instrument to measure the difference between the baseline voltage (prior to an EtO signal) and the peak EtO signal, without measuring the signal following the peak maximum. Once the peak has been reached, the column backflushing operation can begin immediately to prevent other compounds from being detected by the TGS.

Linear calibrations were obtained for EtO over concentration ranges of 0.1 to 10 ppm. The calibrations were performed for 0.1 to 10 ppm EtO due to the fact that EtO concentrations measured in hospital air are extremely low, and frequently are not above the LOD (Lee, 1990, personal communication). Also, OSHA TWA and STEL values fall in the 0.1 to 10 ppm range.

The work begun in Phase I to evaluate interferences and their effect on the measurement of EtO was continued in this Task. A survey of hospitals identified common airborne contaminants which have caused commercial instruments to set off a false EtO alarm. Examples of alarm-triggering compounds include those present in perfumes and household-type cleaners. Steam has also been known to actuate EtO alarms. All of these substances were tested by injecting typical concentrations in the instrument. In addition, the response of the TGS to carbon dioxide was tested. Carbon dioxide is mixed with EtO at a ratio of 10% EtO to 90% carbon dioxide to form an alternate sterilizer gas. Freon-12 was again tested, this time over a wider range of EtO concentrations, to further characterize the effect of Freon on the EtO signal. Freon-12 is also a common dilution gas for EtO in commercial sterilization systems, at a ratio of 88% Freon-12 to 12% EtO.

1. Column Packing Comparison

Several types of column packing materials have been used for EtO analysis by gas chromatography (Bond and Dumas, 1982; Binetti et al., 1986; Allen et al., 1987). The 10% SP-1000 on 80/100 Supelcoport packing (Supelco, Inc., Bellefonte, PA) was chosen for initial testing of EtO separation at room temperature. Other packings included 0.8% THEED on 80/100 Carbopack C, 5% Fluorcol on 60/80 Carbopack B, and 60/80 Carbopack BHT. These column packings were selected for the following reasons:

- The SP-1000 material had been used successfully in the Phase I work.
- The THEED material is made specifically for EtO analyses by Supelco.
- Fluorcol was recommended as a superior column packing for EtO analyses by Steger et al. (1988).
- Carbopack BHT is used in conjunction with the PID by NIOSH.

The Fluorcol column was eliminated early in the testing because EtO eluted very late as a broad tailing peak. A new column packing material recently introduced by Supelco, Inc., Carboxen-1000, was obtained later and tested because of its ability to separate permanent gases, light hydrocarbons, and light polar compounds. This packing was supplied in a coarse mesh size (45/60), which would result in a lower pressure drop than with the finer mesh packings listed above. Unfortunately, a 5-ft column packed with 45/60 mesh Carboxen-1000 did not effectively elute EtO at temperatures of 55°C or 150°C. The length of all columns was initially 10 ft, however shorter columns were tested later because less pressure was required to maintain 30 cm^3/min of carrier gas flow. The length of the column is a critical factor for optimum EtO resolution. Excessive column length can result in long retention times, but a column which is too short will not give adequate separation of the species of interest from other components.

A comparison of column packing operation was performed using a varying EtO concentration. Figure III-6 shows the peak height as a function of EtO concentration for SP-1000, THEED, and Carbopack BHT column packings. While linear calibrations were obtained for all columns (r^2 = .998 to .9999), the largest EtO signals were observed with the THEED column. Limits of detection were determined by measuring the background noise (signal fluctuation before EtO elution from the column) on the highest sensitivity scale, and estimating the EtO concentration that corresponded to twice the noise level. These values were 0.1 ppm for SP-1000, 0.3 ppm for Carbopack BHT, and 0.05 ppm for

THEED. The THEED also has the lowest working temperature of the three, which reduces the risk of thermal decomposition of EtO with attendant loss of sensitivity.

The performance differences between the three columns became more pronounced when they were tested at an EtO concentration of 10 ppm. Peak heights (Figure III-7) and widths at half-height (Figure III-8) as a function of column temperature were compared. The THEED column was superior to the SP-1000 and Carbopack BHT columns in EtO signal magnitude, particularly at ambient temperature. The THEED column also produced the sharpest EtO peaks at the lowest temperatures. The differences in peak quality and magnitude were obviously due to the resolution capabilities of the columns with regard to EtO.

The retention time of 10 ppm EtO on the SP-1000, THEED, and Carbopack BHT columns as a function of column temperature is shown in Figure III-9. The Carbopack BHT column was inferior to the SP-1000 and THEED columns with regard to retention time.

Each of these figures illustrates the superior performance of the THEED column packing, which was chosen for the prototype instrument.

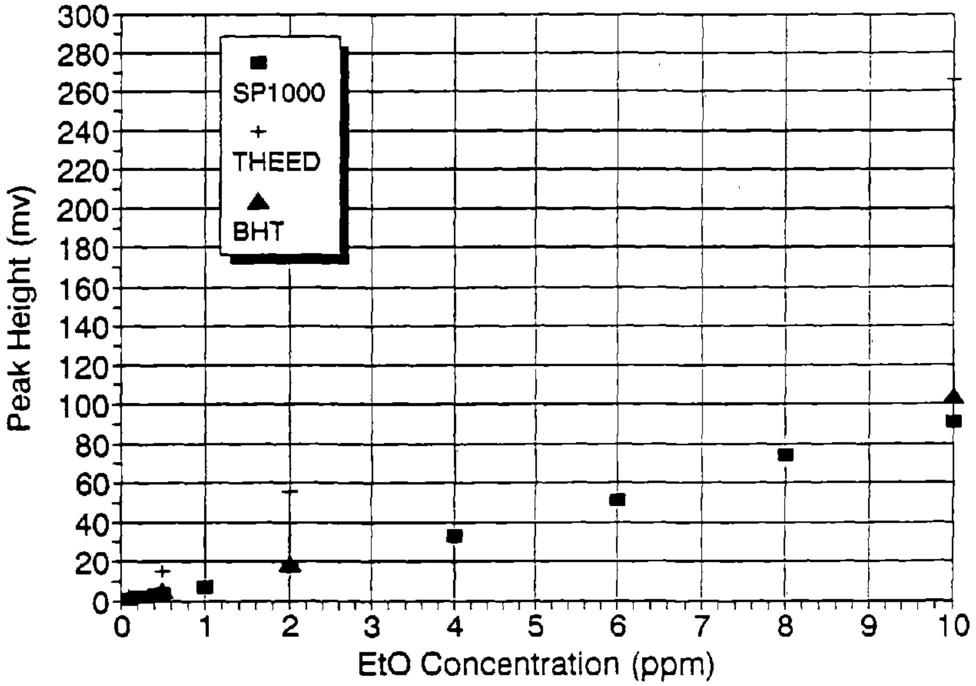


Figure III-6. Peak Heights for Candidate Column Packings

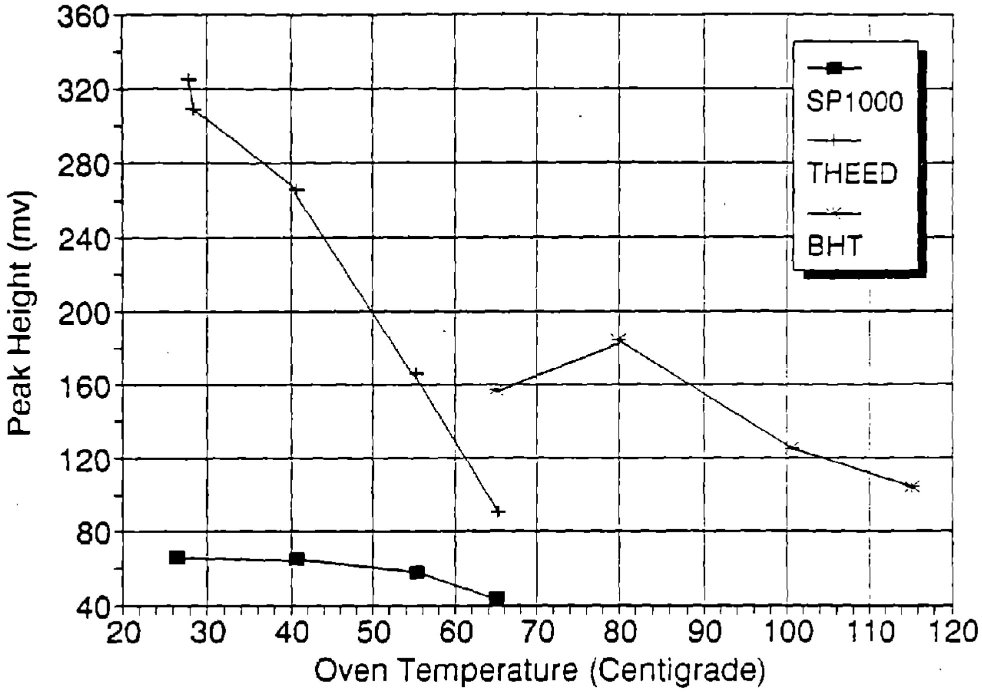


Figure III-7. Effect of Temperature on Peak Height

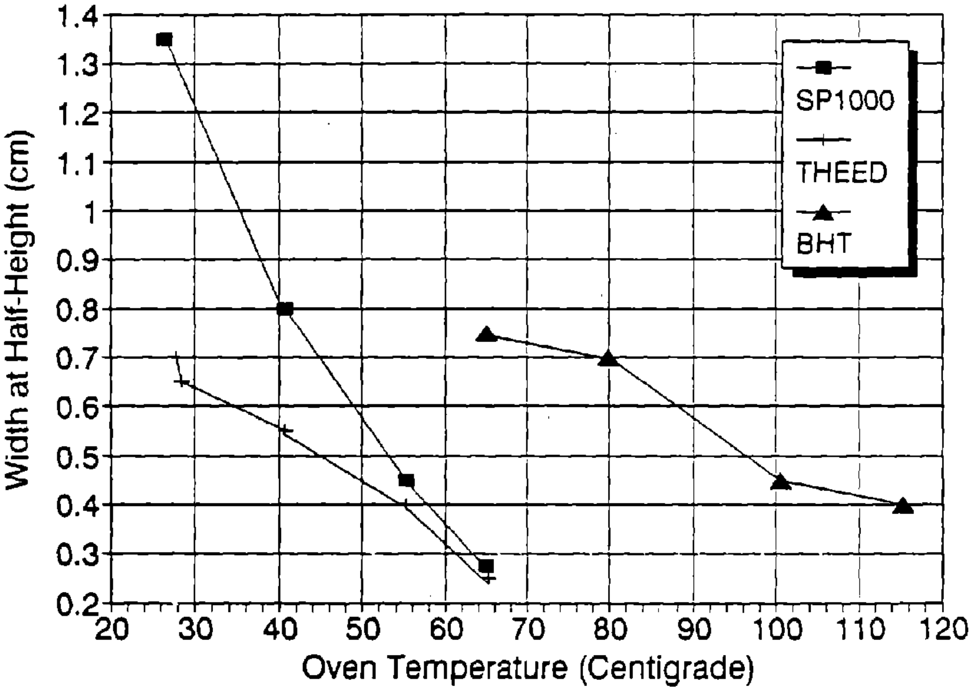


Figure III-8. Effect of Temperature on Peak Half-Width

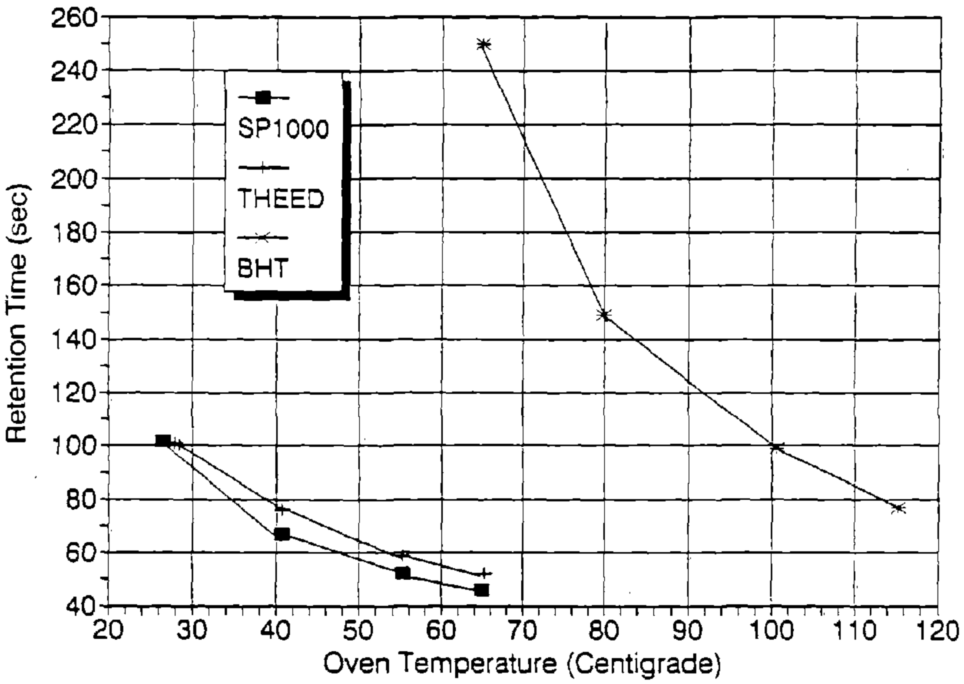


Figure III-9. Effect of Column Temperature on Retention Time

2. TGS Sensor Operation

The effect of column temperature on the EtO retention time, signal magnitude, and peak sharpness (determined as the width of the EtO peak at 50% of the peak height) was evaluated. In addition to varying the column temperature, the air carrier gas flow rate was varied from 15 to 30 cm^3/min. EtO calibration curves and limits of detection (LOD) were determined for each column. Peak height and peak area calibration curves were compared.

Calibration curves were generated using the SP-1000 column at 65°C to compare the TGS 812 and 822 responses. As shown in Figure III-10, the TGS 822 gave a slightly larger signal at the higher concentrations, but the calibrations are essentially identical. The correlation coefficient for both curves was 0.998. The limit of detection (LOD) for the TGS 812 was determined to be 0.2 ppm and for TGS 822 was 0.1 ppm. Because of its slightly better response to EtO, TGS 822 was used almost exclusively for the component selection and optimization testing. For the prototype instrument, the TGS 812 sensor has proven to be less sensitive to baseline shifts in resistance and has since demonstrated an LOD of less than 0.1 ppm.

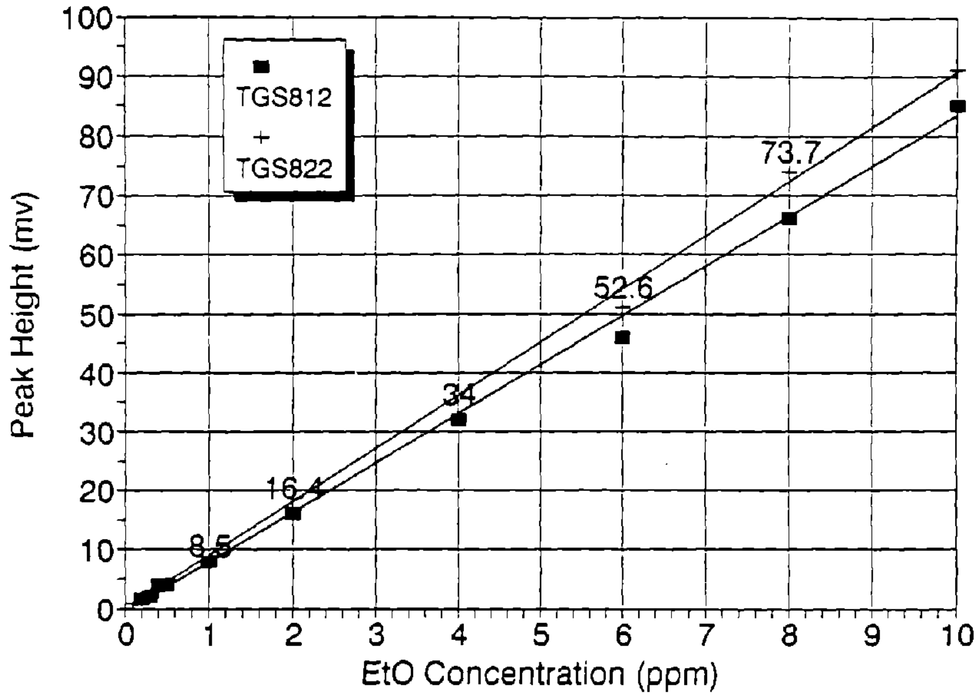


Figure III-10. TGS Sensor Output Comparison
SP1000 Column at 65°C

3. TGS Sensor Operating Temperature

Sensor operating temperature experiments were performed with the THEED column. The linear relationship between heater voltage and sensor operating temperature was confirmed (Figure III-11). It was noted that the peak magnitude leveled out above the sensor operating temperature of 297°C (Figure III-12), instead of increasing as expected. The problem of EtO adsorbing to the sensor was confirmed, when the time required for the TGS signal to return to the baseline level after EtO had been measured (sensor recovery time) was found to decrease with increasing sensor operating temperature (Figure III-13). **A compromise operating temperature of the TGS was set at 338°C, which corresponded to a heater voltage of 5 VDC.**

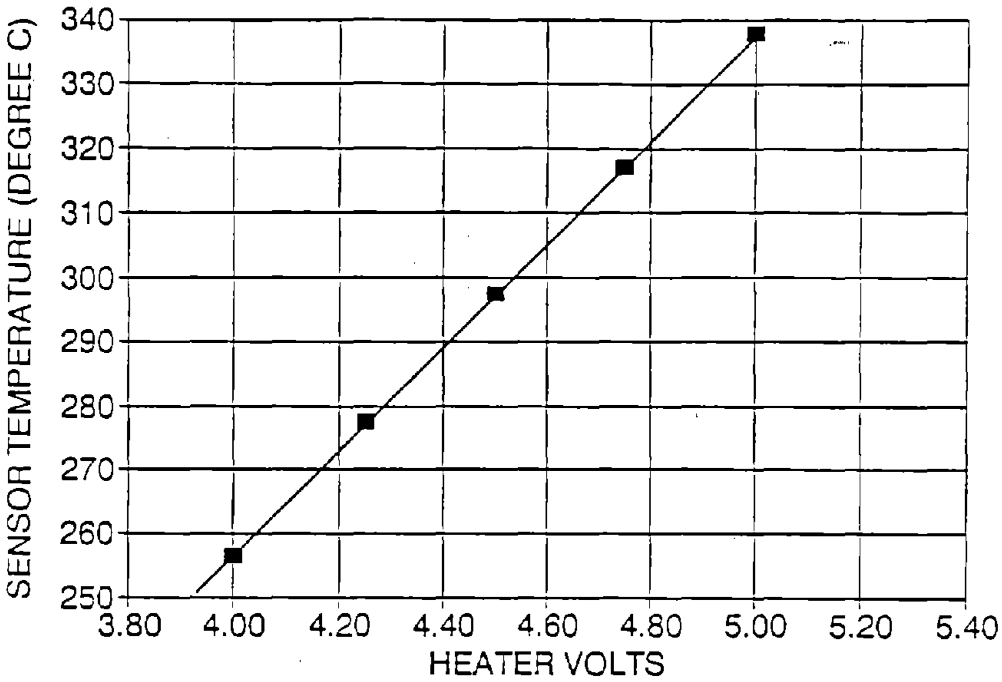


Figure III-11. Sensor Heater Voltage Effect on Temperature

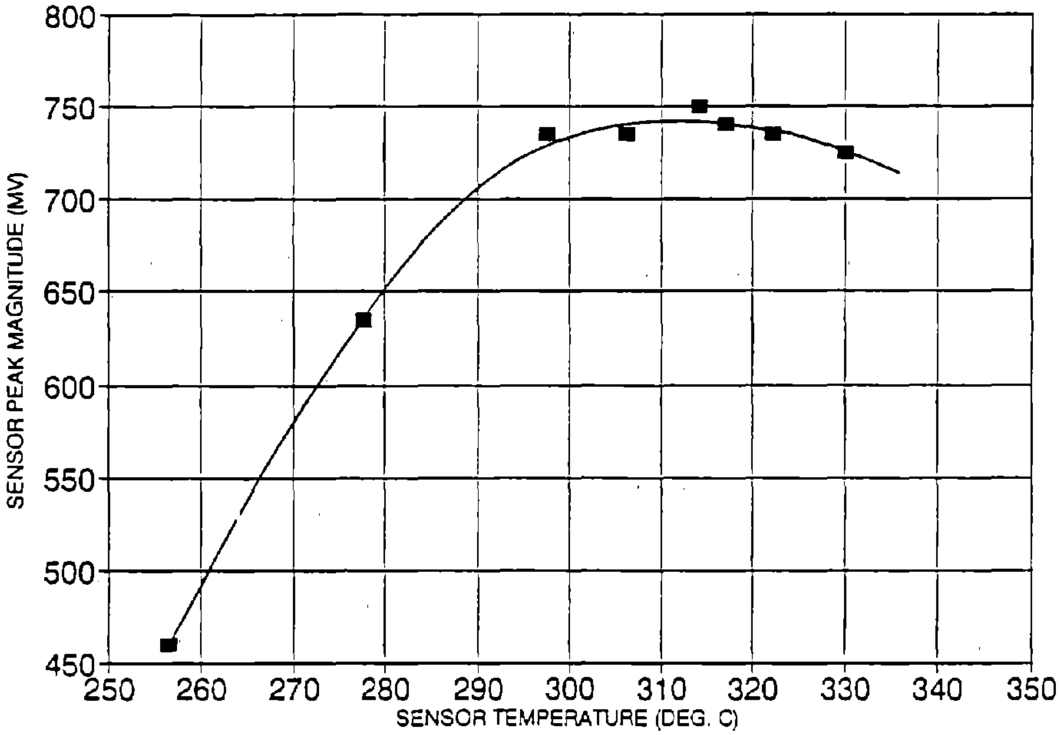


Figure III-12. Sensor Temperature Effect on Sensitivity to EtO

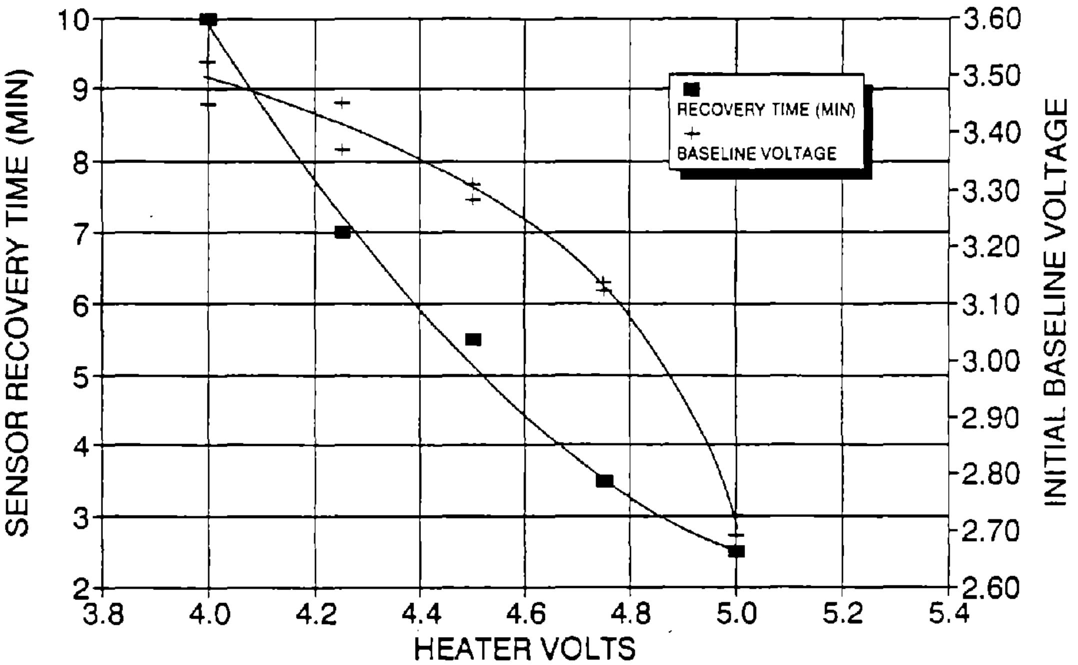


Figure III-13. Effect of Heater Voltage on Sensor Recovery Time

4. Column Temperature

A 0.1-10 ppm EtO calibration was performed at 3 different column temperatures using the THEED column. These results, shown in Figure III-14, confirm the data of Figure III-7 which showed increasing sensor signal strength with decreasing column temperature. The column temperature, however, does not affect calibration linearity.

Based on these data, the design for the prototype specified a 50°C column temperature.

5. Column Flow Rate

The carrier gas flow rate through the Carbopack BHT column at 115°C was varied to investigate the effect on EtO retention time and signal magnitude (Figure III-15). It is apparent that the 30 cm^3/min flow rate results in the fastest elution of EtO with the largest signal magnitude. **All experiments have been conducted using 30 cm^3/min column flow.**

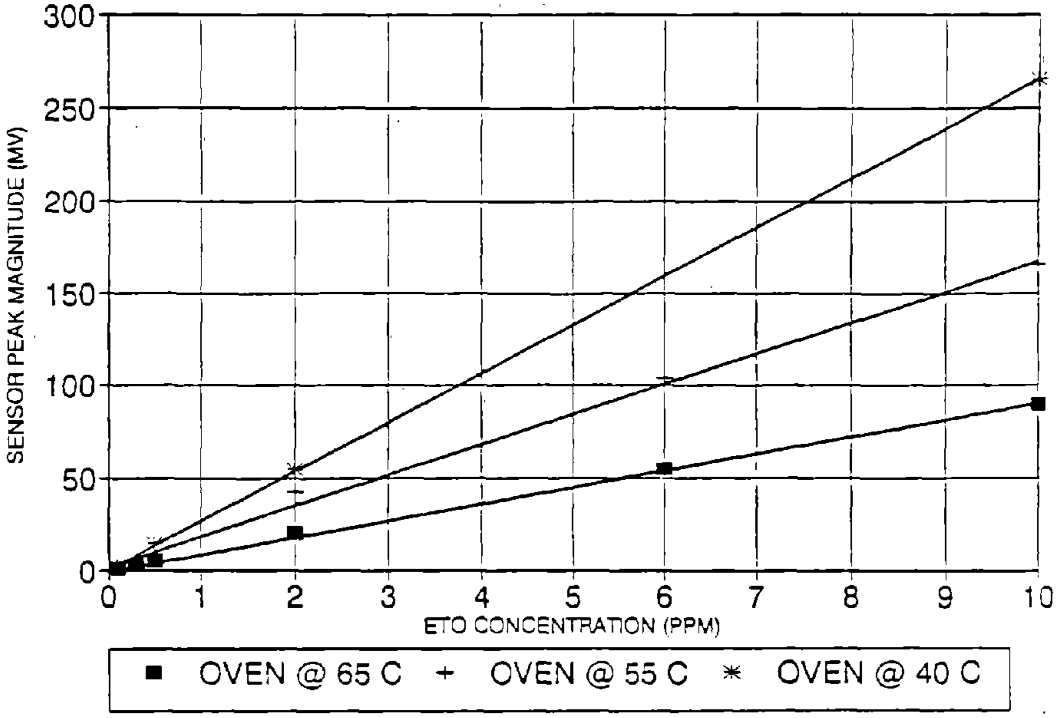


Figure III-14. Effect of Column Temperature on Sensor Output

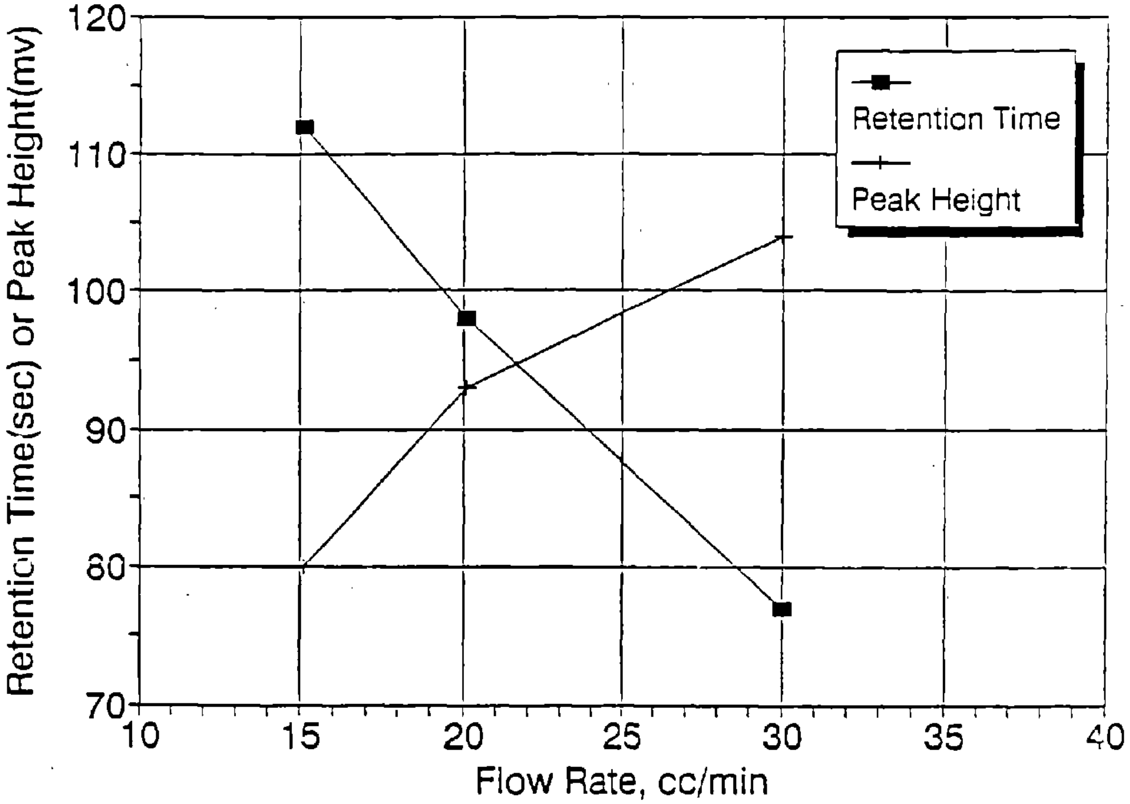


Figure III-15. Impact of Flow Rate on System Performance

6. Column Length

One problem with the column was the 60 psi head pressure required to maintain a 30-cm^3/min flow through the 10-ft THEED column (Figure III-16). This relatively high pressure would require the use of a more sophisticated pump, an expensive and delicate component in the commercial instrument. In order to decrease the column pressure, it would be necessary to either decrease the column length, increase the size of the column packing, or both. Figure III-16 shows the decrease in pressure with various column lengths. A 2.5 ft column gave the desired pressure, but a short column could affect EtO resolution. Therefore, it was necessary to analyze potential interfering compounds to determine retention times and resolution from EtO.

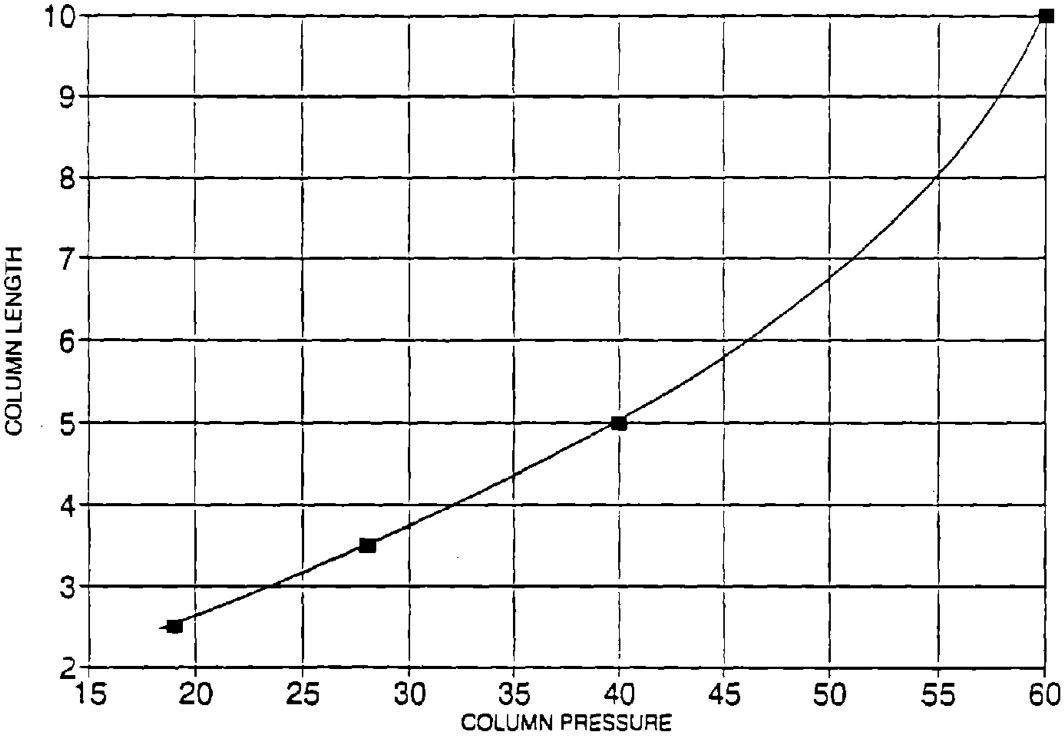


Figure III-16. Injection Pressure Requirements for Separation Column

In summary, the column parameters for the prototype instrument,based on the component tests, were chosen as:

- THEED column packing;
- TGS operating voltage of 5 VDC, resulting in an operating temperature of 338°C;
- Column temperature of 50°C;
- Column flow rate of 30 cc/min;
- Column injection pressure of 20 psi;
- Column length of 2.5 ft and diameter of 0.125 in.

These values were used in the initial configuration of the prototype instrument; as the unit was subjected to an extensive test program, changes were made in the configuration. These included reducing the column flowrate to about 20 cc/min. and increasing the TGS operating voltage to 5.5 VDC.

7. Resolution of EtO from Interferences on the THEED Column

One of the most important objectives of this research program was to demonstrate the ability of the EtO monitor to discriminate between EtO and interfering gases that would typically be present in the vicinity of an EtO sterilizer. One gas which is commonly mixed with EtO as a sterilization mixture is Freon-12, or dichlorodifluoromethane, at a ratio of Freon-to-EtO of 88:12. This mixture is generally referred to as 12/88. Other compounds which might be present in the hospital air are alcohols such as isopropyl alcohol (IPA). Although typical concentrations of IPA in hospital air could not be identified, the Threshold Limit Value for IPA is 400 ppm. This would presumably be the maximum concentration of IPA that would be present in the air in the vicinity of an EtO area monitor.

The TGS is capable of detecting a wide variety of organic and inorganic gases, including propane, alcohols, ethers, and ammonia. The TGS 812 is highly sensitive to propane and butane, while the TGS 822 is particularly sensitive to organic solvent vapors. In order to assure that the TGS is measuring EtO selectively, the chromatography column must be extremely efficient at separating EtO from potential interfering compounds.

A wide variety of compounds may be present in the gas phase in hospitals. Compounds which have been known to trigger false alarms in commercial EtO instruments include those present in perfumes (alcohols) and household-type cleaners (chlorine, ammonia). The contaminants chosen for testing in this program were isopropanol, methanol, ethanol, acetone, ammonia, chlorine bleach (sodium hypochlorite), and water. In addition, carbon dioxide and Freon-12 (dichlorodifluoromethane) were tested because these compounds are routinely mixed with EtO as a commercial sterilization gas supply.

Isopropanol, methanol, acetone, and bleach (sodium hypochlorite) were prepared by injecting 0.1 ml of liquid compound into a 45-liter Tedlar bag filled with compressed air. Freon-12 and ammonia were available as 1000 ppm compressed gas standards. Pure carbon dioxide was also tested to determine sensor response. Water vapor was generated by bubbling air through a container filled with water, followed by flow through the injection valve.

The TGS responded to all compounds except carbon dioxide. EtO was well-resolved from all compounds on the 10-ft THEED column, except ammonia and Freon-12 (Table III-2). Although the ammonia retention time is 30 seconds longer than that of EtO, ammonia does not give a sharp signal. This is probably due to ammonia adsorption to either the column or TGS, or both. The ammonia signal begins at 1 min, then does not peak for 45 seconds. This would clearly obliterate an EtO signal. In addition, 1000 ppm ammonia appeared to have a long-lasting detrimental effect on the TGS, in which sensitivity to EtO decreased and did not recover over a period of two weeks. The TGS was then replaced with a new sensor. Acidic traps such as H_3PO_4 on activated carbon are available that would take out ammonia before it reaches the sensor.

With the good resolution obtained with the 10-ft THEED column for most interferences, the column length was decreased to 5 feet. At a column temperature of 27°C, EtO (2 ppm) and acetone (1000 ppm) were analyzed and found to be well-separated with retention times of 49 and 239 seconds, respectively.

Table III-2. EtO and Interferences on 10-ft THEED Column

TGS822 Temperature: 320°C; Column Temperature: 40.7°C;
Column Flow: 30 cm^3/min

Compound	Concentration (ppm)	Sensor Signal (millivolts)	Retention Time (seconds)
EtO	10	267	76
Freon-12	1100	40*	81
Ammonia	1000	585	105
Acetone	≈680	1360	335
Methanol	1230	1380	592
Water	----	545*	660

*Analyzed after ammonia; signal probably less than it would have been before ammonia was run

The column length was further decreased to 3.5 feet, and excellent resolution of EtO from interfering compounds was maintained. A chromatogram of all compounds tested is shown in Figure III-17, and the data for responses obtained when the compounds were analyzed individually is given in Table III-3.

Table III-3. EtO and Interferences on 3.5-ft THEED Column.

TGS 822 Temperature: 333°C; Column Temperature: 27°C

Compound	Concentration ppm	Sensor Signal (millivolts)	Retention Time (seconds)
EtO	10	350	48
Freon-12	1100	230	40-58
Acetone	1000	3550	219
Methanol	1000	3550	587
Sodium hypochlorite	1000	520	743
Isopropanol	1000	440	745
Ethanol	1000	3600	1620

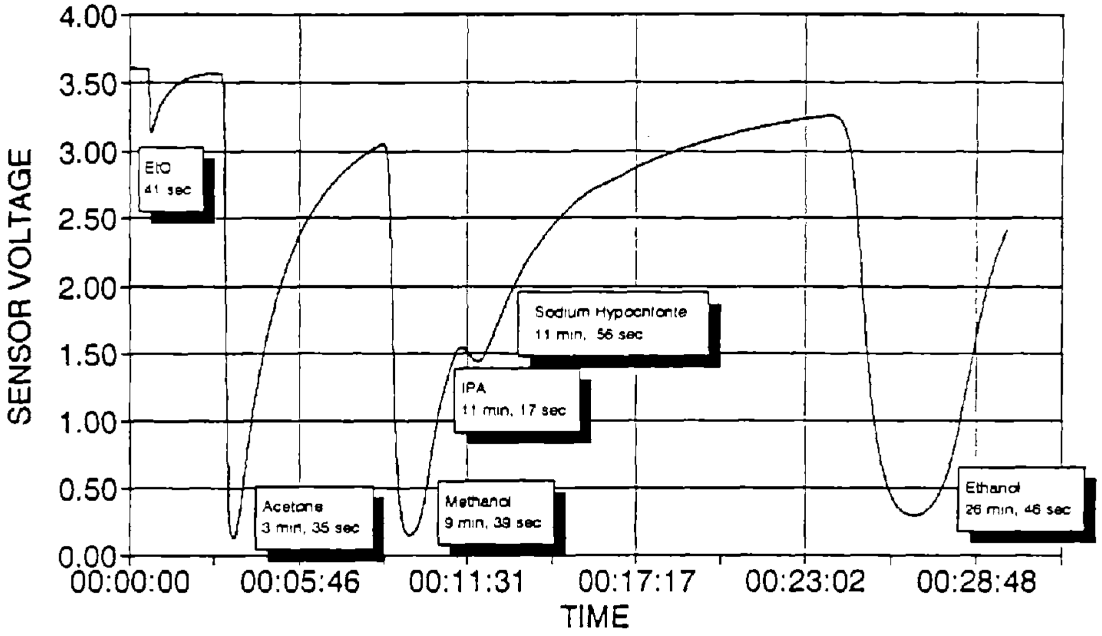


Figure III-17. Elution of Potential Interferents with EtO

Freon-12 co-elutes with EtO, but the signal is much smaller than that of EtO. In sterilization applications, the Freon-12/EtO sterilizing gas mixture consists of 88% Freon-12 and 12% EtO. Since the control systems for EtO removal are ventilation-based, it is unlikely that a high concentration of Freon-12 would be present without a high concentration of EtO also being present. If 5 ppm EtO were present (the high alarm level for the EtO instrument), the Freon-12 concentration would be 37 ppm. According to the data in Table III-3, the response factor for Freon-12 is 0.2 mv/ppm, compared to 35 mv/ppm for EtO. This would correspond to 7.4 mv for 37 ppm Freon-12 and 175 mv for 5 ppm EtO. Therefore, even at a concentration of 37 ppm, Freon-12 should not interfere with the EtO measurement.

Subsequent analyses of EtO and Freon-12, however, showed that Freon-12 affects EtO quantitation. It appeared that Freon-12 "enhanced" the TGS response to EtO, but it is more likely that residual Freon-12 was adding to the EtO peak height. This was observed when EtO in the range of 0.1 to 10 ppm was analyzed with Freon-12 at an EtO-to-Freon-12 ratio of 12:88. The length of the THEED column had been decreased to 2.5 feet in order to attain a desired column pressure of 19 psi. The sensor temperature was set at 338°C. The calibration data for EtO alone at 30°C and 41°C, and EtO in the presence of Freon-12 and acetone at 30°C, are shown in Figure III-18. The retention time of EtO at 30°C and

41°C was 18 sec and 15 sec, respectively. The higher EtO response with Freon-12 present is apparent, but may be within normal EtO calibration variability.

Also in Figure III-18, the EtO calibration curve at 41°C indicates a much lower signal response than the curve at 30°C. The difference in EtO signal between the two temperatures was not as large in earlier calibrations. The reason for the large difference is not known, but may be reasonably postulated as due to thermal decomposition of EtO at higher temperatures.

EtO was thus shown to elute from the selected separation column at times much quicker than any interferent that would be typically found in a medical facility. Further interferent testing was performed on the assembled prototype instrument to confirm this component test result.

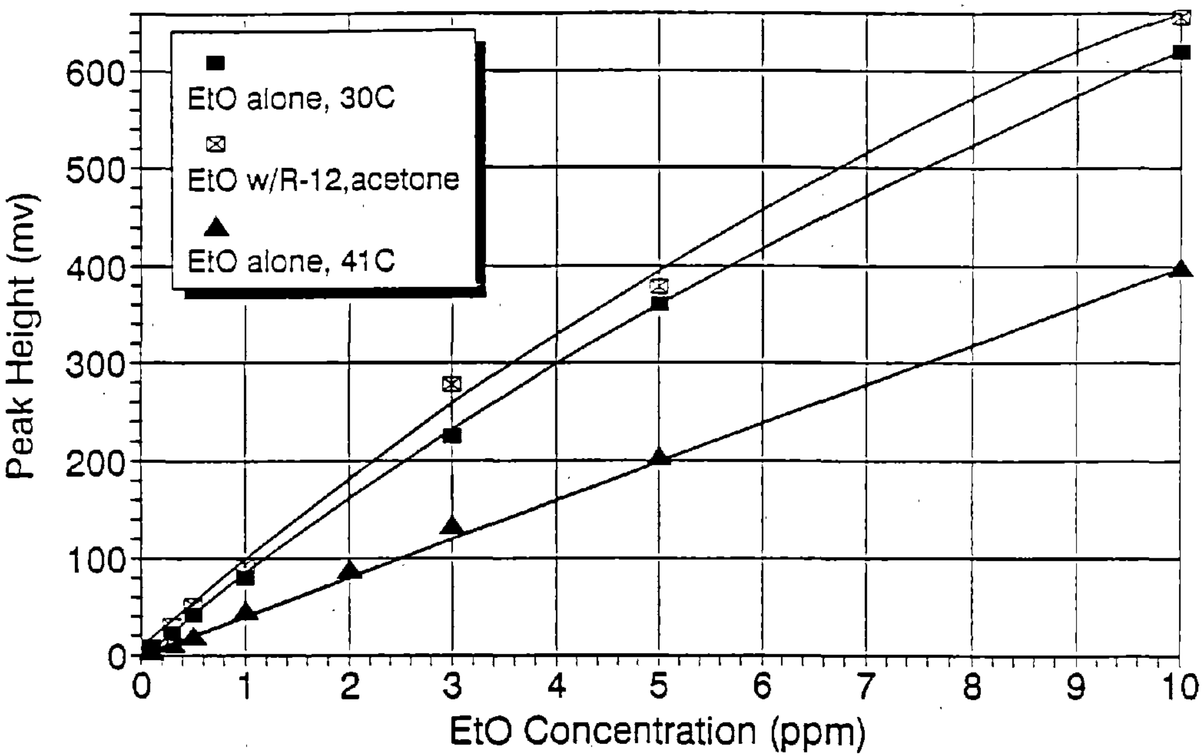


Figure III-18. Effect of R-12 Freon on EtO Peak Height

C. TASK 3: OPTIMIZATION OF SYSTEM FLOW CHARACTERISTICS

The purpose of this Task was to optimize the selection and placement of flow system components in order to maximize the quantitative measurement of EtO and minimize the effects of interfering substances such as water vapor (or steam) and combustible gas phase species in the carrier gas. Combustion of the interfering compounds, followed by complete removal of water from the carrier gas stream was the desired goal.

The primary components fabricated and tested in this Task were the combustibles trap and the dryer. The purpose of the trap was to catalytically combust all organic species in the carrier gas to carbon dioxide and water in order to provide a clean, consistent carrier gas to establish a stable baseline for the TGS. In the initial prototype design, the trap was to be placed at the pump exhaust, and the dryer followed the trap to remove water vapor before the air sample reached the column. Various combinations and configurations of dryers were tested in this task.

The effect of humidity on the resistance of the TGS 822 has been investigated by the manufacturer, Figaro Engineering. Results indicated that at 20°C the baseline sensor resistance decreased by 36% as relative humidity increased from 35% to 100%. A change in humidity in a work area where the EtO monitor may be located, such as a sterilization area, would be expected if a steam sterilizer was present. Therefore, humidity variation is a concern in the design and operation of an EtO monitor.

In the Phase I work, humidity changes in the air were compensated by removing the water vapor before the air stream reached the TGS. This was accomplished by inserting Nafion permeable membrane tubing (0.32-cm diameter) surrounded by calcium sulfate desiccant into the flow system. The Nafion tubing permitted the selective passage of water vapor, and the desiccant surrounding the Nafion produced a water vapor gradient on the exterior of the Nafion tubing. The water vapor concentration in the sample air stream was higher than that in the air outside the tubing, which had been dried by the desiccant, and the gradient was thus directed outward. The effect of the Nafion/calcium sulfate dryer was to remove all water vapor from the air stream as it passed through the Nafion, and provide a constant low relative humidity air stream for the TGS. The drawback of this dryer design was the requirement for replacement of the calcium sulfate desiccant as it became saturated. An alternative configuration was tested in this task.

A major consideration in the design of the flow system was the material and size of tubing to be used. As mentioned earlier, studies have shown that materials such as stainless steel interact with EtO, causing poor precision when used as sample injection loops (Allen, et al., 1987). To minimize EtO adsorption problems, 3.2 mm (0.125 in) Teflon tubing was used in the entire flow system, and the tubing length was minimized, especially between the three-way valve and the column.

1. Combustible Trap Experiments

The first combustibles trap used platinum on an alumina carrier as the catalyst. Tests with interferents showed that there was no reduction of organics at the outlet of the combustor. Another catalyst containing palladium was then obtained and used for subsequent experiments.

The combustibles trap design is shown in Figure III-19. The catalyst is 1% palladium on alumina, composed of 2 to 3 mm-diameter pellets. About twelve grams of catalyst was placed in a container that consisted of a length of one half inch diameter stainless steel tubing fitted with a compression fitting tee on each end for an approximate total length of 8 inches. One tee was capped on one side of the run, and a 0.25-in diameter heater rod was inserted in the run of the second tee and sealed. Carrier air flowed in the branch of one tee and out the branch of the second tee. This trap configuration minimized local heating in the vicinity of the trap, and minimized the power required to heat the catalyst to operating temperature.

Experiments to assess the performance of the trap were conducted with compressed air, noting the change in the TGS baseline voltage as a function of combustor temperature. These results are shown in Figure III-20. A peak in baseline voltage is observed around 300°C, indicating the cleanest background air. The decrease in baseline voltage above 300°C may be due to ammonia from the palladium deposition process offgassing from the catalyst. Since the TGS sensitivity to EtO increases as the baseline voltage increases, a 300°C combustion temperature should provide the largest EtO signals.

The trap temperature was varied from ambient to 400°C to determine the temperature necessary to obtain complete conversion of all compounds to CO_2 and H_2O. Combustion of interfering species was tested by observing the TGS signal due to the interferent with and without the trap in line.

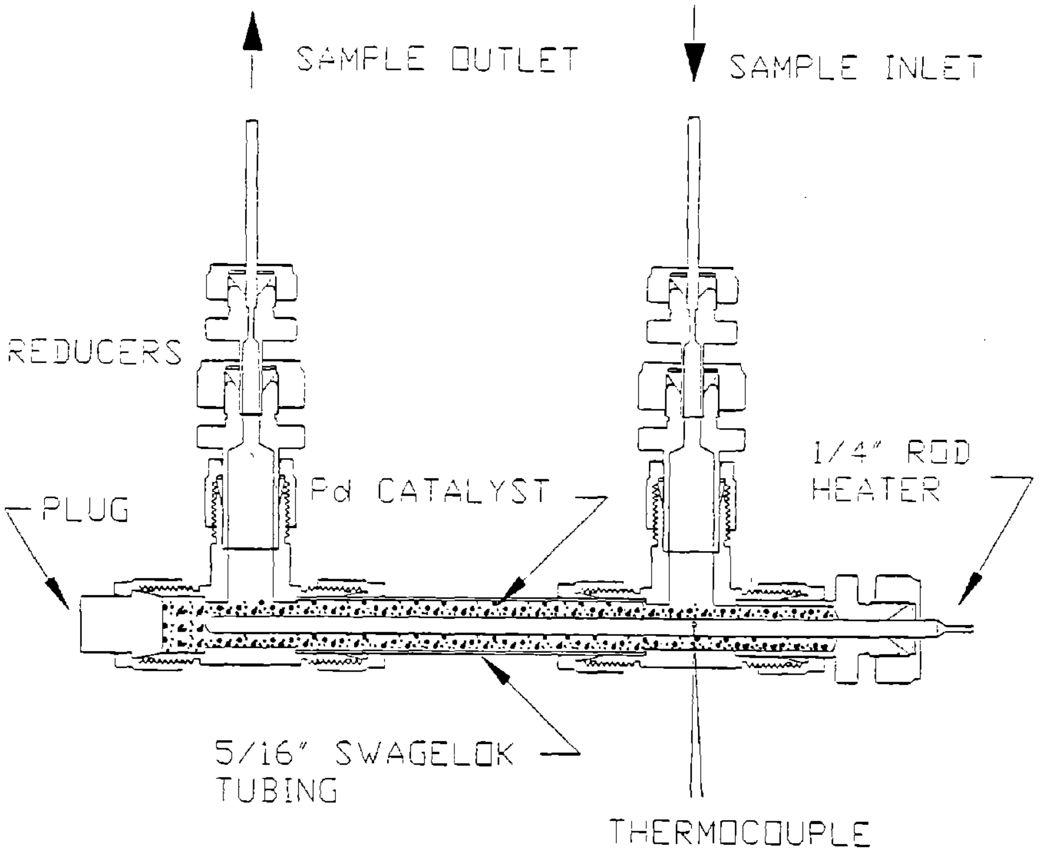


Figure III-19. Design of the Combustibles Trap

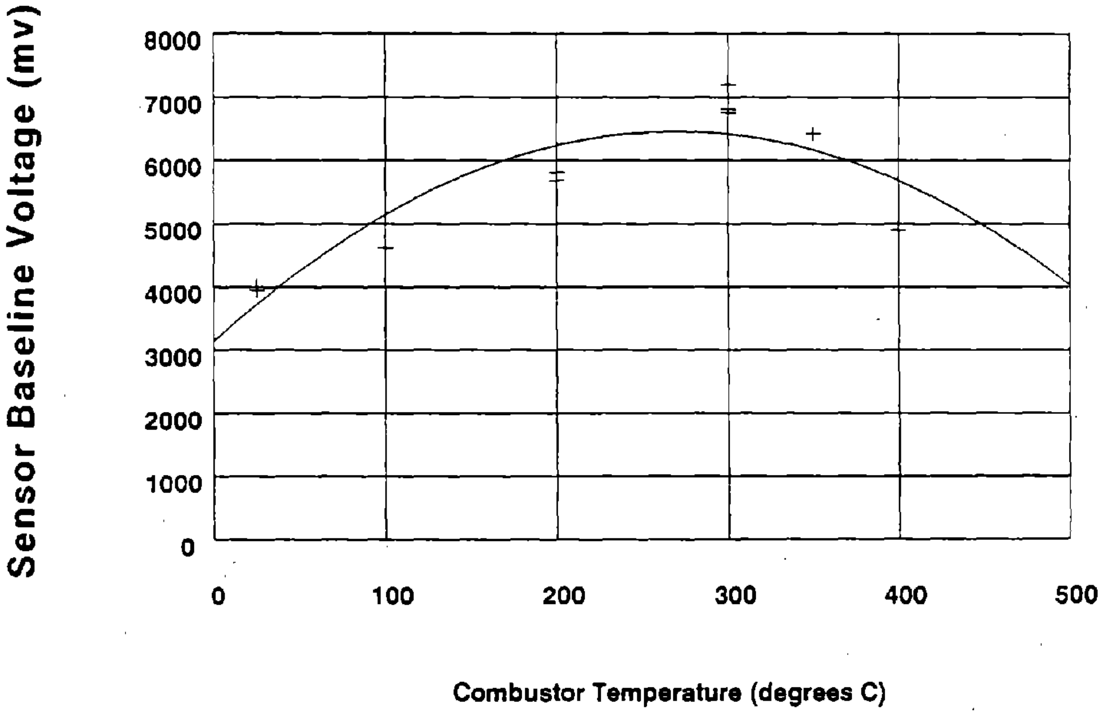


Figure III-20. TGS Baseline Voltage Response to Combustor Temperature

For all compounds except isopropanol and Freon-12, the interferent signal disappeared with the trap in line, regardless of the trap temperature. To what degree combustion had occurred and what percentage of the compounds adsorbed on the catalyst is not known.

There was a revision to the combustibles trap design implemented after testing of the prototype EtO monitor was initiated, due to a failure in the heater rod and the discovery of leaks at several joints in the compression tees. The altered design featured welded seams to reduce the potential for leaks, and is described in greater detail in Task 6.

2. Experiments with the Drying System

The method used for drying the sample air was countercurrent flow in a Nafion dryer (Perma Pure Products, Inc., Toms River, NJ). In this type of dryer (Figure III-21), the sample air flows through a 0.32-cm diameter section of Nafion tubing, which is enclosed in a 0.635-cm diameter Teflon tubing shell, before entering the separation column. A purge gas flows over the outer surface of the Nafion tubing in a direction which is opposite that of the sample airflow (i.e., countercurrent). As wet sample air enters this dryer, a water vapor gradient is established across the Nafion membrane toward the dry purge air. The relative humidity of the sample air decreases as it continues through the dryer, since the water vapor concentration of the purge gas is at a minimum at the point of entrance to the Teflon shell. Once the sample air reaches the TGS, the air has been dried to a constant, low relative humidity. The source of the purge gas may be the TGS exhaust air or a sidestream flow from the pump. The advantage of this drying system is that it does not require either auxiliary gas for drying or desiccant, both of which would require periodic replacement.

Due to the poor sensitivity/response characteristics of the humidity sensor originally obtained for these experiments, it was not possible to evaluate the countercurrent Nafion dryer by measuring the change in relative humidity with the dryer in line. Since the TGS 822 responds very sensitively to changes in water vapor concentration, the TGS itself was used as the humidity sensor. The ambient air relative humidity was monitored with a Vaisala HMI 32 humidity meter.

The problem of removing isopropanol from the air stream was solved after consulting the countercurrent dryer literature. The literature stated that alcohols are also quite permeable in the Nafion membrane, and would be expected to be removed from the air stream in the same manner as water vapor. Ammonia and amines are somewhat permeable in the Nafion material. Subsequent experiments showed that the dryer alone removed almost 100% of the methanol and isopropanol from the air stream. The trap and dryer together provided complete removal of most compounds, as expected. The trap was heated to 330°C in these experiments, and the dryer was heated to 37°C.

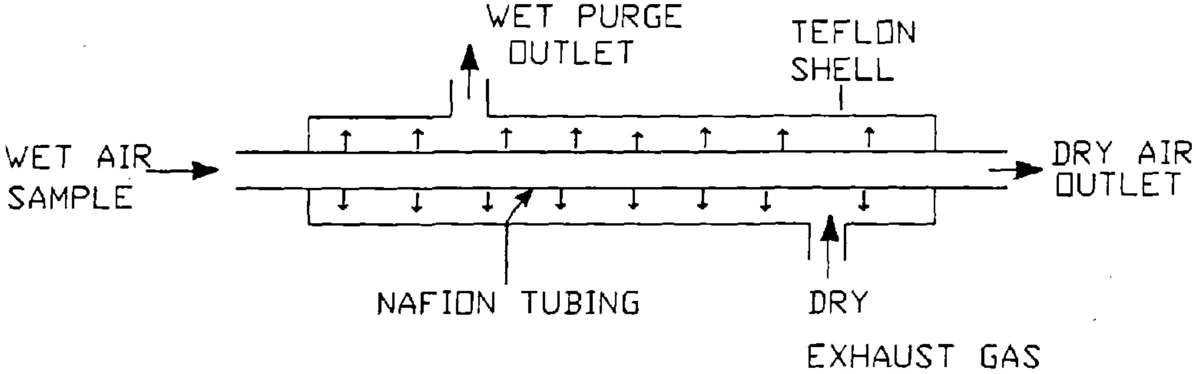


Figure III-21. Schematic of Nafion Dryer Operation

Since Freon-12 elutes so closely to EtO, it is desirable that Freon-12 pass through the trap and dryer so that it is detected as part of the background instead of as a distinct peak. No attempt will be made to remove Freon-12 from the air stream.

Other experiments were conducted to determine the effect of the dryer temperature on the baseline TGS signal. The TGS baseline voltage was measured with both the dryer and trap in line, with the dryer only in line, with the trap only in line, and with neither the dryer nor trap in line. The length of the dryer was three feet. Compressed air flowed through the trap, dryer, 2.5-ft THEED column, and TGS. The relative humidity of the air stream was therefore quite low. The exhaust air from the TGS served as the countercurrent air flow for the dryer. The results of these experiments for three dryer temperatures indicated that there was significant degradation in the sensitivity of the TGS sensor at dryer temperatures above 25°C. The baseline TGS voltage at 37°C dropped to about 2 VDC, so that there was little span remaining in which to detect the presence of EtO in the sample gas stream. This was interpreted as an indication of decreasing dryer efficiency, most likely due to the fact that the partial pressure of water vapor in the outer tubing shell increases with increasing temperature. The vapor pressure gradient across the Nafion, which is the driving force for the water vapor migration, is thus decreased. The dryer will therefore be operated at ambient temperature.

The experimental data also showed the superior baseline voltage obtained using both the trap and dryer. Using the dryer alone gave a much lower baseline signal, and therefore decreased sensitivity to EtO. This is probably due to the fact that the dryer will not remove oxides, halogens, or non-polar hydrocarbons, and these compounds increase the conductivity of the TGS, resulting in a lower baseline signal.

When the compressed air was replaced with a pump, and room air served as the carrier gas, the TGS baseline signal decreased to less than two volts, an unacceptable condition which would result in the inability to achieve the target detection limit of 0.1 ppm EtO. To sufficiently dehumdify room air for use in the monitor, a second countercurrent dryer and a molecular sieve adsorbent were added to the flow system to provide sufficient removal of water vapor. Two one-foot dryers were placed at the pump inlet and outlet, followed by the combustibles trap and molecular sieve adsorbent. Just downstream of the molecular sieve, a portion of the dry carrier air was rerouted to serve as the countercurrent air for the two dryers, while the remainder of the carrier flow went through the THEED column and the TGS at a rate of 20 cm^3/min (Figure III-22).

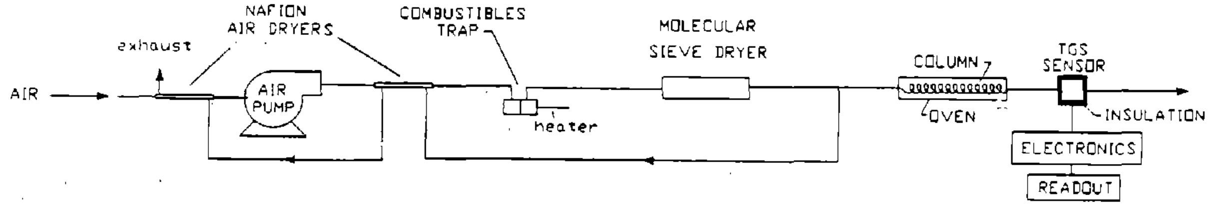


Figure III-22. Flow Schematic for Initial Room Carrier Air Tests

In the original prototype configuration, the TGS exhaust was to be used as the countercurrent air. It was possible that a better baseline signal could be obtained when the downstream side of the TGS was at atmospheric pressure. Also, a higher countercurrent flow rate could be achieved using a sidestream flow of the carrier air before it reached the column. The increase in flow through the system to provide this sidestream offset the benefits of the increase in countercurrent dryer flow.

The flow system configuration shown in Figure II-22 resulted in a steady TGS baseline voltage of 2.4-2.8 volts over a 54-hour period. At the end of this period, the voltage gradually decreased to approximately 0.8 volt as the molecular sieve became saturated and water began to break through. The relative humidity of the room air during this experiment was between 25 and 40%.

In order to increase the time over which the TGS baseline was stable by improving the drying capability of the system, the second one-foot dryer was replaced with a four-foot dryer. This resulted in a higher baseline voltage (3.3 volts) that was maintained over an 8-day sampling period. Breakthrough of water vapor had not occurred at the end of this experimental period, but based on the weight of the molecular sieve measured before and after the sampling period, the adsorbent was 50% depleted at the end of the experiment. The ambient relative humidity was measured as 35%.

In order to maintain continuous drying capability, the flow system configuration would have to include two molecular sieve cartridges, which would alternately provide the final drying stage for the carrier air. While the flow through one cartridge passed through the column, the second cartridge would be heated to dry and regenerate. Solenoid valves would have to be placed after each cartridge to switch the flow direction of the carrier air at regular intervals to provide optimum drying capability and a steady TGS baseline. Due to the complexity and accompanying higher cost of such a flow setup, the flow system for clean carrier air which was originally proposed, consisting of a combustibles trap and Nafion dryer, was installed in the prototype configuration. The results of this testing are given in Section 6.

D. TASK 4: DEVELOPMENT OF A CALIBRATION PROCEDURE

The objective of this task was to determine the most practical and efficient method for calibrating the prototype instrument. It is necessary for a commercial monitoring instrument to undergo simple, rapid and accurate calibration on a regular basis. A review of candidate techniques for a calibration procedure resulted in the recommendation for the use of permeation tubes. Disposable permeation tubes are considered a primary standard because the weight loss of the tubes (containing liquid phase EtO) is an accurate measure of the EtO vapor emitted from the tubes. When a permeation tube is placed inside larger diameter tubing through which clean dilution air flows, a constant mass flux of EtO is passed through the wall of the permeation tube. The concentration of EtO in the dilution gas stream is then an inverse linear function of the dilution flow rate. A range of EtO concentrations may be achieved by changing the flow rate of dilution air over the permeation tube. The permeation rate of EtO from a perm tube is a function only of the temperature at which the tube is held. Thus to maintain a standard, the temperature of the permeation tube must be controlled at the value under which the tube was calibrated by the manufacturer, and that dilution air flow must remain constant.

A commercial, factory-calibrated permeation tube was incorporated in the flow system of the EtO monitor for calibration and testing purposes. The perm tube proved to be a uniform source that was easily installed in the test fixture used in lab experiments. Early tests were performed with a perm tube inserted in a carrier gas tube that was in turn submerged in a constant temperature water bath to maintain a uniform permeation rate in the system. Dilution air flows were checked with a bubble flowmeter, also a primary standard. Later in the prototype instrument testing, a permeation calibration unit, the model 450 Dynacalibrator, was purchased from VICI Metronics.

The model 450 provides separate flow paths for perm tube ventilation and for dilution air streams. The perm tube ventilation and dilution air are mixed at a T on the front panel of the instrument. Two separate dilution air flows are available to the user on the unit; one is a low dilution level flow and the second is a high dilution level. A switch controls the mixing flows, offering STANDBY, ZERO, SPAN1 and SPAN2 settings. The STANDBY mode allows the calibrator to be permanently connected to the instrument under test. At ZERO setting, the flow through the calibrator bypasses the ventilation line from the perm tube chamber. SPAN1 and SPAN2 dilute the ventilation airstream to a low and high level EtO content, respectively. The permeation tube is inserted in a temperature-controlled chamber in the calibrator where the temperature set point accuracy is 0.1°C. The temperature set point must be an integer input to the digital panel potentiometer; the set point must be at least 2°C above ambient to allow for accurate control.

A standard test procedure evolved over the span of testing conducted with the prototype EtO monitor. The instrument cycle was automatically controlled, as described in Section III-E. An additional solenoid valve was wired into the microcontroller, to switch the perm tube flow into and out of the flow circuit of the instrument. Early in the automated testing the overall pattern was to add the perm tube to the flow for seven cycles of the monitor, then switch off the perm tube and flow clean air for seven cycles. Recall that each cycle consists of establishing a flow of clean air over the TGS sensor, injection of a room air sample (that may or may not contain EtO) to the separation column, elution of the EtO from the column through the sensor to determine the EtO concentration, and backflush of the column to purge residual compounds and water vapor that have the potential to foul the sensor. The data was then analyzed by independently averaging the net sensor signals for the two conditions, and subtracting the average "clean" signal for the seven clean cycles from the average "EtO" signal for the seven EtO cycles. The resultant signal strength was used to establish a calibration for the instrument. Calibration data and more details of the process are presented in the discussion for Task 6.

A similar process has been specified as part of the final prototype instrument configuration. A perm tube of known EtO concentration is switched into the flow of the instrument to re-calibrate the sensor several times an hour. This is needed to adjust for the drift in the sensor baseline signal, and for the variance in ambient temperature and humidity conditions, which also affect sensor baseline output.

E. TASK 5: FABRICATION OF THE PROTOTYPE ETO MONITOR

The components tested in the previous tasks and selected for use in the prototype instrument design were incorporated into a self-contained instrument package. The prototype instrument used the TGS model 812 gas sensor, the THEED separation column, the combustibles trap followed by a Nafion dryer, and a pump to move air through the system. The prototype device included a backflush mode as part of the operating cycle in order to remove gases from the separation column, the presence of which could reduce the sensitivity of the TGS sensor to EtO.

The operating cycle of the prototype was controlled by a programmable microprocessor that communicated with the user via a vacuum fluorescent display and an RS232 serial communications port to a personal computer. All electronics for the control and communication functions were designed and assembled as part of the fabrication of the prototype. These included audio alarms and messages sent to the display to indicate that the device had measured EtO concentrations which exceeded regulatory limits. The programmability of the microprocessor control allowed the operating cycle of the prototype to be easily modified, and the sensor output to be recorded in memory for later download to a personal computer. The components were small and lightweight enough to be placed directly in the instrument frame. The exhaust flow from the system was monitored using a small adjustable rotameter located on the front panel.

The prototype design focused on continuous operation with the ability to produce a permanent record of eight-hour EtO time-weighted averages and fifteen-minute EtO short-term exposure levels, and to generate alarms when the statutory limits are exceeded. The alarm system consisted of 1) a flashing warning message and intermittent "beep" audio tone when the ambient EtO concentration exceeded the 0.5 ppm action level; and 2) a red light and constant audio alarm which activated when the ambient EtO concentration exceeded the 5 ppm STEL. Both alarm levels were actuated in the microcontroller program that directed overall operation of the device.

In addition to the microcontroller, the computer-based data acquisition system first used in component testing was again employed to monitor prototype operation during tests with the permeation tube EtO source. The system was programmed to monitor eight data items:

- The sensor baseline voltage that is fixed at the start of the elution of EtO from the separation column for each cycle by a sample and hold amplifier;
- The sensor signal voltage, which is obtained by subtracting the sample-and-hold baseline voltage from the sensor output during elution of EtO from the separation column. The signal voltage was sampled and stored once per second;
- The temperature of the room air used as the carrier gas in the instrument;
- The operating temperature of the semiconductor detector element in the TGS sensor;
- The relative humidity of the room air, measured with a solid-state sensor;
- The air temperature of the chamber that houses the separation column;
- The temperature of the catalytic combustor in the instrument, measured by a thermocouple in contact with the heater rod in the combustor; and
- The start of injection of a sample into the separation column. This is used as a marker by which to begin timing the delay to the point where the EtO begins to elute from the column, when the sample and hold amp is triggered, and the acquisition of sensor signal values during elution of EtO from the separation column.

The data was logged to a file for transfer to a spreadsheet program for analysis and preparation of graphic outputs. All data files were archived to floppy diskettes so that the data could be reviewed and reduced by alternative methods. This permitted exploration of the impact on detector signal voltage of parameters such as the time interval between the start of elution of the EtO onto the detector and the point at which the output signal is sampled for calculation of the EtO concentration in the sample airflow.

1. Signal Processing Electronics

There are two types of sensor signals that are monitored by the EtO instrument's microprocessor control unit. The first is a type K thermocouple, and the second is the TGS sensor that acts as the EtO detector element. The thermocouples must be referenced to an ice point, linearized and amplified to the 0-5 VDC full scale input needed by the microcontroller. Similarly, the TGS sensor signal must be processed prior to being input to the microcontroller.

The thermocouple ice point reference, linearization and scaling is done on a single integrated circuit (IC) chip. The device takes the millivolt-level thermocouple signal as input, and produces a linear voltage output of 10 mv per degree Centigrade. This linear voltage is connected to a single-ended analog-to-digital convertor input on the microprocessor for monitoring the temperature for the catalytic combustor and the separation column heater in the system. Control of the heaters is maintained in another circuit on the IC chip. The temperature control point is set with a potentiometer that is wired to the IC.

The TGS sensor signal conditioning electronics are more sophisticated. Figure III-23 presents a schematic of the elements of the circuit. An amplifier converts the resistance output of the TGS sensor to a voltage, which is then immediately inverted, since the input to the microprocessor must be in the range of zero to five volts DC. The inverted signal is split, where one leg is input to a sample-and-hold amplifier, and the other is connected to a difference amplifier where the output from the sample-and-hold amp is subtracted to obtain a signal that is equal to the change in sensor output at the elution of EtO from the separation column. This signal is then input to the microprocessor analog-to-digital convertor circuit to record and scale the TGS sensor measurement of EtO concentration. The sample-and-hold amp trigger is an output from the microprocessor that is sent at the completion of the sample injection.

2. Microcontroller Operation

The control mechanism for the EtO monitor is a Blue Earth Research (BEaR) Micro 440 programmable controller. This unit has eight analog input channels, twelve digital input/output lines, two RS 232 serial communications ports, a real time clock, and 32kB of battery-backed (nonvolatile) memory. A block diagram of the Micro 440 is presented in Figure III-25. Most of these features are used in the instrument. The TGS sensor output and several thermocouples are attached to the analog input channels. The display is wired to one of the RS-232 communications ports; user selections from menus are indicated via digital inputs from buttons on the front panel. Digital outputs are used to switch the several valves employed in the flow path of the instrument. The microcontroller is supplied complete with an on-board interpreter BASIC programming language. A block diagram of the microcontroller is presented in Figure III-24.

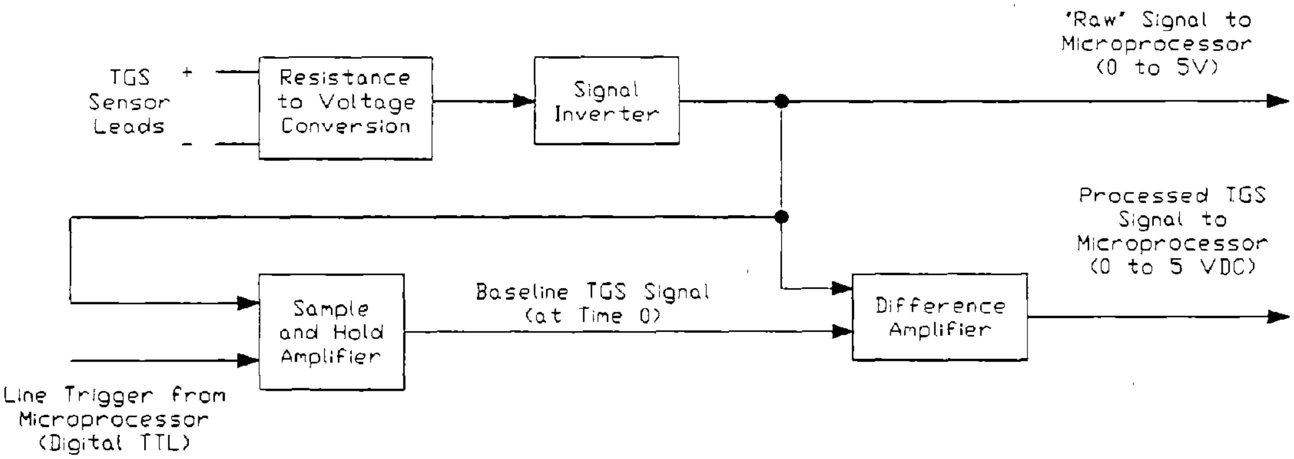


Figure III-23. TGS Signal Processing Electronics

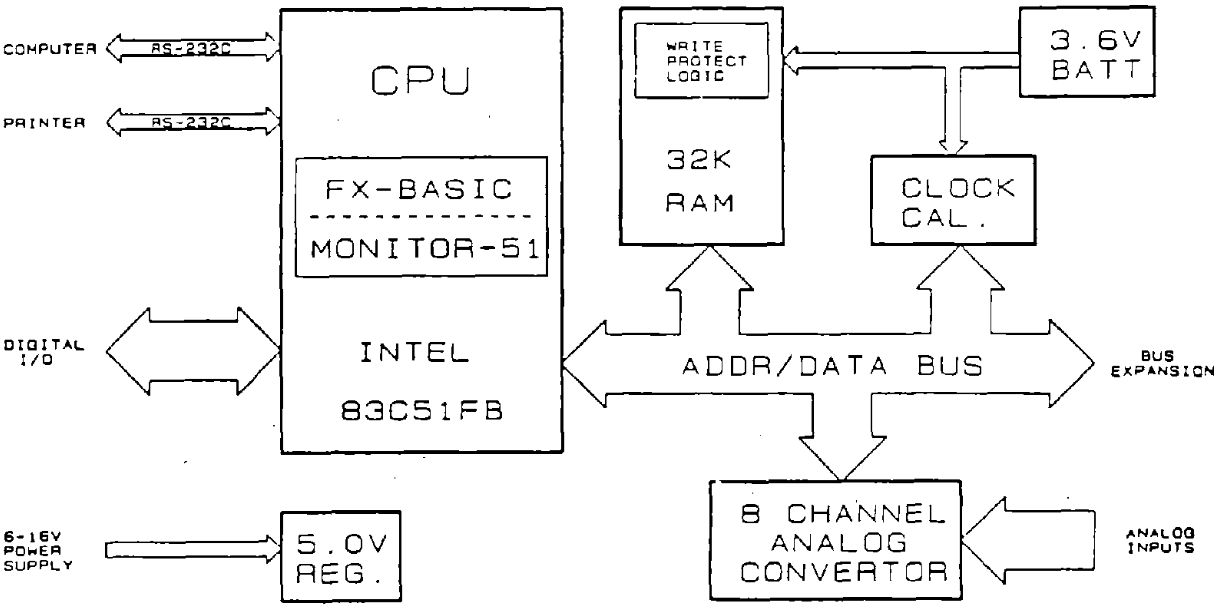


Figure III-24. Block Diagram of the Micro 440 Microcontroller

The Micro 440 is programmed to perform a wide range of functions in the operation of the EtO monitor:

- It actuates the flow control valves to direct the flows of carrier and sample air in the instrument;
- It monitors the the TGS sensor output and is programmed with the calibration equation to convert the processed TGS signal into EtO concentration levels;
- It drives a vacuum fluorescent display to show updated EtO concentrations for each sample;
- It calculates and stores fifteen minute and eight hour EtO concentration averages, and prints them on the vacuum fluorescent display;
- It downloads stored data to a personal computer for permanent archival storage;
- Finally, it constantly reviews system parameters for correct operating range. If out-of-range conditions are detected, an error message is sent to the display to indicate that repairs are needed.

The microcontroller is programmed in BASIC, which allows easy modification of the program to change parameters such as the cycle time for the sequence of flow configurations, and the selection of intervals after sample injection when data is taken to define the baseline and sample signal levels of the TGS sensor. There is a serial port on the microcontroller that allows programming and monitoring of operation via a personal computer that is running appropriate software.

3. Instrument Operating Cycle

Four flow configurations comprise the operating cycle of the instrument. The configurations are controlled by a series of solenoid valves in the instrument; the valves are operated via the digital outputs of the microcontroller. The configurations are defined in reference to the air flow at the entrance to the separation column, and are described below.

- Configuration 1: Ambient air flows through the combustibles trap and Nafion dryer to provide carrier (clean) air to the TGS sensor to establish instrument baseline signal; at the same time, a sample of room air is drawn through the sample loop to charge it in preparation for injection into the separation column.

- Configuration 2: Flow through the instrument is switched to inject the sample of room air from the sample loop into the separation column. This is done by rerouting the clean air flow to the upstream side of the sample loop; the clean air flow through the sample loop then carries the sample to the separation column.
- Configuration 3: Revert to carrier (clean) air downstream of the sample loop to move the sample through the separation column until any EtO present is detected;
- Configuration 4: Reverse carrier air flow through the separation column to backflush to remove components from the column.

In Configuration 1 (Figure III-25), ambient air is drawn into the flow system by the pump. The air passes through the combustibles trap, where all compounds except Freon-12 are converted to CO_2 and H_2O at 270°C. The carrier air then passes through a Nafion countercurrent dryer. The clean, dry carrier air passes through the 2.5-ft THEED column (temperature = 50°C) at a flow rate of about 20 cm^3/min before it flows past the TGS 812 sensor, operated at a constant heater voltage of 5.5 VDC. Simultaneously, suction from the pump draws ambient air through a sample loop of approximately 5 ml volume. The baseline TGS signal is measured just prior to sample injection. Flow in this configuration is maintained for 40 seconds.

The ambient air in the sample loop is swept to the column for 5 seconds by a flow of carrier air in configuration 2 of the operating cycle. Valve positions and the flow path for this configuration are illustrated in Figure III-26.

Configuration 3 (Figure III-27) is identical to the flow path of configuration 1 as clean carrier air sweeps the sample through the column. This flow lasts 13 seconds, the time required for the EtO signal to peak. The baseline voltage of the TGS sensor is subtracted from the sensor output via the sample-and-hold circuit described earlier.

Just after the EtO peak reaches a maximum, the flow is switched to configuration 4 (Figure III-28). In this mode the column is backflushed to remove residual water and other contaminants before they reach the TGS. The duration of the backflush cycle is 90 seconds. The indicated times for the several flow configurations are for a separation column length of two feet and a gas flowrate of 20 cc/min.

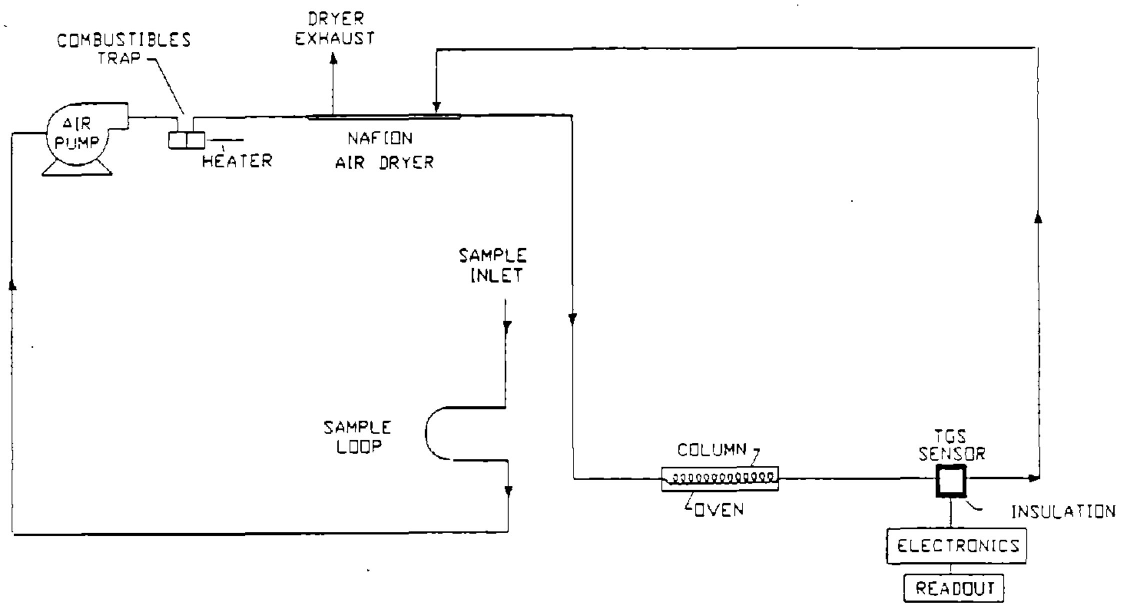


Figure III-25. Schematic for Flow Configuration 1

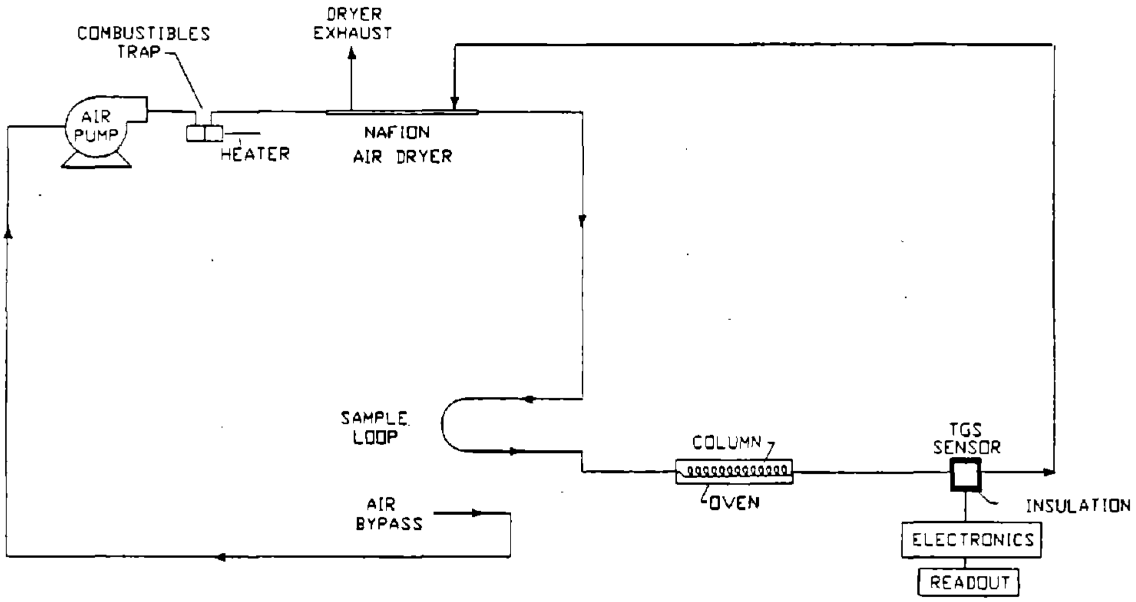


Figure III-26. Schematic for Flow Configuration 2

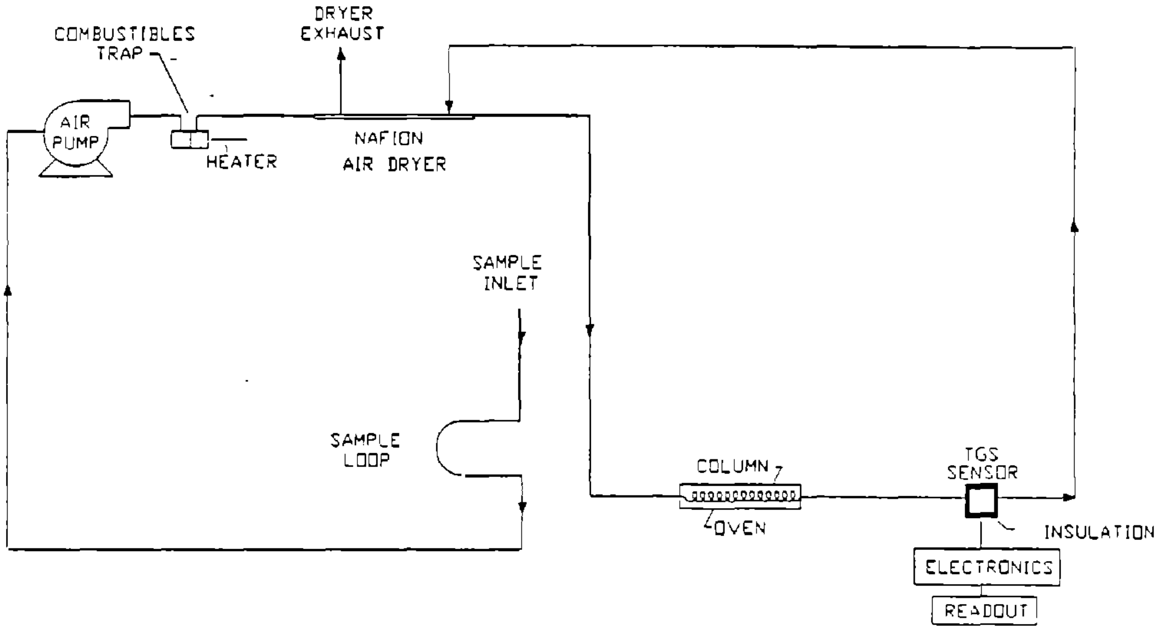


Figure III-27. Schematic for Flow Configuration 3

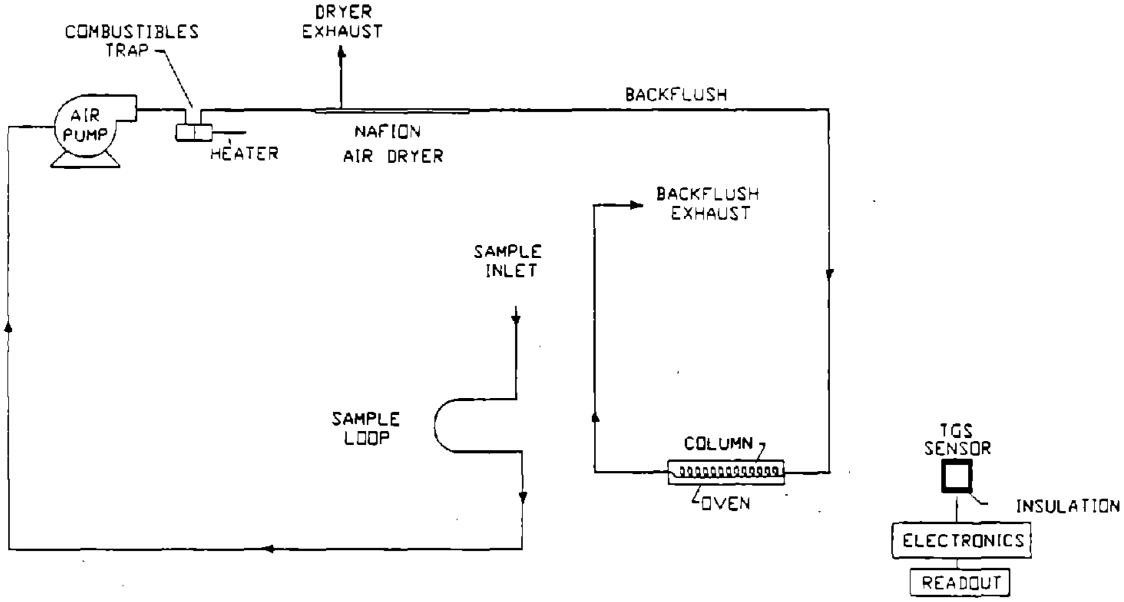


Figure III-28. Schematic for Flow Configuration 4

The instrument calibration cycle is activated on demand, via a switch on the front panel of the instrument. There is a subroutine in the microcontroller software that controls the calibration process. The EtO permeation device, which generates 5 ppm EtO at a flow rate of 20 cm^3/min, is attached to the sample air inlet to the sample loop. In addition to the permeation source measurement, a zero EtO concentration is obtained by taking a reading during a clean air cycle. These two measurements thus provide a two-point calibration curve consisting of a zero and fixed known concentration, from which a linear calibration can be constructed (Section 2).

The complete prototype system is shown in Figure III-29. This instrument design is only slightly different than originally proposed. In the design presented in the Phase II proposal, the ambient air sample passed through the pump to the column, bypassing the combustibles trap and dryer. As the prototype was being assembled and tested in this task, water droplets were observed between the pump and combustibles trap. This observation was not surprising, due to the fact that the compressor raises the partial pressure of water vapor in the sample, and saturation can occur at room temperature; that is, water will exist in a liquid state at a pressure of 20 psig and temperature of 25°C. The pressure would have to be lowered to about 2 psig at a temperature of 40°C, or the temperature of the system raised to 120°C, in order to keep the water vapor partial pressure below saturation.

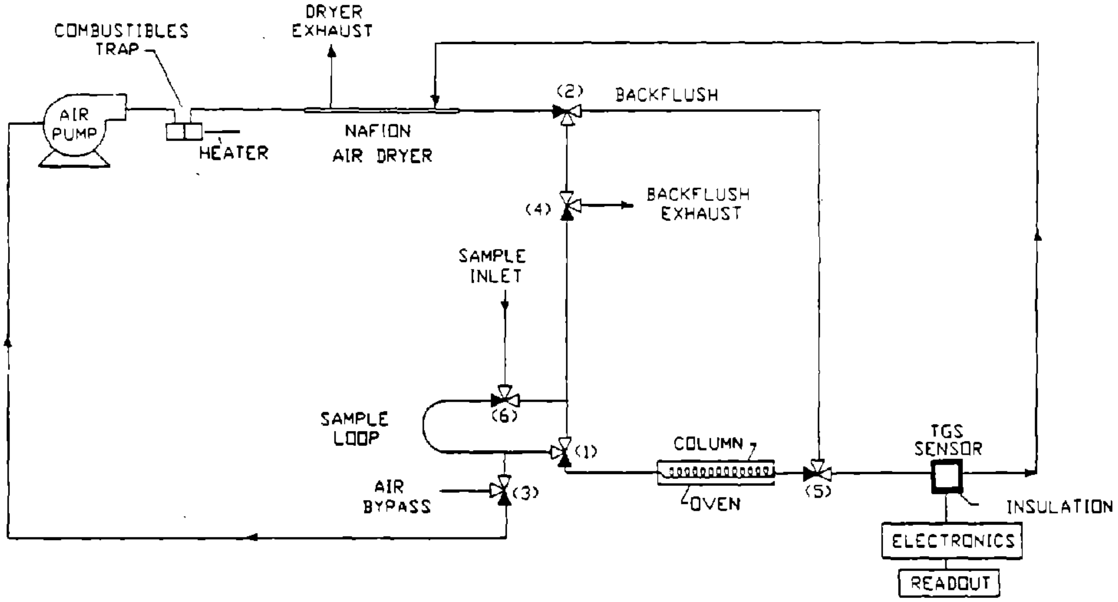


Figure II-29. Flow Schematic for Prototype EtO Monitor

This was a problem with the original flow configuration, as the system pressure could not be lowered, unless the pump was placed downstream of the detector. This would require an extremely leak-tight system, a difficult task to accomplish. A heated pump, on the other hand, would destroy EtO. In the present prototype design, the sample air stream is injected without passing through the pump, avoiding potential loss of EtO to the pump. The Nafion dryer is used to remove water vapor from the carrier gas flow after it passes through the combustibles trap.

F. TASK 6: LABORATORY EVALUATION OF THE PROTOTYPE

Testing of the prototype EtO monitor was performed as the instrument was being assembled and experiments on the system components were being completed. The EtO permeation tube calibration source acquired in Task 4 was used as the EtO standard for the tests.

OSHA requires that an EtO monitoring device be accurate to within ±25% for 1 ppm EtO and to within ±35% for 0.5 ppm EtO, at a confidence level of 95% (Dept. of Labor, 1984). In the past, the accuracy of a new instrument has been determined by comparing EtO quantitation using the new instrument with that of an accepted instrument for EtO measurement, such as a gas chromatograph with flame ionization detection. However, there is currently no validation procedure for a real-time monitor. Therefore, laboratory tests were performed on the prototype EtO monitor using the permeation calibrator to generate known concentrations of EtO in air.

1. Experiments Performed Using Compressed Air; Dryer and Combustor Bypassed

Several experiments that were performed in Task 2 were repeated in this task. Compressed air was used as the carrier gas in these tests, and the dryer and combustor were removed from the carrier gas flow path. The experiments investigated operation of the TGS sensor over a range of heater voltages (and corresponding sensor temperatures), variation of the temperature of the separation column, and variation of the flow rate to maximize the best EtO signal and signal-to-noise ratio of the sensor.

As the sensor voltage was adjusted from 4.9 VDC to 5.5 VDC (corresponding temperatures of 325 to 375°C), an increase in the sensor signal for a 6 ppm EtO standard was observed. This agrees with the first set of data obtained in Task 2, but not with the second data set, which showed a leveling-off of the EtO signal with increasing sensor temperature (Figure III-12). The discrepancy may be due to different TGS baseline voltages for the Figure III-12 data set, and the fact that the maximum TGS temperature tested in Task 2 was 338°C. For this experiment, the TGS baseline was zeroed at each temperature tested. As data from previous tasks show, the baseline signal affects the EtO peak magnitude. The operating voltage of the TGS was changed to 5.5 VDC (nominal 375°C operating temperature), although the lifetime of the sensor at that temperture will probably be shorter than at 5 VDC (338°C).

When the column temperature was investigated over the range of 30 to 70°C, an optimum signal for 6 ppm EtO was observed at 50°C. This contradicts earlier data. Again, the differences may be due to different baseline voltages in the earlier data sets. The operating column temperature in the prototype was then set at 50°C for all additional testing.

The carrier flow rate was adjusted to 10, 20, and 40 cm^3/min as 12 ppm EtO was sampled by the instrument. Although 40 cm^3/min resulted in the fastest elution of EtO, the largest EtO signal was produced at a flow of 20 cm^3/min. The 20 cm^3/min flow was therefore used in all subsequent experiments with the prototype instrument.

Another test was run to investigate the impact on sensor performance of humidity of the air in the ambient sample. The instrument was configured to operate on compressed air, with a sample injected at the designated time in the flow cycle. The sample contained humidified room air doped with a fixed concentration of EtO from a permeation tube; the humidity was varied by passing the room air through a water bath maintained at a temperature to saturate the gas stream for the target humidity. Measured voltages from the TGS sensor are plotted in Figure III-30. The humidity in the small sample (about 2 ml in volume) is the only difference in the data points that are shown. Two voltages are presented: the "baseline", or reference voltage that is the minimum voltage from the detector after the injection is complete and before any EtO begins to elute from the column; and the peak voltage, which is the difference between the maximum sensor voltage and the reference voltage.

The baseline voltage is seen to decrease with increasing humidity. The effect of this decreased baseline on the detected EtO peak voltage is apparent on the other curve: the peak signal decreases somewhat proportionally. The change in signal level implies that the instrument should be operated in humidities that are as low as possible. In any case, the quality of the measurements will be increased in an environment where the humidity is fairly constant. Certainly, the humidity variation in sensor response can be accommodated in the calibration of the instrument, when periodic calibrations are carried out on site at the user's installation.

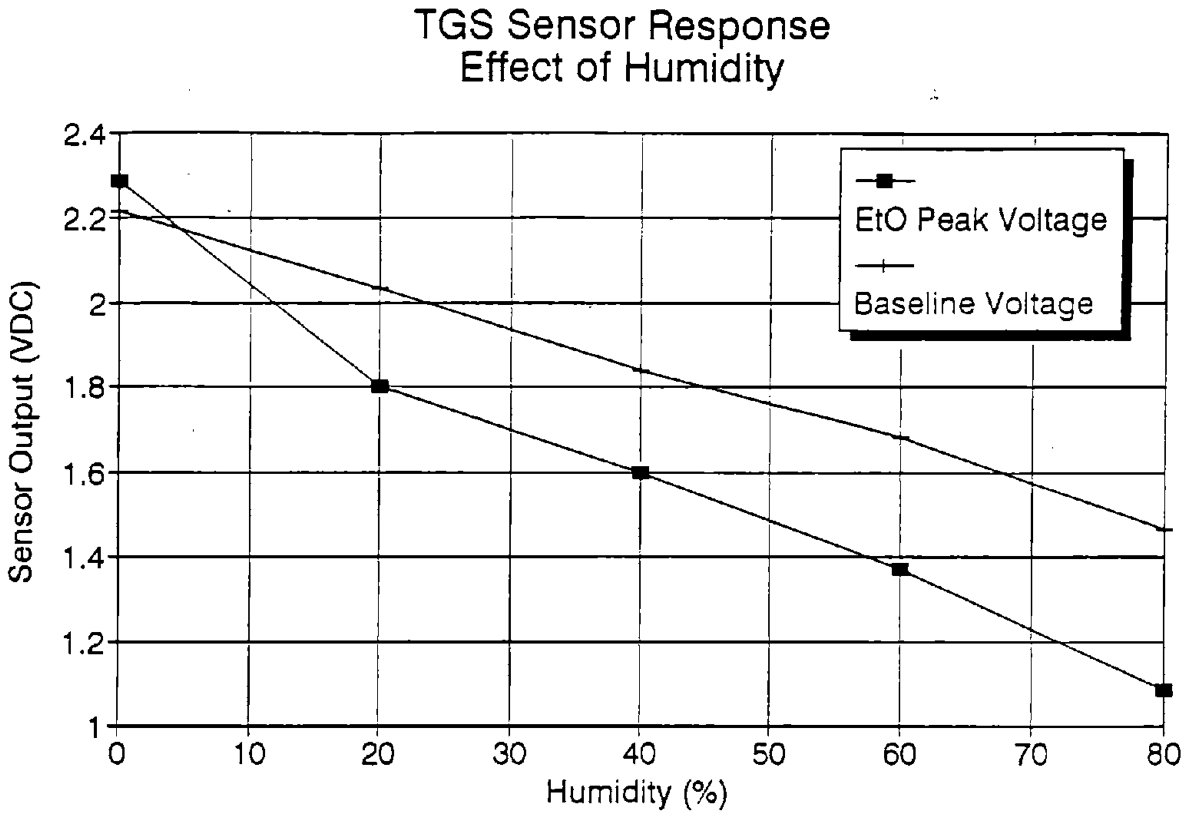


Figure III-30. Effect of Humidity on TGS Sensor Response

2. Experiments Performed with Complete Prototype Instrument

The prototype EtO monitor was tested to determine its response to interferent species. Tests were conducted separately with methanol and ethanol at concentrations of 1000 ppm. Typical TGS sensor signal output time histories are presented in Figure III-31. There is a small signal from the clean air injection, probably due to the effect of the humidity in the ambient air sample. The EtO injection at 2 ppm creates a definite response in the TGS sensor; the two interferents each create a dramatic shift in the sensor signal. The interferents are not of concern because of the time at which they elute from the separation column. As is quickly seen, the EtO peak is reached about the time that the methanol and ethanol begin to elute from the column. Thus in typical operation, the instrument would be switched to the backflush configuration about the time that the interferents would begin to contact the TGS sensor, so that no contamination of the sensor with interferents would ever occur.

The Figure also illustrates typical timing for the used for the calculation of output signal from the sensor during EtO elution from the separation column. Since the separation column is very repeatable in its elution of component gases, the times at which the sensor output is read for each injection can be preprogrammed, once the separation column has been characterized. The TGS sensor output in the prototype instrument was sampled every second, so that the output waveform could be defined, and the sample times selected to maximize the signal used to calculate the EtO concentration in the ambient air. The "baseline" or reference voltage is taken at time T_0 as shown in the Figure, and a second voltage is measured at time T_1, near the elution peak. The sensor signal used to determine EtO concentration is the difference between the signal strengths at times T_1 and T_0.

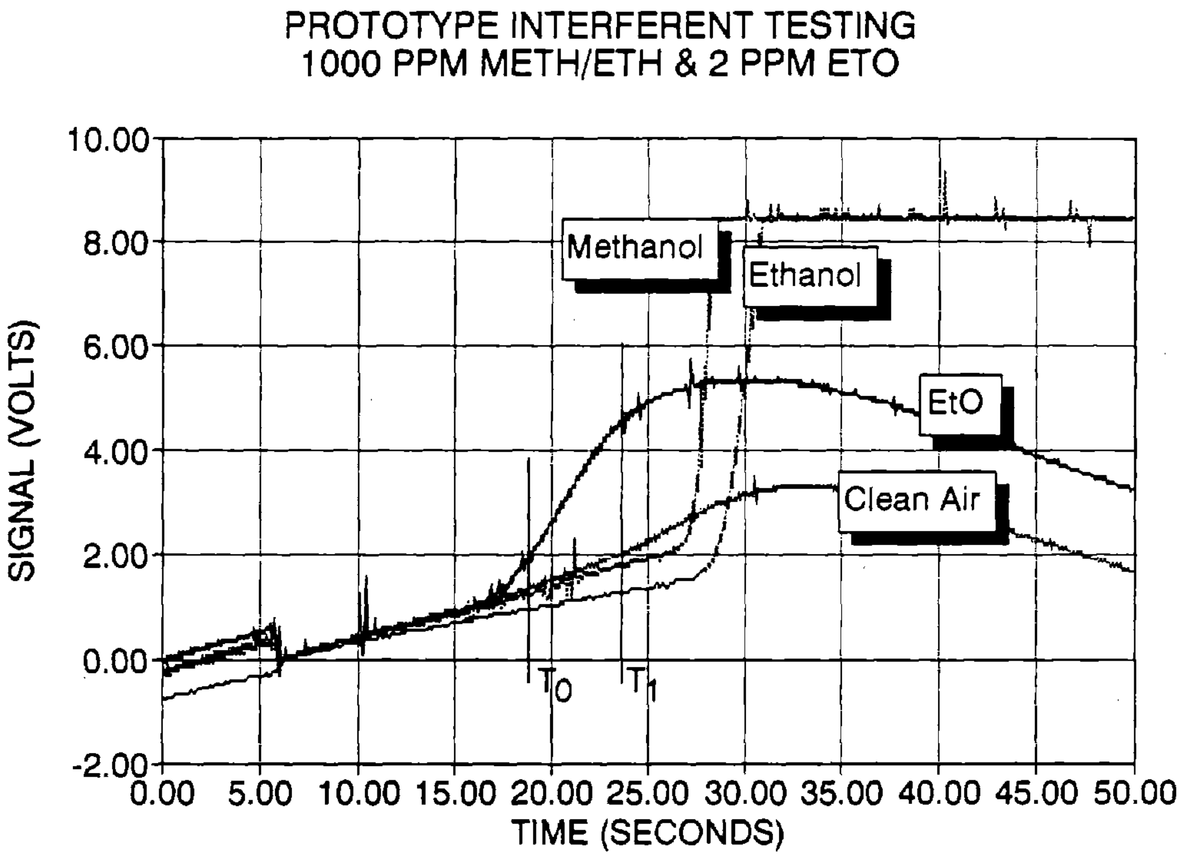


Figure III-31. Chromatograms Showing Interferent Elution from Column in Prototype EtO Detector

The prototype has demonstrated good resolution of EtO from all interferences except ammonia. As stated in Section 5, EtO elutes at 27 seconds. Freon-12 and acetone elute at approximately 70 seconds and 80 seconds, respectively. As observed in Task 2 experiments, ammonia eluted as a broad peak beginning at about 12 seconds into the run.

Operating the TGS at 375°C results in faster recovery of the sensor following exposure to ammonia than operating at lower temperatures, as in Task 2 experiments.

Additional tests of the complete prototype instrument were dedicated to refinements in the program of the microcontroller that operated the instrument. Elements that were investigated included the timing for the switching of valves that controlled the flow configurations in the operating cycle, timing of data samples from the TGS sensor, menus and program control communications via the serial display, and "bulletproofing" of the program.

The importance of timing of the valve switching is seen in Figure III-31 (above), where the backflush must be initiated before the interferents start to elute. In addition, the backflush must be long enough to assure that interferents are removed from the column before the succeeding air sample is injected into the separation column. Thus the cycle timing must be readjusted if there is a change in the length or type of separation column used in the instrument.

The data sampling times were also investigated. The objective of this series of experiments was to identify the sample times that provided the greatest signal-to-noise ratio (S/N) for the instrument. This is important because the lower limit of detection of the sensor is directly related to the level of noise that is measured in the signal. The "signal" here is calculated as the difference in the sensor output near the start and peak of the sensor output when exposed to clean air. In fact, the noise on the EtO curve just as the EtO begins to elute from the column is seen in Figure III-31. Since data was available in one-second sample intervals, different interval combinations could be evaluated to identify the sample times that resulted in the maximum S/N.

The prototype instrument also provided an opportunity to tinker with the user interface, that is the mechanism by which a user interacts with the instrument. Provision was made in the microprocessor programming for the user to switch between "calibration" and "operating" mode in the the instrument, to set date and time for the internal clock, and to initiate a data download via a serial communications port to a personal computer or printer. The initial menu scheme was found to be somewhat clumsy, and was revised to facilitate use by persons not familiar with computers.

Finally, the microcontroller was found to occasionally "hang", or to become inoperative when subjected to certain sample and/or sensor output conditions. There is a feature in the microprocessor that is called a watchdog timer; when enabled, the watchdog timer keeps track of microprocessor operation, and if there is no activity for a user-specified time period, the program is reset, or restarted at the beginning. This function allows the microprocessor to "fix" itself when an upset condition is encountered. The watchdog timer feature was enabled for the EtO control program, and eliminated the problem with random system "hangs".

G. TASK 7: FIELD EVALUATION OF PROTOTYPE

To complement the laboratory testing, it was initially proposed that the instrument would be tested at several hospital sterilization facilities in the Denver metropolitan area. In fact, the director of Central Processing at Porter Memorial Hospital in Denver had been contacted and had expressed interest in testing the ADA EtO monitor in her sterilization area. However, due to possible liability issues, it was decided that testing in a laboratory environment would allow the prototype instrument to be evaluated over a carefully controlled range of EtO exposure levels without risk to hospital personnel.

Testing was conducted over a nine week period to determine the long-term performance of the prototype instrument. The prototype instrument was set to operate under its microprocessor control, with the sensor output also connected to a data acquisition board in a personal computer. The data system then logged sensor output voltages on one second intervals during the elution phase of the flow cycle of the instrument. Data was downloaded daily, and analyzed to establish a statistical data file with which the overall performance of the prototype could be evaluated. The objectives of this test sequence were threefold: to demonstrate the long-term, unattended operation of the instrument; to gather sufficient data to generate a calibration curve; and to confirm that the instrument could consistently detect EtO levels of 0.2 ppm.

Sensor Output Signal

In order to calibrate the instrument and to evaluate the signal-to-noise ratio, a standard methodology was developed for the determination of the output signal from the solid-state sensor that detected the presence of EtO. As described earlier, the voltage output from the sensor was processed via an electronic circuit to generate a voltage signal that was monitored by the microcontroller. The "signal" was determined as the difference in this output voltage at two different times during elution from the separation column. The low voltage point was taken early in the elution, just as the sensor output signal began to rise above its baseline level. The second voltage point was sampled a few seconds later, as the sensor output neared its peak level.

The sensor output was sampled once every second after the initiation of injection into the separation column, until the backflush of the column was initiated in the control program. In order to maximize the signal magnitude and resolution, an analysis program was run on the data. The program calculated signal strengths for a range of time differences between the initial (early) sensor voltage and the second (rising) voltage. This difference was then also computed for conditions with no EtO in the flow; that is, for a "clean air" case at the same time sample points. Since there was no EtO in the "clean air" case, that signal represents the noise, or inherent variability in the sensor signal.

The EtO signal was divided by the "clean air" signal to obtain a signal-to-noise ratio (S/N) for the instrument. The S/N was calculated for different pairs of sample points (different time intervals between initial and rising voltages, and different start times for the voltage sampling) over several hours of instrument operation. The maximum S/N ratio over the test period was then found from among the calculated S/N ratios for the timing pairs examined, and that timing (start time and time interval between samples) was used in the calculation of signal levels for all subsequent testing in the long term performance evaluation.

Test Results

The long term testing was conducted for approximately six weeks in a configuration where the separation column was 0.6 m (2 ft) in length, and two additional weeks in a configuration with a 1.8 m (6 ft) column. The column was changed when an unknown interferent was identified as elutriating at about the same time as the EtO, which was seen as a large variation in the EtO signal at a fixed EtO concentration. Minor changes were made in the instrument configuration during the testing period, including some changes in the plumbing and "fine tuning" of the programming for the microcontroller that operated the unit. The testing was ended when a digital output in the microcontroller that operated one of the flow control valves in the instrument failed.

A summary of results from the long term testing is presented in Figures III-32 and III-33. The calibration data is shown in Figure III-32 for both the 2 ft and 6 ft separation columns. It is quickly noted that the signal strengths are much greater for the shorter column, but that there is also more scatter to the data. The decreased signal with column length is a logical result of the increased transit time and the fact that the elution is spread over a greater time when the column is lengthened. The scatter in the 2 ft data is attributed to a suspected interferent that was eluting at the same time from the 2 ft column as the EtO. Indeed, this was a primary driver tc the installation of a 6 ft column.

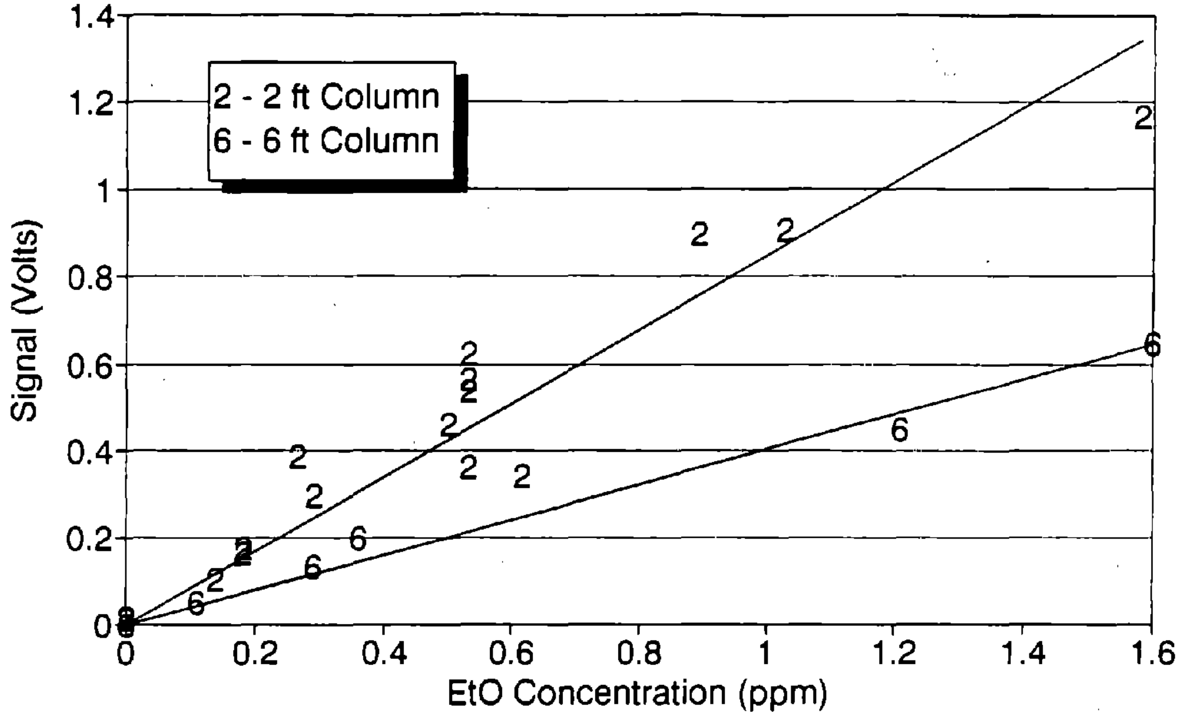


Figure III-32. Long-Term Prototype Test Calibration Results

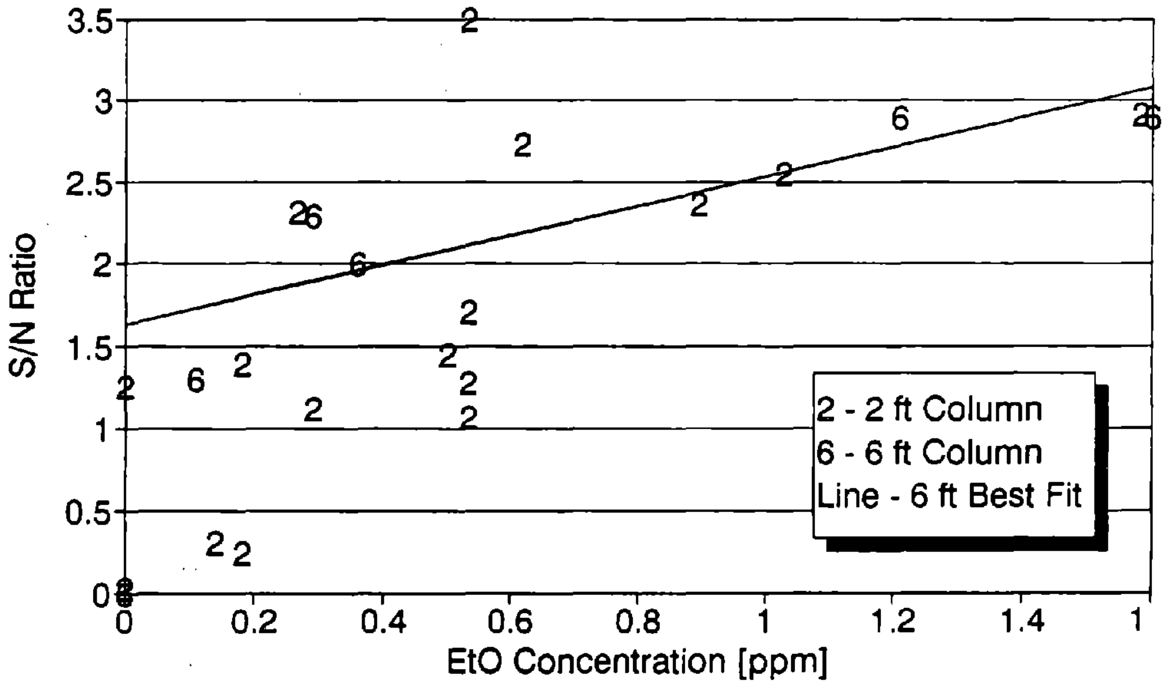


Figure III-33. Signal-to-Noise Ratios for Long Term Testing of Prototype EtO Monitor

The value of the 6 ft column is better illustrated in Figure III-33, where the signal-to-noise ratio is plotted as a function of EtO concentration. The scatter in the 2 ft column data is particularly disturbing at concentrations below 0.5 ppm, where most of the data shows a S/N of less than 1.5; at concentrations below 0.2 ppm, there are numerous data points with a S/N ratio of less than one, which indicates that the presence of EtO in the sample gas stream could not be definitively detected.

The 6 ft column, on the other hand, shows much less scatter and generally higher S/N levels. The line of best fit indicates a S/N of over 1.5 at the target lower limit of detection of 0.1 ppm, and there is a data point at that concentration with a measured S/N of 1.3. The performance of the longer column is thus confirmed, and the 6 ft column was selected for the final configuration.

Near the end of the long-term evaluation tests in the lab a new flow cycle was programmed for the instrument. In the modified cycle, the injection and carrier sweep configurations (2 and 3 in the Task 5 discussion) were combined. This was possible because the fixed volume of the sample loop limited the quantity of sample that was injected into the separation column. The clean gas flow that carried the sample into the separation column continued to flow through the now-purged sample loop. By eliminating the switch to remove the sample loop from the flow path, a pressure spike that was generated in the switching process was deleted from the flow. This spike sometimes affected the output of the TGS sensor as it was transmitted through the separation column in the gas flow.

H. TASK 8: FINAL INSTRUMENT DESIGN

The operating principle and basic design of the prototype EtO monitor were validated in the Phase II testing discussed previously. Extended testing of the prototype instrument in the lab presented the opportunity to gain insight into the routine operation of the unit, and suggested design modifications that would simplify the design and improve the reliability of the hardware. In particular, two alternate flow schemes were developed that reduced the number of valves needed and simplified the flow paths in the instrument. Based on the results of the laboratory component and system studies, minor modifications to the prototype design were proposed in order to improve the performance and lower the cost of a production instrument.

The prototype EtO monitor hardware is shown in the photos of Figures III-34 and III-35. The container is approximately 23 cm wide by 20 cm high by 41 cm long, and operates on 110 VAC. In the front view the display is visible, as are several calibration switches that control the menu-driven user interface. On the back there is a connector to a serial port that permits communication between the internal microprocessor and a personal computer. This port can also be connected to a printer for the preparation of hard-copy log reports of instrument measurements. In Figure III-35 the interior of the instrument is seen. The solenoid valves are mounted in a row at the top of the unit, and the tubing that connects the flow paths is also seen. The signal conditioning and control electronics are housed in two secondary containers mounted at the left side of the housing. The internal box on the right side is a small oven that houses the separation column, temperature controller and heater relay. The pump that provides the flow through the instrument is located just above the fan grating seen in the back cover in the foreground. The overall layout is very compact, with easy access for maintenance. It is believed that the production instrument could be easily housed in a container of this size.

The only significant change in the design of the final instrument from that of the prototype shown in the photos is in the layout of the flow path. The design has been optimized to reduce the number of valves required for the several flow configurations in the cycle of operation. Fewer valves in turn means fewer connections, which are potential leak points, and fewer parts, which impacts component and assembly costs. A permanent calibration permeation tube has also been added to the flow path. The cycle itself has been simplified, with only three configurations: forward flow/sample acquisition, sample injection, and backflush.

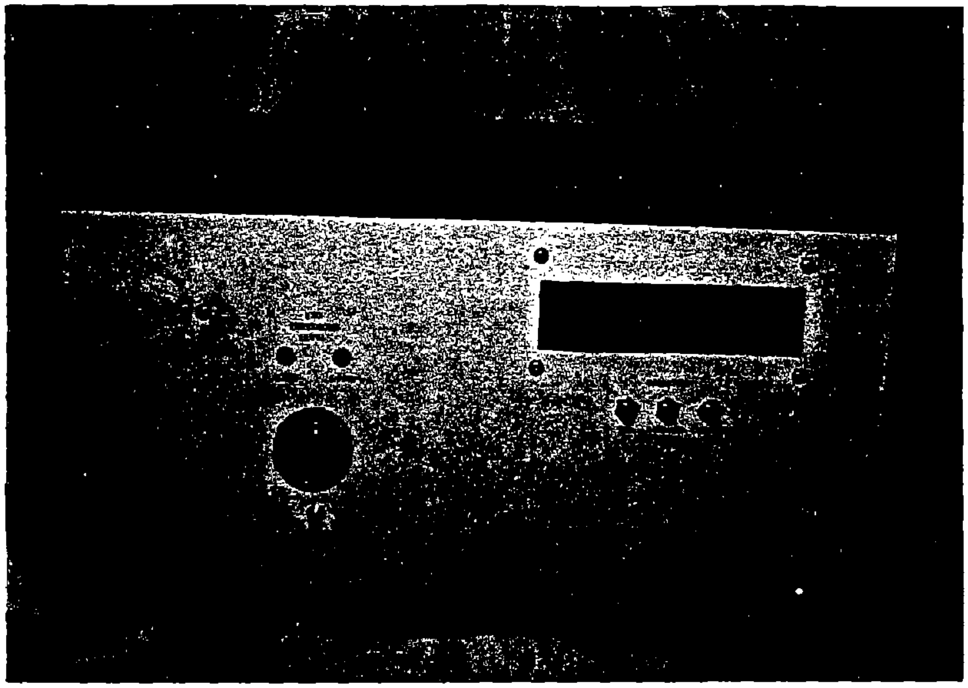


Figure III-34. Front View of the Prototype EtO Monitor

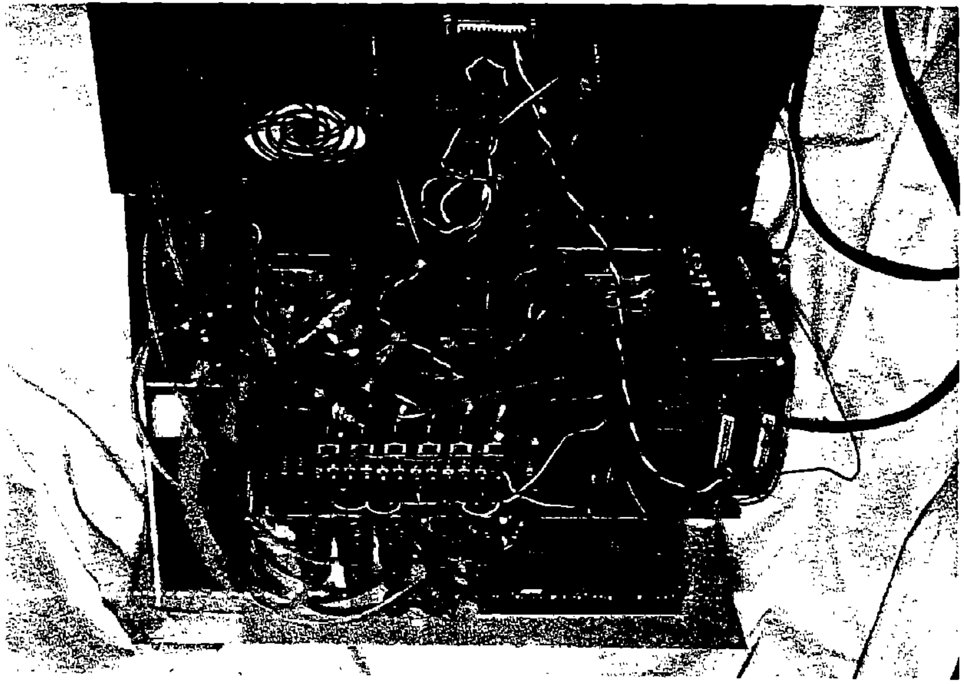


Figure III-35. Interior View of the Prototype EtO Monitor

Two options are offered for the final design; in the first, the separation column is installed in the same manner as in the prototype, while in the second, the separation column is split. The split column allows the backflush to be initiated earlier in the flow cycle, so that the total cycle time is cut in half. In one additional feature of the second option, a valve is installed just upstream of the solid-state TGS sensor, and is used to control the flow of gas across the sensor. For most of the flow cycle the flow is bypassed around the sensor so that the device is not exposed to interferent or contaminated gases. This should maximize sensor response to the presence of EtO in the sample.

Single-Column Flow Layout

The single-column design, presented in Figure III-36, requires four valves to direct the flow through the instrument. After passing through a filter to remove any particulate material in the ambient airstream, the flow is split. Flow restrictors are installed to equalize the flows in the two flow paths. In the carrier gas flow path, the ambient air passes through a chamber that houses a permeation tube which is designed to add EtO in a carefully controlled concentration to the flow stream. During normal operation of the instrument, this EtO is removed in the combustibles trap and Nafion dryer. In calibration mode, the EtO-doped sample is routed to the sample loop by valve A. The known concentration from the perm tube is then added to the ambient EtO (if any) to perform a calibration by the method of standard additions.

At the start of the flow cycle, the valves are in the positions shown in the Figure, the default configuration when no power is applied to the valves. Valves B and C are installed such that there is a known flow through the sample loop that is combined with the ventilation flow for the perm tube and passed into the inlet side of the pump. The combined flow then moves through the combustibles trap, where it is heated to destroy any EtO or other organic compounds in order to provide a clean carrier gas to the separation column. The carrier flow then passes through the Nafion dryer to reduce its water vapor content. This is important since the water vapor affects the separation in the column as well as the response of the solid-state sensor to EtO. In this configuration, valve D routes the carrier gas flow through the separation column in the forward direction.

The second configuration in the flow cycle is the sample injection. Valves B and C are actuated, and the sample loop is inserted into the flow downstream of the Nafion dryer and upstream of the separation column. The sample is pushed onto the column by the carrier gas flow, which continues as the sample traverses the column and the separation of species is accomplished. The carrier gas "purges" the sample loop in this configuration while the separation is completed. The TGS sensor baseline is recorded just after actuation of the injection configuration so that the change in signal level due to the presence of EtO in the sample can be determined.

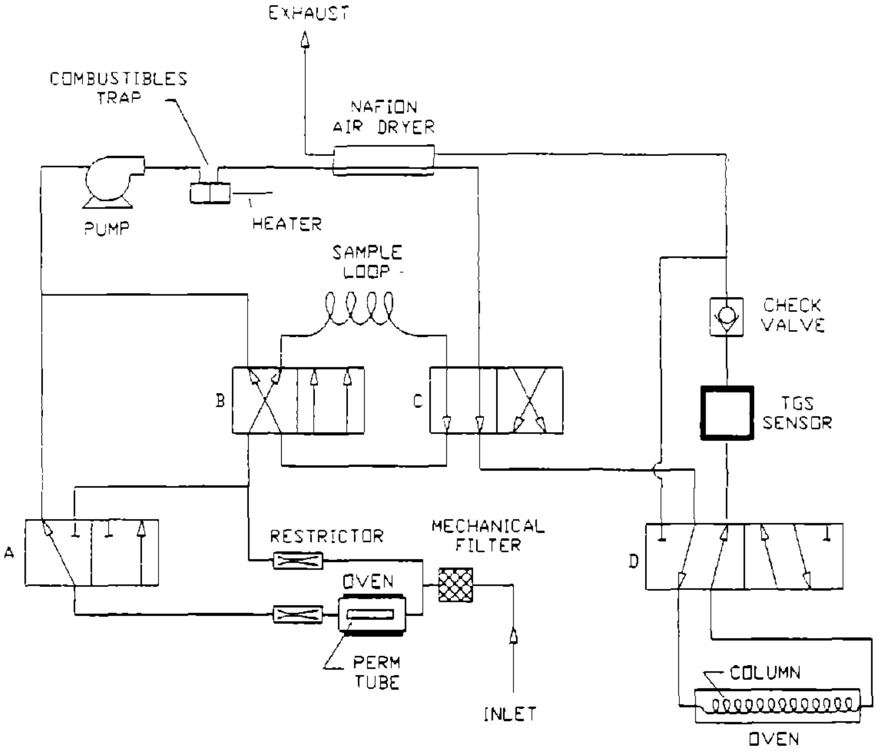


Figure III-36. Single Column Flow Schematic

Just after the EtO peak has been detected by the TGS sensor, the flow is switched to the final configuration in the cycle. The sample loop valves B and C are returned to their normal positions (as shown in the figure), and valve D is actuated. Valve D reverses the flow in the separation column, to backflush interferents and any moisture that may have been deposited in the column. A check valve is installed downstream of the TGS sensor in order to prevent inadvertent contamination of the sensor from the backflush exhaust. Backflush continues for a period somewhat longer than the injection time in order to assure that the column is cleaned of all contaminants.

The single-column flow layout for the final design is configured such that there is always a countercurrent flow in the Nafion dryer, a condition that was not the case in the prototype layout. This minimizes the amount of water vapor that is injected to the separation column, which is important since the water vapor lowers the signal baseline of the TGS sensor and therefore reduces the sensitivity of the instrument.

Split-Column Flow Layout

The split-column flow layout uses five valves and is shown in Figure III-37. The design tradeoff here is a requirement for an additional valve over the single-column layout, resulting in a significantly shorter cycle time since the backflush of column 1 occurs while column 2 is eluting the EtO to the TGS sensor. This layout also features a valve that bypasses the flow around the TGS sensor for most of the cycle; this keeps the sensor clean, and maximizes the sensitivity to EtO by permitting operation at relatively high baseline voltage (corresponding to high resistivity in the TGS sensor).

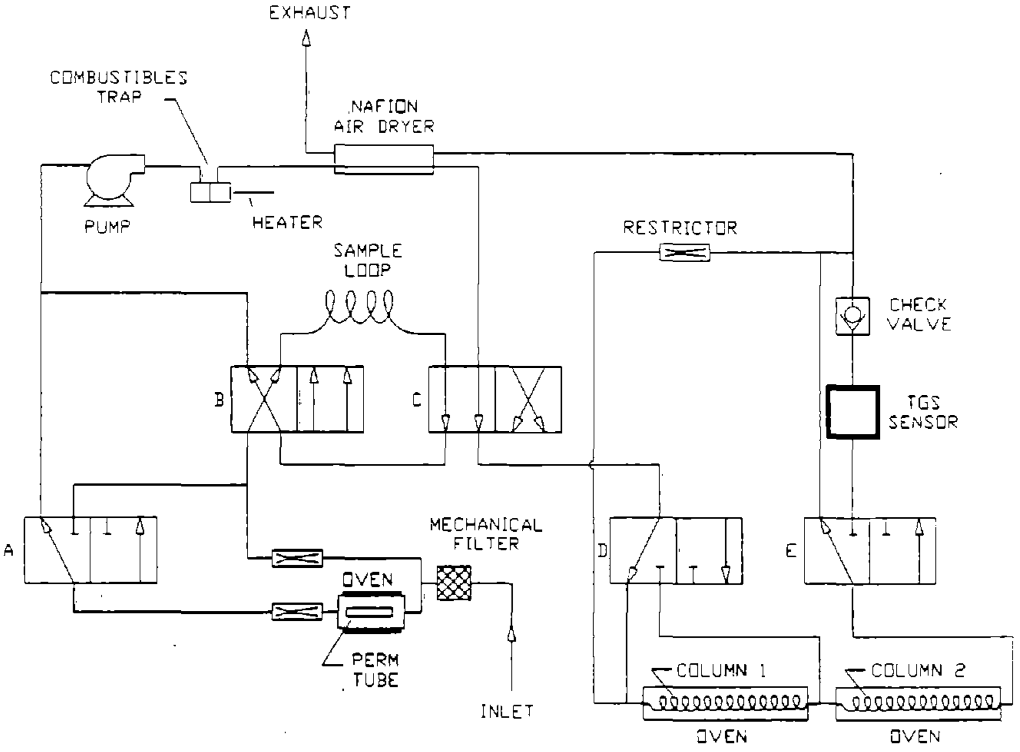


Figure III-37 Split-Column Flow Schematic

The three flow configurations in the split-column layout are similar to those in the single-column option. In normal operation, valve A remains in the shown position where the room air that ventilates the perm tube is directed through the combustibles trap and Nafion dryer to provide clean carrier air to the separation column. The other half of the split flow at the entrance to the device is passed through the sample loop to accumulate a sample for later injection to the split separation column. Restrictors are used to control the flows in the two paths downstream of the mechanical filter. Valves B and C are positioned in their deactuated states as shown during this flow configuration in the instrument cycle. The flow through the two separation columns is in the forward direction (toward the TGS sensor); valves D and E are in their deactuated states (as illustrated in the Figure). Valve E in its deactuated state bypasses the flow around the TGS sensor so that it is not exposed to gas flow that could contaminate the sensing element during sample acquisition.

In the second flow configuration, a sample is injected at the top of the split separation column (i.e., top of the left column, labeled "column 1" in the schematic). Valves B and C are actuated to insert the sample loop in the flow path downstream of the Nafion dryer and upstream of the backflush valve D, which remains unactuated. At a preprogrammed time after the start of injection, valve E actuates to direct the flow from the outlet of the separation column across the TGS sensor. This must be done within a few seconds after the start of injection since a baseline voltage must be obtained before any constituents of the sample begin to elute from the column. Valve E remains open during the elution to direct the flow across the TGS sensor where any EtO eluted from the separation column is detected.

The final flow configuration is initiated before the EtO peak has reached the TGS sensor. This is possible because with the split column, Column 1 (lefthand) can be backflushed while the EtO is undergoing separation in Column 2 (the righthand). The flow in Column 2 continues to move the EtO toward the sensor, even as Column 1 is being backflushed. Any residual contaminants in Column 2 will be moved through during the succeeding sample acquisition flow, and will not affect the sensor since Valve E will bypass the flow during the sample acquisition; the net result is that Column 2 never requires backflushing. It it believed that the limited exposure of the TGS sensor will also result in more stable operation and less drift over time in the instrument.

Preliminary Cost Estimates

Lists of the components that would be required to build the single-column and split-column versions of the final design have been compiled, and are presented in Tables III-4 and III-5. Estimated costs for each component are also included. A modest discount for

Original Equipment Manufacture is taken, and a multiplier of five is applied to arrive at a target sales price for the instrument. From the data included in the tables it is seen that the final EtO monitor could be profitably sold for about $5,000.

Before commercial production of an instrument could be initiated, several issues require resolution. These include a full test of the revised flow scheme (whichever is selected), a re-calibration to reflect the split flows, modifications to the microcontroller software to operate the valves, and a several month reliability test of an instrument built to the production specification.

Table III-4. Preliminary Cost Estimate for Final Configuration A

System Component	Number Required	Unit Cost	Total Cost
Mechanical Filter	1	$8.00	$8.00
ETO Perm Tube	1	$120.00	$120.00
ETO Perm Tube Block	1	$20.00	$20.00
Flow Restrictors	2	$2.00	$4.00
3-Way Solenoid Valves	1	$37.00	$37.00
Feed Pump	1	$80.00	$80.00
Combustor Heater	1	$25.00	$25.00
Air Purifier Catalyst	1	$10.00	$10.00
Catalyst Tube	1	$5.00	$5.00
Insulation	1	$5.00	$5.00
Combustor Control Circuit	1	$25.00	$25.00
Nafion Dryer System	1	$125.00	$125.00
4-Way, 4-Ported, Solenoid Valves	2	$65.00	$130.00
4-Way, 5-Ported, Solenoid Valves	1	$54.00	$54.00
GC Column and Packing	1	$20.00	$20.00
GC Oven Enclosure	1	$10.00	$10.00
Temperature Controller	1	$25.00	$25.00
TGS Sensor Block	1	$20.00	$20.00
TGS Sensor	1	$1.00	$1.00
TGS Thermocouple	1	$2.00	$2.00
Check Valve	1	$3.00	$3.00
Flow Detection Thermistor	1	$5.00	$5.00
Hookup Tubing (feet)	20	$1.00	$20.00
Compression Fittings	20	$5.00	$100.00
Wire and Sockets	1	$50.00	$50.00
Control Computer	1	$200.00	$200.00
Input/Output Module	1	$80.00	$80.00
System Readout Display	1	$50.00	$50.00
Monitor Case	1	$25.00	$25.00
BASIC PROJECTED PARTS COST			$1,259.00
ASSUMED COST MULTIPLIER	5		
OEM DISCOUNT ON PARTS (%)	15		$1,070.15
PROJECTED PRODUCT SALES PRICE			$5,350.75

Table III-5. Preliminary Cost Estimate for Final Configuration B

System Component	Number Required	Unit Cost	Total Cost
Mechanical Filter	1	$8.00	$8.00
ETO Perm Tube	1	$120.00	$120.00
ETO Perm Tube Block	1	$20.00	$20.00
Flow Restrictors	3	$2.00	$6.00
3-Way Solenoid Valves	3	$37.00	$111.00
Feed Pump	1	$80.00	$80.00
Combustor Heater	1	$25.00	$25.00
Air Purifier Catalyst	1	$10.00	$10.00
Catalyst Tube	1	$5.00	$5.00
Insulation	1	$5.00	$5.00
Combustor Control Circuit	1	$25.00	$25.00
Nafion Dryer System	1	$125.00	$125.00
4-Way, 4-Ported, Solenoid Valves	2	$65.00	$130.00
GC Column and Packing	1	$25.00	$25.00
GC Oven Enclosure	1	$10.00	$10.00
Temperature Controller	1	$25.00	$25.00
TGS Sensor Block	1	$20.00	$20.00
TGS Sensor	1	$1.00	$1.00
TGS Thermocouple	1	$2.00	$2.00
Check Valve	1	$3.00	$3.00
Flow Detection Thermistor	1	$5.00	$5.00
Hookup Tubing (feet)	20	$1.00	$20.00
Compression Fittings	20	$5.00	$100.00
Wire and Sockets	1	$50.00	$50.00
Control Computer	1	$200.00	$200.00
Input/Output Module	1	$80.00	$80.00
System Readout Display	1	$50.00	$50.00
Monitor Case	1	$25.00	$25.00
BASIC PROJECTED PARTS COST			$1,286.00
ASSUMED COST MULTIPLIER	5		
OEM DISCOUNT ON PARTS (%)	15		$1,093.10
PROJECTED PRODUCT SALES PRICE			$5,465.50

I. TASK 9: REPORTING

This final report comprises the documentation of project activities to design and test a prototype EtO monitor. The details of the component selection, system design, prototype fabrication, and comprehensive testing are presented in the report. The final report also includes a design for commercial instrument and a list of components identified for installation in that design.

ADA has conducted initial discussions on the commercialization of the EtO monitor with a major commercial safety equipment manufacturer under the terms of a confidentiality agreement. These talks have continued through the completion of the Phase II research, and represent a possible mechanism for commercial production and sale of the EtO monitor technology.

This final Phase II report constitutes the deliverable product of this project.

IV. CONCLUSIONS AND RECOMMENDATIONS

The most important finding from this research is that the best features of two types of commercial EtO area monitors can be combined into one instrument that eliminates the drawbacks of the commercial monitors.

Several continuous monitors on the market employ solid state semiconductor sensors, but the lack of a scrubber or column in these instruments results in severe interference problems. Gas chromatographs offer specificity and sensitivity, and some even offer continuous operation, but all commercial gas chromatographs require cylinder gases. Flow systems and detectors for gas chromatographs are considerably more sophisticated and thus more difficult to operate and more expensive than the simpler solid state sensors.

Low cost and specificity for EtO are the two main characteristics hospitals look for in an EtO monitor, and it is anticipated that the prototype EtO monitor developed in Phase II will be able to achieve these goals as a commercial instrument. Opportunities to produce the commercial instrument, in partnership or under licensing agreements with existing instrument manufacturers, continue to be actively pursued.

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VI. ACKNOWLEDGEMENTS

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Dr. Cynthia Benner was the original Principal Investigator on the Phase I and early Phase II research. Dr. Mark Burkhardt was the perseverent chemist who worked with the experimental configuration until EtO was successfully eluted from a separation column; this critical step was the key to the Phase II proposal.

Dr. Don Stedman served as a consultant, who demonstrated a knack to identify problem areas and managed to focus the effort on the task at hand. Dr. Jim Armstrong contributed to the hardware design and data analysis over the course of the project.

Most of the prototype fabrication and all of the system electronics designs were completed by Mr. Frank Sagan. Much of the component evaluation work was performed by Mr. David Holloway; Mr. Patrick French conducted the prototype long term evaluation testing and developed the final flow configurations for the instrument. The programming of the microcontroller was performed by Mr. Paul Manning.

EQUIPMENT INVENTORY
GRANT NO. 2 R44 OHO 2662-02A1
DEVELOPMENT OF A LOW COST ETHYLENE OXIDE DETECTOR

ITEM 1: PERMEATION TUBE GAS CALIBRATION DEVICE

Description: Calibration device (DYNACALIBRATOR) manufactured by VICI Metronics, to contain permeation tubes at controlled temperature in flowing gas stream of known flowrate to provide calibration gases of variable and known concentration. Model No. 450-18-YS.

Manufacturer Serial Number: M-1120

Acquisition Date: December, 1991

Acquisition Cost: $6000

Percentage of Federal funds used in acquisition: 100

Condition of item: Good

ITEM 2: GAS CHROMATOGRAPH

Description: Single column gas chromatograph, manufactured by SRI, equipped with temperature programmed oven and FID detector. Model No. 8610-10.

Manufacturer Serial Number: 488

Acquisition Date: November, 1990

Acquisition Cost: $4995

Percentage of Federal funds used in acquisition: 100

Condition of item: Good

50272-101

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7. Author(s) Hyatt, D., R. Stewart, and J. Butz

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13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words) An effort was made to design, test and build a prototype ethylene-oxide (75218) (EtO) monitor for use in hospitals where exposure to EtO is possible during the sterilization of equipment. In the model, room air serves as the carrier gas. The device operated continuously as a direct reading instrument and consisted of a combustibles trap and a dryer, a Teflon gas chromatography column, a solid state gas sensor and a programmable microcontroller to control various items throughout the cycle. EtO could be detected at a concentration of 0.2 parts per million (ppm). A digital concentration reading was updated every 2 minutes. Values of EtO concentration were computed and stored for 15 minutes and for determinations of the 8 hour time weighted average readings. It was anticipated that the commercial cost of the instrument would not exceed 5,000 dollars. It was also expected that this device would overcome the shortfalls of some of the commercial instruments now available in the area of interferences from other compounds.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Grant, Grant-Number-R01-OH-02662, End-Date-05-31-1992, Grants-other, Health-care-facilities, Air-quality-monitoring, Air-sampling-equipment, Gas-detectors, Chromatographic-analysis

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages 83
	22. Security Class (This Page)	22. Price

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