PAMSGRAM

VOLUME 18

PLEASE DELIVER TO ALL INTERESTED PARTIES IN YOUR OFFICE

JUNE 1, 2000

SUPPLEMENTAL INFORMATION ON THE OPERATION OF THE OZONE PRECURSOR SYSTEM

The operation, QA/QC and maintenance of the Perkin-Elmer ATD 400 Air Monitoring System are typically customized.

This document provides general advice that is within the scope of the Technical Assistance Document (TAD) for the Sampling and Analysis of Ozone Precursors (EPA-600-R-98/161, September 1998) for PAMS. The document does not supersede the advice and recommendations of the TAD or the vendor and should be used in conjunction with the vendor supplied operation manuals.

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1 INTRODUCTION

The purpose of this document is to provide the operator with additional information about the function of the ozone precursor system components shown in the block diagram below (Figure 1.1), together with advice on the limitations and potential failure modes. Chapter 1 includes a brief introduction and step-by-step summary of the system operation. Chapter 2 provides operational details of most of the system components. Chapter 3 describes the typical operational scenario of the system and suggests schedules and some protocols for the analysis of samples other than the required ambient air samples.

The Perkin-Elmer Ozone Precursor System is an adaptation of the standard Automated Thermal Desorber Model ATD 400 to include a special means for introduction of ambient sample air. This is achieved via a modified internal standard valve mounted at the rear of the ATD 400, which incorporates a dehumidifying system. The ATD 400 desorber is connected to the gas chromatograph via a heated transfer line. Carrier and combustion gases and dry zero air supplies are derived from both cylinders and generators. Separation of the target analytes is achieved through the use of a dual-column system with column switching. The system includes two flame ionization detectors (FIDs) for signal detection. Voltage signals from the detectors are collected by a dual-channel buffered digital-to-analog interface, which supplies data to a personal computer running the Turbochrom® data handling software. Data telemetry is accomplished by modems and terminal emulation software.

1.1 BLOCK DIAGRAM OF THE SYSTEM

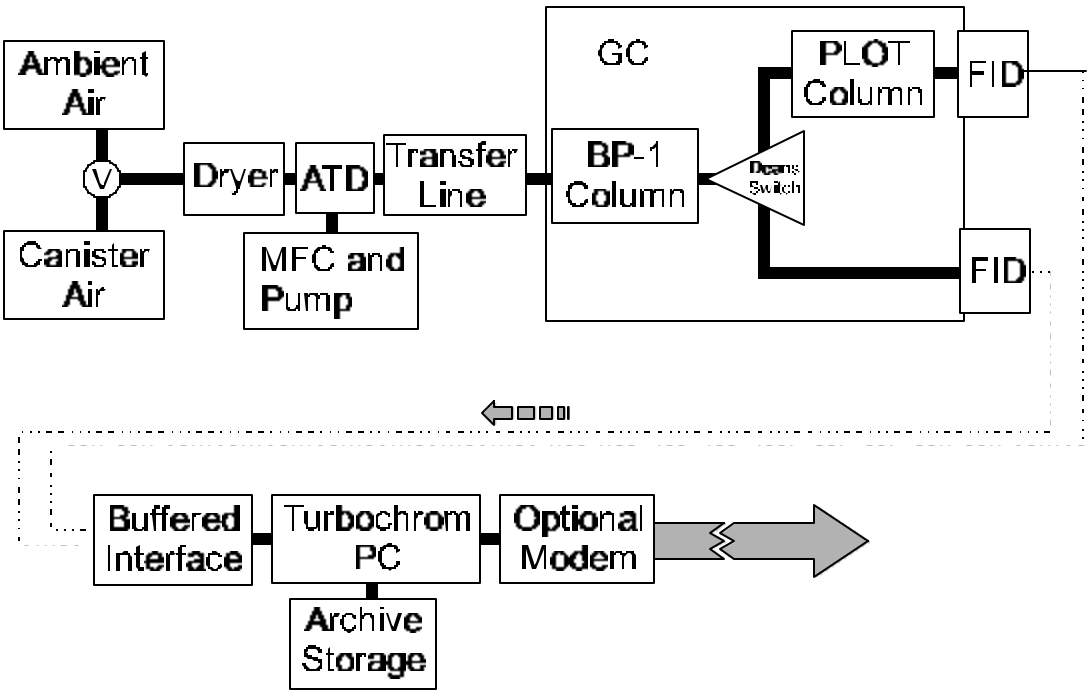

Figure 1. Block diagram of the "On-Line System"

1.2 STEP-BY-STEP SUMMARY OF OPERATION

Step 1. Ambient air (AMBIENT) or air from a CANISTER enters the DRYER by means of an MFC (Mass Flow Controller) and PUMP and is trapped by the ATD unit. Forty minutes of sample air is collected at a flow rate of 15mL/min., for a total volume of 0.6 liters. This number is chosen to ensure that acetylene cannot break through the trap sorbent bed at the highest expected ambient levels.

Step 2. The sample is injected into the TRANSFER LINE and subsequently into the GC using split injection where it enters first the BP-1 COLUMN. This separates the hydrocarbons in order of their boiling points (equivalent to their carbon number series) from C_2 (e.g. ethane) to C_{11} (undecane).

Step 3. The first compounds to elute out from the BP-1 column are switched by a Deans' Switch to the PLOT (porous layer open tubular) column, where they are separated and then detected by a FID (Flame Ionization Detector). This column is designed to separate the light hydrocarbons. Thus ethane, ethylene and acetylene (all C_2 compounds) are separated from each other. The actual reference chromatogram varies from system to system. A representative chromatogram may be seen in Appendix B of your Perkin-Elmer Ozone Precursor Manual Part Number 0993-8970.

Step 4. The later eluting compounds from the BP-1, (hexane to nonane) are switched by the Dean's switch back to a second, separate FID.

Step 5. The electrical signals from the FIDs are sent to a BUFFERED INTERFACE, which converts the analog data to digital data.

Step 6. Turbochrom® data acquisition and processing software running on a PC processes the data and converts it into concentration information for each compound in the sample. This is stored in the ARCHIVE STORAGE device, and may also be transferred to your office via modem (if you are using one) and terminal emulation software such as PCAnywhere.

2 OPERATIONAL DETAILS OF COMPONENTS

2.1 NAFION DRYER

The de-humidification device used is a semi-permeable membrane (Nafion ® by Permapure Inc, Toms River, NJ). It consists of a stainless-steel tube with a coaxial tubular membrane. Dry air flows around the outside of the membrane to carry off moisture. Ambient air sample flows through the center of the membrane, as shown below:

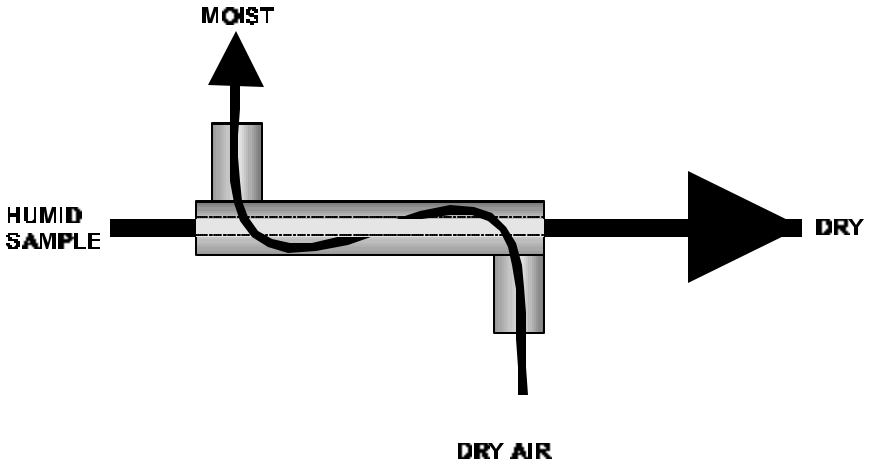

Figure 2. Nafion semi-permeable membrane dryer

Dry air at a flow rate of about 250 mL/min., flows around the outside of the membrane from the back (exit end) to the front (counter-flow). Moisture in the incoming air selectively permeates through the membrane, where it is expelled to vent thus drying the incoming sample air. The dryer will pass almost all normal hydrocarbons with the exception of isobutylene, which is removed almost entirely from the chromatogram. Substituted hydrocarbons, which tend to be polar, are expected to be affected to some degree.

2.1.1 OVERHEATING/DRYING OF THE MEMBRANE

Some have suggested that the dryer performance may be improved by heat cycling. ***The manufacturer specifically recommends against this***. Heat cycling and desiccation causes the membrane to swell and contract, eventually leading to discoloration, degeneration and loss of efficiency.

2.1.2 LONGEVITY

Experience has shown that the drying device is robust under normal use. Replacement on an annual basis is recommended, preferably at the start of each season.

2.1.3 FAILURE OF THE ZERO AIR SUPPLY

If the zero air is not sufficiently dry (dewpoint <-100°F) the sample air cannot be purged of moisture, which may lead to icing of the peltier cooling system. This is usually manifested as a difficulty cooling rapidly to the setpoint of -30°C on the ATD. You may observe data being acquired at successively later times in the hour, e.g.:

File 1	Collected at 10:22 a.m.
File 2	Collected at 11:22 a.m.

File 3 Collected at 12:22 p.m.
File 4 Collected at 13:24 p.m.
File 5 Collected at 14:26 p.m.
File 6 Collected at 15:28 p.m.
File 7 Collected at 16:30 p.m.

Notice the minutes increasing. As soon as you see this - STOP SAMPLING and fix the problem. Failure to do so will damage the ATD. Check for the cause of the failure of the dry zero air (such as broken or split tubing, broken compressor, stuck drain valve on the compressor or zero air generator, etc.).

Procedures for drying the peltier cooler are complicated. The easiest way is to re-establish a dry zero air supply, then leave the ATD 400 turned OFF for two hours or more (or *as long as possible*). Resist the temptation to open the peltier cooler housing, as this damages the sealing gaskets. The dry air will remove any moisture as long as the ATD is not powered on.

2.2 BRIEF DESCRIPTION OF THE ATD 400 OZONE PRECURSOR SYSTEM

The Automated Thermal Desorber, Model ATD 400, is a system for the pre-concentration of a gaseous sample using solid sorbents and the subsequent injection of that sample into the inlet of a gas chromatograph (GC). In this specific application, many of the standard features of the ATD are not used (the autosampling capability and the sample tube, for example). The design and description of the ATD is covered comprehensively in your ATD 400 Users' Manual (Part No.L427-9050) and in the Ozone Precursor Operation Manual (Part No. 0993-8970). A brief description of the important functional features follows:

The ATD 400 incorporates a small glass trap packed with two sorbent materials, one of which is a form of graphite and the other is carbon molecular sieve. During sampling, 600 cc of standard gas or ambient air is drawn through this trap by a small vacuum pump. The trap is cooled electrically to -30°C and this causes the volatile organic compounds (VOCs) in the air to adsorb strongly onto the surface of the sorbents. At the end of the sampling period, the flow is stopped. The VOCs from the 600 cc sample are therefore trapped on these sorbent materials. A valve in the ATD then operates to reverse the direction of flow. The trap is then heated, and the VOCs are desorbed and swept into the transfer line and onto the analytical column of the GC system. Refer to Figures 1.6 through 1.8 in the Ozone Precursor Manual.

Unless otherwise advised, use the ATD settings recommended by the manufacturer in the Ozone Precursor Manual, Section 3.

2.2.1 SORBENT TRAP FAILURE

The sorbent trap material is held in the trap by a glass wool plug at the entrance/exit end, and a glass wool plug and spring at the other end. During the collection and analysis cycles, the system pressure cycles from a vacuum to ~48psi. This can cause eventual failure of the trap if the packing becomes loose. Material displaced from the trap will contaminate the sample lines within the ATD. The onset of failure is manifested by the degradation of peak shape on the BP-1 column (excessive tailing of peaks), while the PLOT column peaks remain relatively sharp. In addition, there may also be the loss of recovery of some compounds, especially the higher molecular weight hydrocarbons (C_6, benzene and up).

Stop the system immediately. If you have not changed a trap before, call a instrument Service Representative.

2.2.2 PELTIER TRAP ICING

The causes of icing in the Peltier trap stem range from poor zero air quality (not sufficiently dry), to leaks in the trap enclosure and plumbing. It is essential that ~160 mL/min. of dry air (dewpoint <-100°F) is supplied to the trap box at all times.

NOTE: Early ATD 400 systems had a purge flow of 30 mL/min.. All ATDs should now have been modified to increase the flow to 160 mL/min..

If icing is suspected, **stop immediately**, and turn the ATD OFF. This is the only way to remedy the situation: as long as the ATD is ON the ice will continue to form.

2.2.3 STUCK TUBE

At the start of the run, the ATD 400 loads an empty sample tube and performs a leak-test. The leak-test is only performed for the first run after the STOP key has been pressed. For PAMS applications, this empty sample tube is loaded and remains in place for subsequent sample runs. After many hours of sampling it is possible for the sample tube to refuse to unseal when the ATD is stopped. When this occurs the ATD may halt with an error message. Do not switch the unit back ON until the dropped tube is retrieved or serious damage may result to the elevator mechanism. Before continuing you must check the tube status, and replace seals and components that may have become damaged. It is also a good idea to check for dropped tube caps.

To avoid this condition, replace the tube seals at intervals of once per month. Take advantage of down time during routine off-line maintenance. Never handle the tube at the ends. Finger oils can cause the tube to stick. A glass tube is preferred to metal since it conducts less heat to the seals. Use the lowest leak-test sample tube temperature possible (100°C recommended).

2.2.4 CONTAMINATED OR DAMAGED TRAP FILTER DISKS

Small glass-fiber disks are inserted in the end fittings of the trap. These must be present and clean. Contamination of one of these disks by sorbent particles will lead to a loss of compounds (poor recovery), since the material does not get desorbed. Generally only the higher molecular-weight hydrocarbons will be affected (C6, benzene and greater).

2.2.5 LEAK FAILURES

The ATD will test itself for leaks at the start of sampling, i.e. when you first press the green button to start. Thereafter, no leak checking is performed since the tube is not unloaded. If system leaks occur, they will be from devices such as the rotary valve or fittings, resulting in poor recovery of all analytes from both columns.

2.2.6 INABILITY TO RESOLVE ETHANE FROM METHANE

Resolution of these lightest target compounds is achieved only if the desorption flow is sufficiently high. Closing the outlet split completely will reduce the trap flow to equal the column flow. This is insufficient. Correct operation requires some small additional flow of about 3.5 ml/min. This reduces the effective sample amount injected to 600 x 3.5/6, or about 350 ml. See "Setting Up the ATD Method" in the User Manual Section 2, Page 15.

2.2.7 CONTAMINATED TUBE FILTER DISK

The sample tube holder, rear jaw contains a glass fiber filter disk. Check and change this disk periodically, especially when changing tube seal o-rings. See also Section 6.1.2 of your ATD 400 User's Manual, Part Number L427-9050.

2.3 MASS FLOW CONTROLLER (MFC)

The mass flow controller measures the flow of air by the pressure drop across a venturi. Any change in flow causes a corresponding change to the measured pressure drop. Electronics measure this change via a pressure transducer, and a compensating circuit causes the flow to increase or decrease to restore equilibrium.

2.3.1 MASS FLOW CONTROLLER FAILURE

The mass flow control (MFC) devices installed in these systems may eventually exhibit a failure in which the displayed flow gradually drops off over time, and there is an inability to adjust the setpoint to a higher value. Eventually the MFC cannot sustain the 15 mL/min. required to collect sample.

The MFC is rated for up to 100 mL/min. when put into service. Diminished flow goes unnoticed until it drops below the desired set-point of 15 mL/min.. The reason for the gradual failure is that the thermostatically-controlled valve loses its span calibration over time, aggravated by the fact that the pressure differential across the device is less than the amount specified by

the manufacturer. [This is why connecting a canister (higher pressure) to the standard port sometimes causes the readout to immediately display a nonsense value.]

The best advice is to return the MFC to Tylan for re-calibration. Contact your Ozone Precursor system Service Representative if system is still under warranty or the Tylan Corporation directly. It is extremely rare that a MFC suffers a "hard" or permanent failure.

Alternative MFC devices may be available, but not yet recommended by the ATD manufacturer.

2.4 GAS CHROMATOGRAPH (AUTOSYSTEM GC)

The GC uses two FIDs (Flame Ionization Detectors) for reading the chromatographic signal. An FID responds to carbon, so the larger the number of carbons in the molecule, the larger the signal will be. In theory, molecules with 6 carbons, C_6 (hexane for example), will generate about twice the signal as C_3 (propane) for the same amount.

The GC is equipped with a Deans' Switch, which is a fluidic valve located at the exit of the BP-1 column. It is not a complicated device in principle, but it can be difficult to assemble and re-assemble without the proper knowledge. It uses a switching pressure supplied by the carrier gas and a second pressure regulator to send the eluent from the BP-1 to the FID directly or to the PLOT column. This second regulator pressure is termed the "mid-point" pressure supply.

The GC must be temperature programmed from 46°C to 200°C according to the manufacturer's directions. **Under no circumstance should the upper temperature limit of 200°C be exceeded, as this will cause irreversible damage to the PLOT column.**

2.4.1 NO SIGNAL (FID FLAMES)

Check that you have the FID flames lit. This is commonly done by holding a cold surface (mirror or shiny wrench) over the FID chimney to observe the condensation from the moisture in the flame. Alternatively, you can look at the FID signal on the autozero page of the GC display. On Range 1 and Attn. 1, the signal should be about 0.4 mV. If it is below 0.4 mV, the flame is out.

Newer GCs from Perkin-Elmer have an auto-ignition feature, which is enabled prior to the beginning of a run. If the flame has gone out, the software in the GC (if enabled) will attempt to re-light the detector during the equilibration period prior to allowing the GC to become Ready. This takes about 30 seconds. If the flame cannot be lit the GC will not become Ready.

Common reasons for the flame to be extinguished are humidity (inadequate drying) and lack of hydrogen or air fuel gases, or the wrong ratio of hydrogen to air. If the flame goes out consistently during a run, it is very likely that the incoming sample contains too much water. The water on a GC column will expand with such force during temperature programming that it will literally blow the flame out.

Note that the gas mixture must be enriched in order to ignite the flame. If you are doing it manually, follow the instructions in the GC manual to lower the air pressure (air flow) to enrich the flame, and do not forget to increase the pressure after the flame has ignited.

2.4.2 NO SIGNAL (BROKEN COLUMN)

Check that a column has not broken. If necessary, open the oven, disconnect the column from the detector, put the end in a non-polar solvent such as pentane and see if you get bubbles.

2.4.3 NO SIGNAL (MIDPOINT PRESSURE)

Check the midpoint pressure. If it is too high the carrier gas cannot flow down the BP-1 column. The pressure should not be more than 5 PSIG higher than the midpoint pressure recorded in your instrument log.

2.4.4 GC WILL NOT BECOME READY

Look on the GC display to see what is preventing the Ready condition. Generally it will be a device in the GC, such as a heated zone (heater has broken); Turbochrom® is not ready (which means the interface is not ready); the sequence has ended; or the ATD has not cooled down due to icing.

2.4.5 GC DOES NOT COOL FAST ENOUGH

There is a window of about 8 minutes for the GC to recycle from 200°C back to the Ready condition. If the ambient air temperature is too high it will inhibit cooldown. Also check the operation of the oven vent or cooling door.

2.4.6 NO PEAKS

Check that the ATD trap has not cracked. You will generally hear gas escaping in the vicinity of the cold trap compartment if the trap is cracked.

2.4.7 POOR COMPOUND RECOVERY

Symptom: the low molecular weight compounds are attenuated. This means that the light compounds are not being properly trapped. Check the trap low temperature and make sure it is getting down to -30°C. Check the trap packing. To check the trap packing, turn off the ATD 400 and removing the trap as described in Chapter 6-2 of the ATD User's Manual.

Symptom: the heavier molecular weight compounds are attenuated. If only the *Standard* exhibits this problem, then the standard is not being properly humidified. If the *Sample* also exhibits the problem, then the trap is probably failing/failed. Check the trap packing. To check the trap packing, turn off the ATD 400 and removing the trap as described in Chapter 6-2 of the ATD User's Manual.

2.4.8 BASELINE DISTURBANCE ON ONE CHROMATOGRAM

This may be due to a bad hydrogen regulator (there is one for each FID). The particular regulators used in the Perkin-Elmer GCs have a diaphragm that can become displaced when the control knob is turned. The displaced diaphragm prevents the regulator from working properly, causing pulses in pressure from 1 to 10 minutes in duration. Other causes of baseline cycling, including the zero air system, can cause confusing diagnoses. A good baseline is achievable.

2.4.9 BASELINE DISTURBANCE ON BOTH CHROMATOGRAMS

This may be due to a bad air supply (there is one for both FIDs). This can be very difficult to diagnose, and difficult to resolve. There are many causes. Check with your Perkin-Elmer Service Representative.

2.4.10 LEAK CHECKING

The best method of determining leaks is to use the "leak down" method. The system is first pressurized and then the pressure is monitored over time. If the internal pressure decays, there is a leak. If it maintains pressure, the system is leak-free.

Do not use isopropanol or other polar solvent as a leak checking solution for this system. Inadvertent contamination of the PLOT stationary phase can cause permanent damage to it. If possible, use an electronic helium leak detector. They are available from most chromatographic supply houses. If you have to use a solvent, pentane is recommended. If you have to use a polar solution, use methanol/water 50:50 v/v, which can more easily be removed from the PLOT column. Soap solution and other preparations run the risk of contaminating the system.

2.4.11 DESCENDING BASELINE

If the first 15 minutes of the run show a baseline that is gradually descending, the hydrogen and air fuel gas ratio is wrong. Following the procedure provided in the GC manual, reset the flows to the correct values. Do not try to economize on the consumption of air! The new Whatman zero air generators are capable of supplying up to 1500 mL/min., which should be sufficient for the normal demands of the AutoSystem GC. (Older Balston units only supplied 1200 mL/min..)

2.4.12 SHARP RISE IN SIGNAL ON THE PLOT JUST BEFORE THE RUN END

A sharp increase in the signal baseline, before the run ends, may be caused by an incorrect setting of the Deans' switch solenoid valve. Examine the baseline at 0.03 minutes prior to the end of the run, and make sure that the baseline signal does not suddenly go vertical just before the run ends. (If necessary, you can extend the Turbochrom run to 48.01 minutes so that you can observe the actual GC run end-point.) If there is a sudden positive rise to the baseline, you have the valve setting wrong. This is an AutoSystem GC phenomenon. The P-E 8000 GC works differently.

Check the valve #2 setting in CONFIG: if it is OFF set it ON, and vice versa. This is quite important.

What is happening is that the Deans' Switch solenoid is being reset to its default state at the end of the AutoSystem GC run. If this is set to the wrong setting, high boiling compounds from the BP-1 column are being switched onto the PLOT column, when the exact opposite is preferred. This will lead to accumulation of aromatic, high boiling compounds on the PLOT column that are difficult (almost impossible) to clean up.

As a general rule, it is good practice to ensure that, *at all times*, the BP-1 flow is being directed away from the PLOT column except when light, normal hydrocarbons are cut to it. This leads to the minimum PLOT contamination and the best performance and longevity. In other words, when the GC is at "Ready" the BP-1 flow should be *away* from the PLOT column.

2.5 970 ANALOG-TO-DIGITAL (A/D) INTERFACE

The interface contains dual channel, analog-to-digital circuitry, memory and an IEEE interface to the PC. The PC sends a sequence, which is a list of analyses that are to be performed. The interface then proceeds to process the incoming analog data every time it receives a start signal from the GC, and associates that data with a line in the sequence. This is a **Run.**

These data are then sent on request up to the PC in packets or bursts of data points (or time slices), which the PC stores under the heading of the Run File Name. This is called raw data, and Turbochrom gives this data the filename extension of .RAW. The PC need not be active in order for the A/D interface to do its job. Once the sequence is downloaded (let's say 200 lines) the interface will acquire data. If the PC is not available the Interface will accumulate data in its on-board memory buffer. When the PC is available it will request the data from the interface by continuous polling. Runs stored in the buffer will be uploaded as a backlog.

If the PC does not request the data the interface buffered memory will eventually fill (about 4 to 6 hours of data) and the interface will stop acquiring data. (The whole system will then stop, since the GC will then not become Ready.)

2.5.1 NOISY BASELINES

Some interfaces exhibit excessive baseline noise if ground current loops exist. Get your Perkin-Elmer Service Engineer to try to fix the problem. Analog cables should be grounded at one end only.

2.5.2 INCORRECT DATE ON DATA

If you see a date like October 32nd on a report, it is because it is more than one month since you downloaded a new sequence. Do not generate sequences of more than one month.

2.5.3 INTERFACE LOCKUPS

The 970 data system uses the IEEE bus. Make sure that your IEEE cable is short and well terminated. Avoid cheap IEEE cables. Eliminate electrical spikes by using the best power conditioner possible (surge and spike protector). Shielded cables should be connected to good grounds.

2.5.4 INTERFACE "NOT READY"

Check to see that Turbochrom is running and a method has been downloaded to the Interface for acquisition. Check to see that the IEEE interface is properly configured. If the Interface is continually being detached, try another Interface.

2.5.5 UNDER AND OVER RANGE

The 970 Interface may not be properly configured. Start Turbochrom again and download a new sequence. In addition, baseline disturbances can cause the interface to signal under and over range. Under range: The FID might not be lit, causing a very low or under-range signal. Over range: Check that the analog cables are connected the right way round. Reverse them if necessary.

2.6 TURBOCHROM DATA HANDLING SYSTEM

The Turbochrom software scans a series of data points (time slices), which represent the chromatogram. Each data point represents an analog voltage acquired at a nominal time into the run. Data are normally acquired at 3 points per second: more is unnecessary for this analysis and less is unsatisfactory. From this data Turbochrom determines the baseline signature and identifies peaks according to the criteria in the Turbochrom Method. With the peak information, Turbochrom is able to then match peaks with a list of pre-defined target components and parameters and calculate the amounts of each based on a previous calibration run (a process known as the external standard method of analysis).

2.6.1 NO PEAKS

Check the system as previously described in 2.5.

2.6.2 NO INTERFACES

Run the Turbochrom configuration program and allow the IEEE bus to be scanned. A working interface will return a valid IEEE address. If there are no interfaces found, power-cycle the interface and check again. If the interface is still not found, restart the computer and run the configuration again. It is sometimes possible for the IEEE port to become locked. In such cases it may be necessary to shut down the computer completely in order to reinitialize the system.

2.6.3 PARALLEL PORT KEY NOT FOUND

Earlier versions of Turbochrom and older computers did not always recognize “LPT1”. Adding a second parallel port card "LPT2" usually fixes the problem. Recently Perkin-Elmer introduced a new active key, which also alleviates these problems (key is round instead of square).

2.6.4 POOR PEAK INTEGRATION

Poor integration can be ascribed to a variety of factors that include baseline noise and other disturbances, poor peak shape, faulty A/D interface, wrong sampling rate, wrong noise and baseline threshold values, poor peak separation, poor column performance (K value). All of these factors should be considered when attempting to integrate the chromatogram.

2.6.5 FILE INCOMPATIBILITY

Each new version of Turbochrom (and each sub-version) employs a different file header format, rendering the data files incompatible with previous revisions. Simply opening a file to view it is enough to make the file unusable by the previous version. Most states do not change their version of Turbochrom unless it is absolutely necessary to do so, so that they can re-examine past data. However, Perkin-Elmer Support personnel cannot trouble-shoot older versions of the program effectively. It is strongly recommended that an original archive is always kept offline so that accidental changes to the source data cannot occur.

2.7 TERMINAL EMULATION SOFTWARE [PCANYWHERE Ò (SYMANTEC)]

The *optional* terminal emulation software allows an external connection to interact with the system via the serial communication port COM1 or COM2. The program must be run on the HOST (the analytical GC system) and the REMOTE (the central office) systems. Each trailer or monitoring site is therefore a HOST.

At its simplest, this system simply allows for the interrogation of the HOST site by the REMOTE in order to view what is going on. More complex setups allow the periodic downloading of data several times a day. This is a complex issue and data integrity considerations are extremely important. An offline storage medium is recommended, such as a zip drive (Iomega Inc.). Tape cartridges are not recommended, since they cannot be well integrated with the operations of Turbochrom.

2.8 MODEMS

Modems convert digital data from the computer into a series of analog signals that can be transmitted over telephone wires. Use the same model of modem at the HOST and REMOTE sites so that they will use the same protocol.

2.8.1 DISCONNECTS

The quality of the telephone line is critically important to the success of a PCAnywhere installation. Ensure that you have the highest quality of telephone line possible. If possible, have another line for a handset so that voice conversations do not conflict. Use the best quality of telephone handset to impose the minimum "ringer equivalence" on the system. This reduces the current in the system and allows the modem to operate more quietly.

2.8.2 LOW CONNECT SPEEDS

It is probably unreasonable to expect connections much higher than 19.2 kilobaud, but some will run as high as 36 kilobaud and others only as fast as 9600 baud. This depends again on the quality of the telephone line. Enabling data compression may help, but some rural telephone systems may be unavoidably slow.

2.9 ZERO AIR GENERATOR

The zero air supply in most field-deployed systems is generated by means of an electrical compressor and zero-air generator, consisting of a catalytic converter and drying unit. The unit that has been selected to meet the criteria of this application is a modified TOC (total organic carbon) zero air generator from Whatman (previously Balston). It is imperative that the air supply used meets the stringent humidity criterion otherwise the system will be adversely affected.

Figure 3 shows a schematic of a typical configuration. Compressed air is supplied to the zero air generator. The zero air generator is able to supply up to 1500 mL/min. of dry (dew point < -100°F) air to power the ATD pneumatics, supply fuel for the dual FIDs, and dry air for the Nafion dryer.

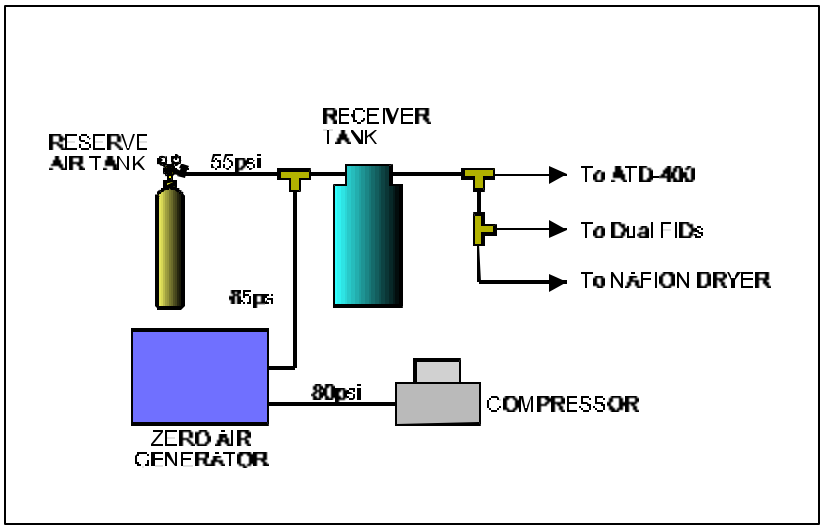

Figure 3. Zero air supply diagram

In the event that a power failure occurs, the zero air generator is "teed" to a reserve air tank as shown. This simple arrangement ensures that the reserve air will automatically start to flow when the delivery pressure drops below 55 psig, and cease when the pressure recovers. This is essential, otherwise the FID flames will go out during a power failure and cannot be re-lit. The newest GCs (1998 vintage) now come with FIDs that re-light if the flame is extinguished, so this may no longer be a serious concern.

2.9.1 EXTERNAL LEAKS

The input stage of the zero air generator features dual, moisture-eliminating, self-venting filter bowls. Over extended periods it is possible for the filters inside these bowls to dry out and leak. This is manifested as a loss in zero air delivery pressure with air escaping from one or both of the black water drainage hoses. You may also notice the compressor running continuously. To remedy this:

a) Switch the zero air generator to OFF.

b) Unscrew and remove the first filter bowl and pour into it about 50 cc of clean water. Replace the bowl, tightening the large locking ring firmly.

c) Repeat for the second bowl.

d) Switch the unit back on, holding a finger firmly over the end of each discharge hose. Allow the internal pressure to rise to about 20 or 30 psi, then remove the finger and relieve the pressure. Water will be expelled (watch where you are pointing the hose), and the filter cartridge should re-seat itself. If not, do it one or two more times.

2.9.2 INTERNAL LEAKS

Some of the internal plumbing is small diameter urethane hose, which can get hot and humid, and then cause leaks. Shut down the unit, revert to tank air, and arrange to have the unit serviced promptly.

2.9.3 PRESSURE CYCLING

There are many reasons why the baselines of the chromatogram can cycle, causing poor integration. One of the reasons is failure of the zero air generator to supply sufficient air through improper setting of the controls. Note the following:

a) The reservoir is designed to eliminate the fluctuations caused by the pulsing of the moisture filters in the zero air generator (you can hear this cycle occur about every five minutes). TOO MANY reservoirs will CAUSE cycling, as one device strives to replenish another. Be careful not to have too many large volumes reservoirs in series.

b) All copper tubing should be examined to ensure that the cut ends are fully open. Most tubing cutters reduce the diameter of the tubing considerably (by at least 50%), creating an impedance at the cut end. When several such pieces are joined together, the result is a system of pinched tubes that considerably diminish the flow of air. This makes it more difficult for the reservoir and pressure regulators to perform their functions adequately and leads to cycling of the baseline.

c) Use only high quality, two stage regulators, making sure that they are supplied with sufficient pressure (a certain minimum pressure drop across the diaphragm is required), and use the minimum number of controls and fittings. Tubing should be kept short and as large a diameter as possible.

2.9.4 DRAINING MOISTURE

The holding tank on the electrical compressor will accumulate condensation, which should be drained at regular intervals. Recent versions of the compressor may include an automatic, electrical solenoid to drain the tank. Periodically check for correct operation. The large, black filters on the rear of the Zero Air Generator (with thick black tubes attached) are designed to expel large water droplets that might escape from the compressor. Make sure that the tubes do not hang over electrical equipment where the drips may cause a problem.

3 SYSTEM OPERATION

3.1 SERVICES AND SETTINGS

The optimum settings for the system are well known, and should not be modified without excellent justification.

The following tables lists the services and settings recommended for various parts of the system.

3.1.1 GASES AND FILTERS

Table 1. Gases and Filters

GAS	SUPPLY	FILTERS	GRADE	USAGE
HYDROGEN	CYLINDER	MOISTURE = P-E # N9301178 HYDROCARBON = P-E # N9301192	UHP (99.999% PURE) <0.5PPM TOTAL HYDROCARBONS	25 - 30 ML/MIN.
HELIUM	CYLINDER	MOISTURE = P-E # N9301178 OXYGEN = P-E # N9301179 INDIC. OXYGEN = P-E # N9301191	<2.0PPM OXYGEN <5.0PPM H_2O	~5 ML/MIN.
AIR	GENERATOR OR CYLINDER	SMALL MOISTURE = P-E #N9301193	<2.0PPM OXYGEN <5.0PPM H_2O	~1350 ML/MIN.

3.1.2 ATD 400 SETTINGS

Table 2. ATD 400 RECOMMENDED PARAMETER SETTINGS

ATD PARAMETER	VALUE	DESCRIPTION
MODE	2	
FIRST TUBE	1	
LAST TUBE	1	
OVEN TEMP	100**	KEEP THE OVEN TEMP DOWN TO AVOID GETTING THE TUBE STUCK. THE TEMP NEEDS TO BE ONLY HIGH ENOUGH TO PREVENT CONDENSATION
DSRB TIME	1.0	DEFAULT MINIMUM
VALVE TEMP	175	
INJ/TUBE	99	INFINITE SAMPLING
TRAP FAST	YES	40degC/SEC
CYCLE TIME	60	SETS HOURLY SAMPLING
TRAP LOW	-30	

TRAP HIGH	325	
TRAP HOLD	5	
INLET SPLIT	NO	
OUTLET SPLIT	YES	NEED 3.5ML/MIN
RECYCLE	NO	
TRANSFER LINE TEMP	200	
MIN PSI	0**	SET TO ZERO TO PREVENT UNFORESEEN HALTS
STD INJ	40	SETS SAMPLING TIME

**These values are different from the User Manual recommendations

3.1.3 GAS CHROMATOGRAPH CONFIGURATION S ETTINGS

TABLE 3. GC SYSTEM CONFIG. SETTINGS

AUTOSYSTEM GC CONFIGURATION PARAMETER	SETTING
SET TEMPERATURE LIMIT	200°C
EQUILIBRATION TIME	0
COOLANT	NONE
INJ 1	NONE
INJ 2	NONE
GAS DISPLAY 1	NONE
GAS DISPLAY 2	PSIG
VALVE 1	NONE
VALVE 2	VALVE
VALVE 3	NONE
VALVE 4	NONE
VALVE 5	NONE
VALVE 6	NONE
DETECTOR 1	FID
FILTER	200 ms
DETECTOR 2	FID
FILTER	200 ms
AUX	NONE
OUTPUT 1	INTEGRATOR
OUTPUT 2	INTEGRATOR
INTEGRATOR OFFSET	5 mV

3.1.4 GC METHOD PARAMETERS

Table 4. RECOMMENDED GC METHOD PARAMETERS

AUTOSYSTEM GC CONTROLLING METHOD PARAMETERS	VALUE
OVEN TEMP 1	46°C**
ISO TIME	15 min

RAMP RATE 1	5degC/min
OVEN TEMP 2	170ºC
ISO TIME 2	0
RAMP RATE 2	15degC/min
OVEN TEMP 3	200ºC ABSOLUTE MAXIMUM
ISO TIME 3	6 min
FID 1 RANGE	1
FID 2 RANGE	1
DET 1 TEMP	250ºC
DET 2 TEMP	250ºC
ATTN	1
ATTN	1

**Value different from the manual. This setting saves about 1 minute during recycle and allows the GC to stabilize faster.

3.1.5 TURBOCHROM METHOD PARAMETERS

Table 5. RECOMMENDED TURBOCHROM PARAMETERS

PARAMETER	VALUE
DETECTOR SAMPLING RATE	3.0 SAMPLES/SEC
BUNCHING FACTOR	3.0 FOR MOST COMPOUND, 1.0 FOR SOME
AREA THRESHOLD	5 times NOISE THRESHOLD
NOISE THRESHOLD	12 TO 20 mV/SEC
RESPONSE FACTOR PLOT COLUMN	~3200 TO 3700
RESPONSE FACTOR BP-1 COLUMN	~2800 TO 3800
DATA COLLECTION TIME	48 MIN

3.2 SAMPLING PROCEDURES

3.2.1 ATD 400 CYCLE

The system is set up initially by the Perkin-Elmer Installation Engineer to sample from the sampling port of the ATD 400 at 60 minute intervals. (Refer to Figure in Appendix C of User Manual 0993-8970 of the User Manual, reproduced below.)

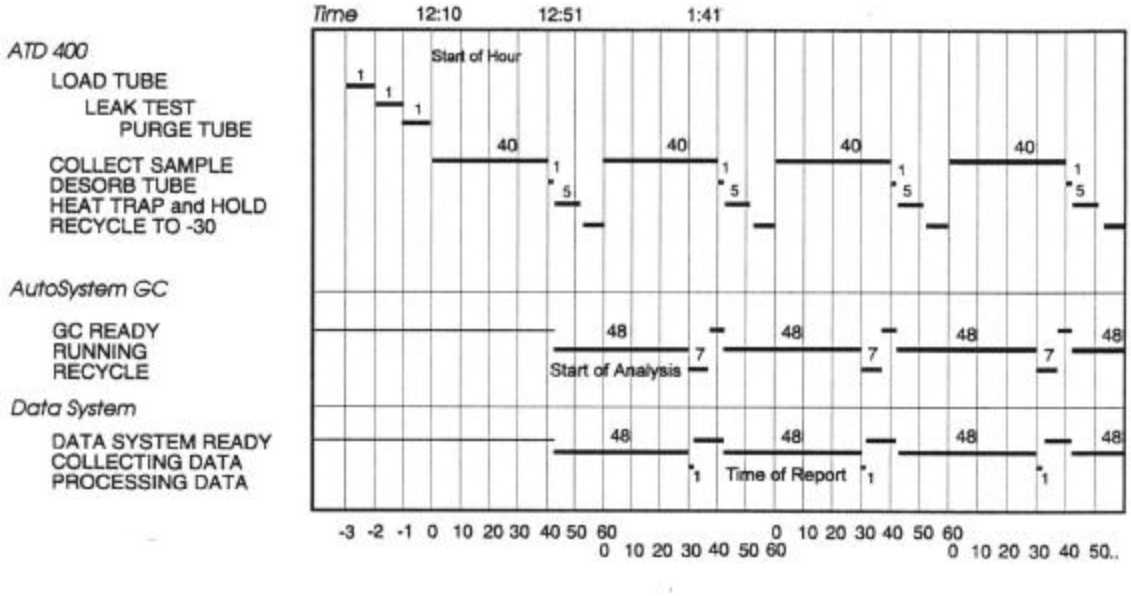

Figure 3. Perkin Elmer On-Line System Timing Diagram

You can see that, once the initial loading and starting of the ATD occurs, a new sample is collected over 40 minutes of every hour. The sample enters the ATD through the SAMPLE port on the back of the ATD On-Line Accessory at the rate set on the mass flow controller control box (15 mL/min.). At the end of 40 minutes the total amount of sample collected is 40 x 15 = 600 cc. The system waits one minute (DESORB TUBE) then injects the sample (HEAT TRAP and HOLD). The ATD then cools down to -30°C and waits. The next sample will then start to be collected exactly 60 minutes after the previous one, and the cycle continues. As long as nothing else occurs, the ATD 400 will continue to collect and inject ambient air samples indefinitely.

3.2.2 GC CYCLE

The GC receives a start signal (contact closure) at the instant the ATD starts heating the trap. The analysis continues for 48 minutes, with the GC temperature rising from 46°C to 200°C. At the end of the analysis the GC has 60 - 48 = 12 minutes to cool down and return to the initial Ready state so the next run can begin.

3.2.3 DATA SYSTEM CYCLE

The Turbochrom 970 A/D Interface starts and stops identically with the GC (i.e. it runs for 48 minutes and waits for 12 minutes in synchronism with the GC as long as it has a valid sequence to execute).

3.2.4 STREAM SELECTION VALVE

Whether the ATD 400 takes a sample from ambient air or from a canister standard is determined by the position of the stream selector valve. The valve is controlled by relays #6 and #7 in the GC, or by timed event from the 970 Interface (as shown in Figure 4) or by manual operation of the 970 Interface relays.

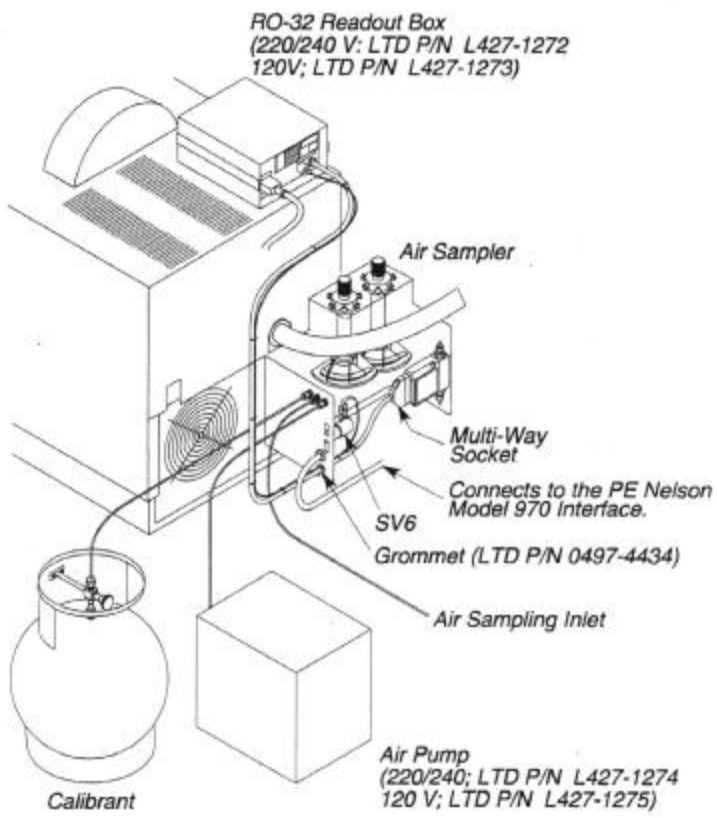

Figure 4. Connections to the on-line valves

3.2.5 "SAMPLING" TIMED EVENTS

It is a good idea to include the following timed event in your analysis:

0.01 minute	Relay 7 On
0.02 minute	Relay 7 Off

(Assuming relay #6 switches to the sample stream)
(Assuming relay #7 switches to the calibration stream)

[Operation of a relay requires two steps - (1) energize and (2) de-energize.] The effect of these two steps is to switch the stream selector valve to the "Sampling" position. The reason for doing this is that the ATD 400 will now always default to "Sampling" if the operator forgets to switch the valve back, and you will only need to use one timed event to take a Calibration Standard aliquot (the second event is now built in). This procedure is shown schematically below.

3.3 TAKING A CALIBRATION ALIQUOT.

Here is the hourly timing diagram for the stream selector valve:

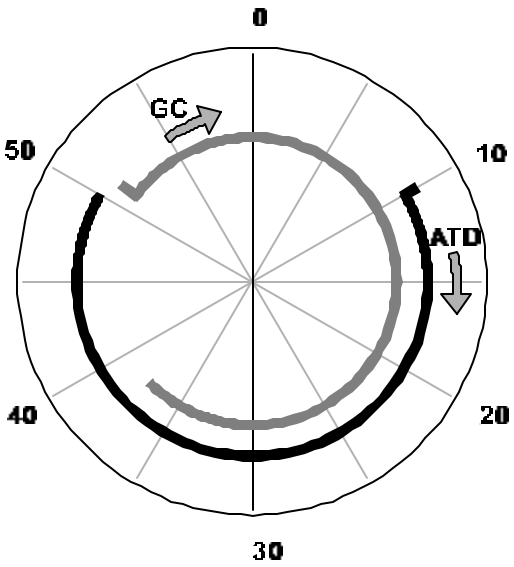

Figure 5 A. Stream Selector Valve Timing

At (say) 10 minutes after the hour the ATD 400 starts to collect SAMPLE. At 51 minutes after the hour the GC starts running. The stream selector valve is set by the timed event at 51.01 to SAMPLE, as shown next:

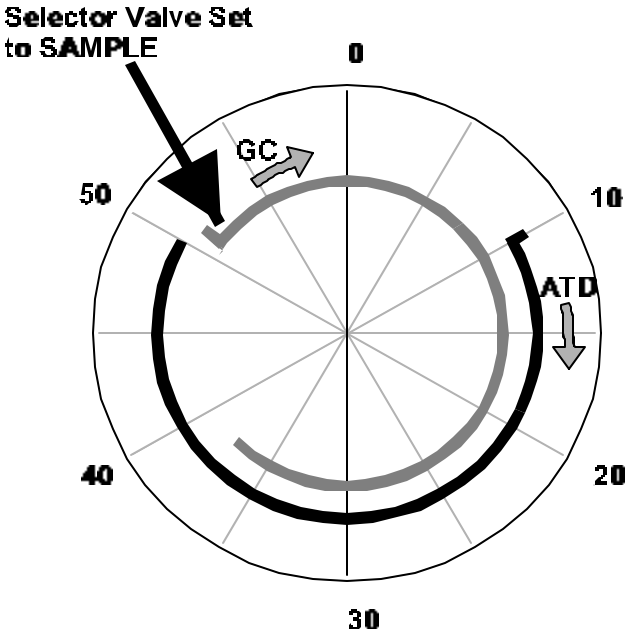

Figure 6 B. Stream Selector Valve Timing

In this case, when the ATD starts to collect again it will be from the SAMPLE stream.

To cause the ATD to collect a canister standard, relay #6 must be operated "after" 51.05 minutes and "before" 10 minutes (i.e. at the top of the hour). **This 19 minute window is the only time that you can change these setting without invalidating the ATD sampling cycle.** In the next example a calibration standard is collected:

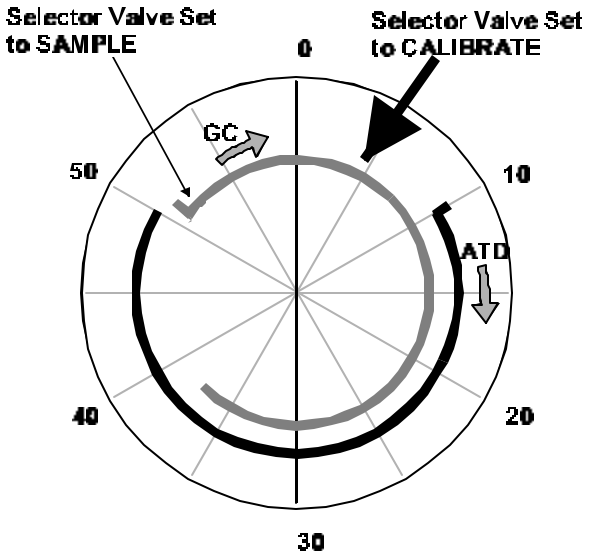

Figure 7 C. Stream Selector Valve Timing

The command to do this is

	Relay #6	ON
	Relay #6	OFF

Or, to do the same thing automatically you would program

4.01	RELAY #6	ON
4.02	RELAY #6	OFF

There is no need to issue the instruction to revert to the SAMPLE stream, because the timed event is now already built in (at 51.01).

APPENDIX A: PAMS AIRS TARGET LIST

Num	Code	Compound
1	43203	Ethylene
2	43206	Acetylene
3	43202	Ethane
4	43205	Propylene
5	43204	Propane
6	43214	Isobutane
7	43280	1-Butene
8	43212	n-Butane
9	43216	trans-2-Butene
10	43217	cis-2-Butene
11	43221	Isopentane
12	43224	1-Pentene
13	43220	n-Pentane
14	43243	Isoprene (2-Methyl-1,3-Butadiene)
15	43226	trans-2-Pentene
16	43227	cis-2-Pentene
17	43244	2,2-Dimethylbutane
18	43242	Cyclopentane
19	43284	2,3-Dimethylbutane
20	43285	2-Methylpentane
21	43230	3-Methylpentane
22	43245	1-Hexene*
23	43231	n-Hexane
24	43262	Methylcyclopentane
25	43247	2,4-Dimethylpentane
26	45261	Benzene
27	43248	Cyclohexane
28	43263	2-Methylhexane
29	43291	2,3-Dimethylpentane
30	43249	3-Methylhexane
31	43250	2,2,4-Trimethylpentane (Isooctane)
32	43232	n-Heptane
33	43261	Methylcyclohexane
34	43252	2,3,4-Trimethylpentane
35	45202	Toluene
36	43960	2-Methylheptane
37	43253	3-Methylheptane
38	43233	n-Octane
39	45203	Ethylbenzene
40	45109	m/p-Xylene
41	45220	Styrene
42	45204	o-Xylene
43	43235	n-Nonane
44	45210	Isopropylbenzene
45	43209	n-Propylbenzene
46	45212	m-Ethyltoluene (1-Ethyl-3-Methylbenzene)
47	45213	p-Ethyltoluene (1-Methyl-4-Methylbenzene)
48	45207	1,3,5-Trimethylbenzene
49	45211	o-Ethyltoluene (1-Ethyl-2-Methylbenzene)
50	45208	1,2,4-Trimethylbenzene
51	43238	n-Decane
52	45225	1,2,3-TrimethyIbenzene
53	45218	m-Diethylbenzene
54	45219	p-Diethylbenzene
55	43954	n-Undecane
56	43141	n-Dodecane*
57	43102	TNMOC
58	43000	PAMHC