Gas Chromatograph Varian 3700 Series
User Manual

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Working with Gas Chromatography

A. Introduction

This manual has been designed in order to serve as a simple guide for the use of the Gas Chromatograph Varian 3700 Series. Here we describe as clear as possible the way the GC should be managed in order to function and what are the parameters that the user should follow when a run wants to be taken.

The main use that is given to this GC is to follow the kinetics from two independent systems: a batch reactor and a high-pressure cell (connected with the RAIRS-UHV chamber). The first system is composed of a dosing line, a quartz reactor (where a supported catalyst can be placed) and a circulating pump. The second one is used to follow the reactions that occur inside the high-pressure cell, where a Pt(111) single crystal is used; this system shares the circulating pump and some of the lines used in the other system.

B. Basic Operations.

The series 3700 Gas Chromatograph is a modular, dual-column instrument comprised of the basic unit to which a broad range of optional modules may be added. The actual instrument is equipped with a FID (flame ionization detector) and ECD (electron capture

detector). However, the detector that is connected to the column and has been used for the type of analysis required is the FID.

The instrument also has removable front-opening door and each heated zone (injectors, detectors, column oven) is insulated to minimize heat-transfer effects between zones. The temperature of each heated zone can be controlled independently. The column that is installed in the system is a 23% SP-1700 on 80/100 Chromosorb PAW (30' x 1/8" OD SS). (Catalog page.pdf) The maximum temperature for this column is 110^{o}C; for this reason, it is recommended not to use temperature ramps that may exceed this value (!!).

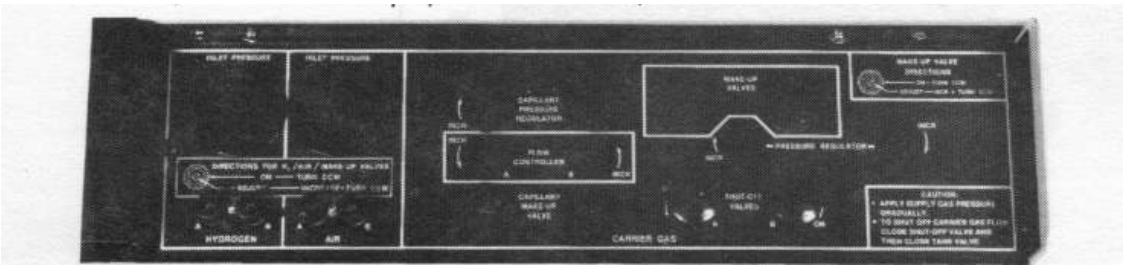
The system is connected to a multimeter, which is capable of transmit the voltage values to a PC via a RS232 connection.

1. Pneumatics.

All instrument gases are connected by means of 1/8" fittings on the rear panel of the pneumatics cabinet. All fittings are labeled for specific gases. For the FID we have installed in the system N_2, H_2 and compressed air. The first gas serves as the carrier while the other two are used for the ignition of the flame in the detector. The inlet pressures set on each gas regulator are the followings: N_2 = 60 psi, H_2 = 40 psi, and Air = 40 psi.

1.1. Gas Flow Adjustment.

All gas flows are regulated at the control panel of the pneumatics cabinet (Figure 1). The procedure outlined below applies to manually adjusted gas flows. Adjust the gas as follows:



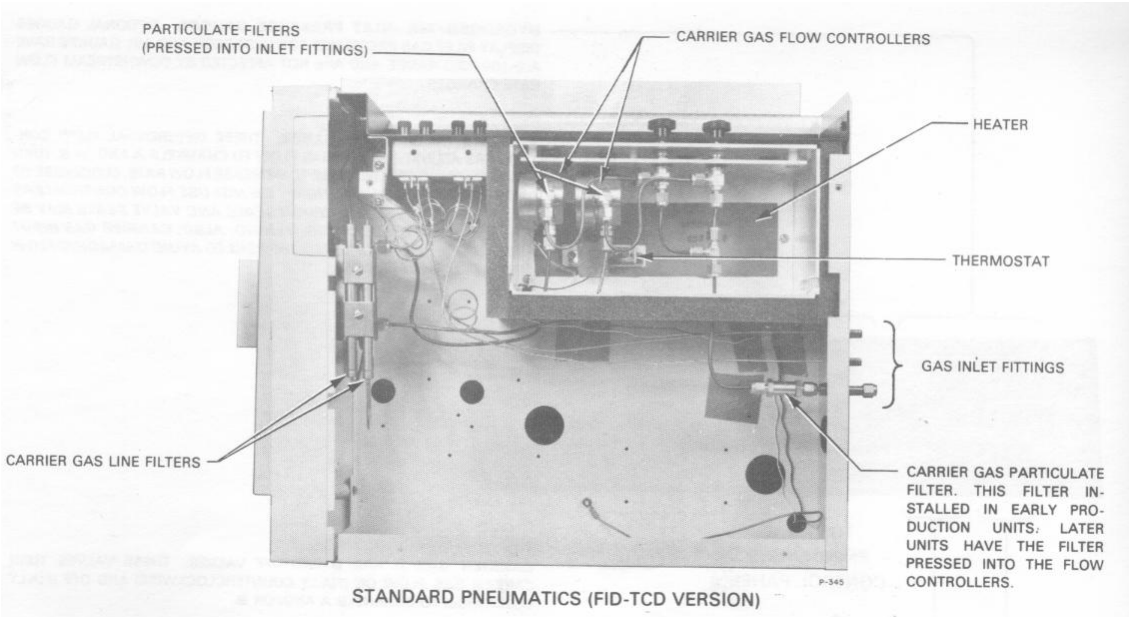


Figure 1. Flow control panel

(1) Set supply pressure of gas being measure to the pressures listed above. Gas pressures are indicated at the second stage regulator gauge on the supply cylinders. The carrier gas pressure can be also checked on the gauge located in the front panel of the GC.

(2) Connect soap-bubble flow meter to the selected detector as shown in Figure 2.

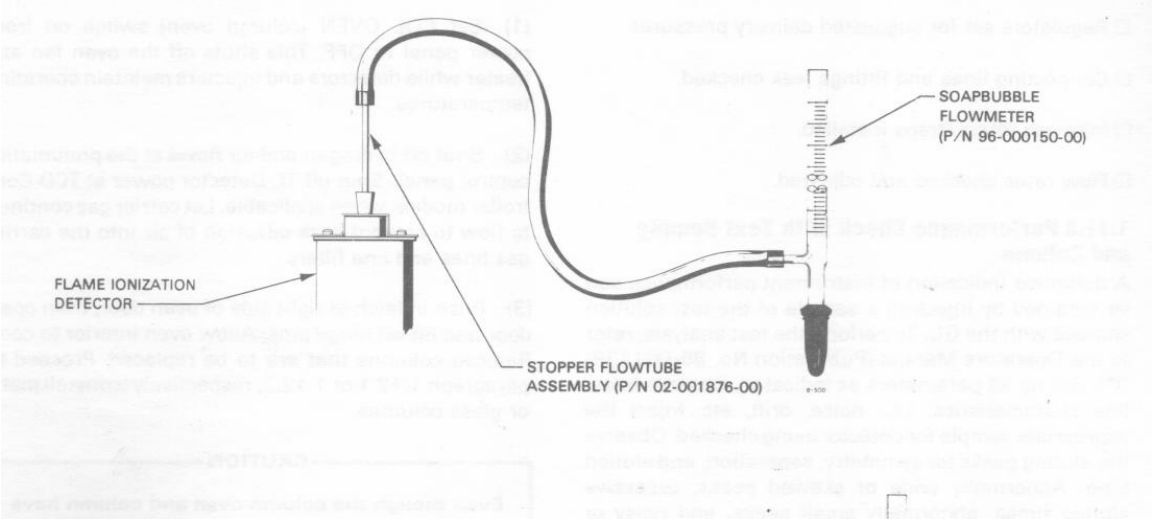


Figure 2. Soap-bubble system.

(3) Turn appropriate gas shutoff valve all the way counterclockwise, the clockwise 1/8 turn.
(4) Force a bubble above the inlet of the flowmeter by squeezing the soap reservoir bulb. Using a stopwatch measure the elapsed time it takes the bubble to move from 0 to 10. Calculate the rate in cc/min. To avoid contamination of cell, do not allow soap solution from flowmeter to flow into detector exit tubes.
(5) Carefully adjust the appropriate gas flow regulator valve to obtain the desired rate. Unless hydrogen flame is lighted immediately after making the flow adjustment, be sure to shut off hydrogen flow. Escaping hydrogen gas is both a waste and a potential hazard.

1.2. Column Installation.

All injector and detector fittings (GC column inlet and outlet) are located on the interior ceiling of the column oven. For this two detector GC, there are two injector (column inlet) fittings (actually, there are four but two are disconnected) and four detector (column outlet) fittings, one each for the two ionization detectors and two for the ECD detector. The injector body that is used is a ¼" OD fitting. The two ionization fittings are also of ¼" OD fittings. In order to install the preconditioned column do as follows:

(1) Set COL OVEN (column oven) switch on front power panel to OFF. This shuts off the oven fan and heater while detectors and injectors maintain operating temperatures.
(2) Shut off hydrogen and air flows at the cylinders (so in that way is not necessary to change the flows for each gas as set before). Let the carrier gas continue to flow to prevent back diffusion of air into the carrier gas lines and line filters.
(3) Push in latch at right side of oven door, then open door and lift off hinge pins. Allow oven interior to cool. Remove columns that are to be replaced.
(4) Stainless steel columns should be installed with stainless steel ferrules and nuts. For best sealing and longest remake life, follow the installation and tightening procedures used for any Swagelok connection. If the column has not been preconditioned, do not

connect the detector en (outlet). Precondition the column at 25°C below the maximum operating temperature of the liquid phase for 10 hours with 10–15 ml/h carrier gas flow. Matching dimensions between column and oven fittings are not so critical since metal columns can be bent to facilitate installation. **Be sure the column is inserted far enough to bottom out against internal shoulders of injector and detector fittings**. This is particularly important for on-column injectors where incomplete or partial insertion into the injector body would destroy the advantages of the on-column mode.

2. Operation.

This section provides brief operating procedures intended to aid the operator in getting the GC set up and into operation as quickly as possible. A most detailed explanation of how to run an experiment using the batch reactor is given in section c of this manual. In order to set up the GC prior an experiment follows the next steps:

1. Open the N_2 carrier gas to the selected pressure (the flow should be set to 25 mL/min).
2. Set oven temperature to 35°C by setting it in the Initial Temp on the Auto Linear Temperature Controller Panel (the temperature can be checked by pressing COL button), and then turn COL OVEN switch to HTR & FAN position.
3. In the Readout Temperature Controller, set the TEMP CONTROL INJ A to 10 (which is 110°C) and the TEMP CONTROL ION DET to 11 (110°C). The temperatures will start to increase and you can check them just by pushing the bottom below the temperature reading screen. Wait until all the red LEDs of Injector, Column, and Ion Detector are turned off. (Less than 20 min)
4. In the meantime, connect the DMM to the PC and open the DMM software. You may start to see some voltage reading (see Figure 3). Do not try to set this value to zero by using the ZERO knob in the FID controller.

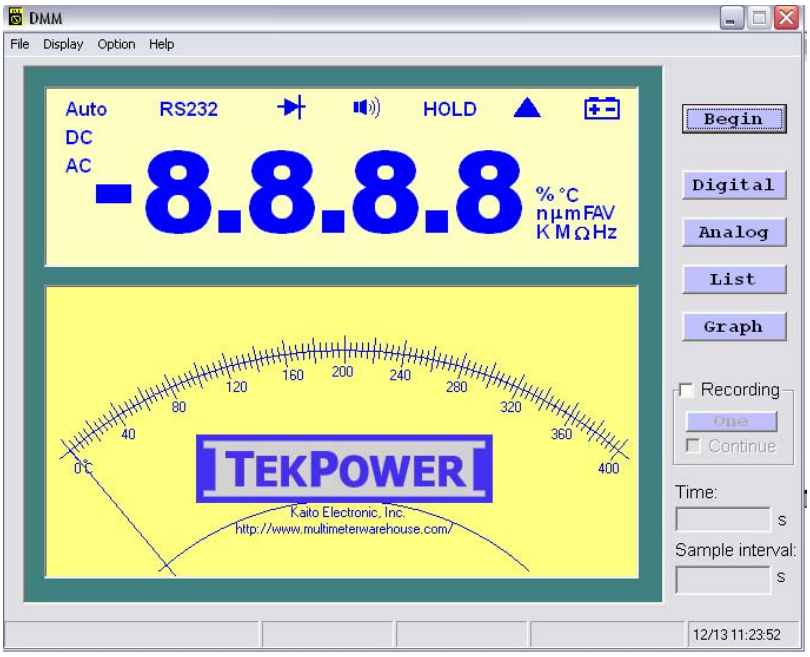


Figure 3. DMM software window.

5. Once the oven, detector and injector temperatures have reached the desired temperature, open the cylinders for Air and Hydrogen. Then turn the IGNITOR switch to A to ignite the flame till the voltage in DMM jumps to around 30. This value will be decreased immediately. You should hear a sound like an explosion; if not, use a metal or a glass material and put it closer to the top of the detector. An indication of water vapor on the surface of the material indicates that the flame is on. If the flame fails to ignite, repeat the procedure one more time. If the problem persists, check the flow for air and hydrogen. Also, the ignition of the flame can be checked with an increase in the voltage reading. Wait for the stabilization of the baseline (approximately 20 min). Once the baseline is stable, you can set the voltage to zero by moving the ZERO knob.

6. Now, everything is ready to run an experiment.

* *FID Setting*	*Attenuator = 1,*	*Range = ECD 10, 10^{-11},*
	Output = positive (+),	*Mode = Ion Det. A.*

C. How to make a run using the Batch Reactor.

The batch reactor consists of the following elements:

- A mechanical pump, used to keep a vacuum on the line of about 10mtorr.
- A circulation pump, used to circulate the gases in the line, while the reaction takes place.
- Seven valves. One is used to connect the dosing line with the mechanical pump; four are used for the dosing of Ar, H_2, O_2 and the probe gas; other connects the dosing line with the sampling loop; and the other two, are used to connect the sampling loop with the quartz reactor. Also, we make use of two other three-way valves that are used to switch the sampling loop from the batch reactor to the high-pressure cell.
- The vacuum pressure and the dosing pressure are followed with a TC and a Pirani gauges. The TC gauge is located in the dosing line and is used to check that a good vacuum is obtained here. The Pirani gauge is used to check the vacuum in the sampling loop and also to check the pressures of the gases introduced in such line (although careful should be taken with this gauge, mostly because its sensitivity depends on the type of gas introduced).
- A 6-way-sampling valve located in the GC, which is used to introduce the gases in the GC for further analysis.
- A quartz reactor, where the catalyst is place.

In order to make a run, the following steps should be followed (the GC is supposed to be ready to be used):

1. Place the catalyst in the quartz reactor. About 3–5 mg of the catalyst is placed in the reactor between some layers of quartz wool above the metal disk placed in the reactor. (The loading amount of catalyst will be depended on the experimental conditions and plans.)

2. The reactor is placed inside the heating jacket and connected carefully with the ultra-torr connectors to the sampling line. The valves are open and the system is pump. The pressure should be below 60 mTorr. If not, check connections or disconnect the reactor and connect it again. Be careful not to break it.
3. Dry the catalyst usually at 150^{o}C for 1 hour.
4. Activate the catalyst via reduction or oxidation cycles at a proper temperature for hours as long as needed. 100 Torr of H_2 may prevent from sintering while the temperature goes up to 350^{o}C for the pretreatment. At 350^{o}C, fill the system up to 400 torr of the gas and turn on the recirculation pump.
5. After the pretreatment of catalyst, wait until the temperature comes back to 100^{o}C (or any desired reaction temperature.)
6. Turn off the circulation pump and then evacuate the system.
7. Once the vacuum is reached, the gases can be introduced. The gases with lower partial pressure are introduced first (usually Ar is the last one to be introduced due to the high partial pressure use). The dosing line is isolated from the mechanical pump by closing the proper valve. The valve of the probe molecule is introduced until the desired pressure is reached in the Pirani gauge; the valve that connects the dosing line with the sampling loop is closed (check that the pressure in the sample loop is stable). Evacuate the dosing line (check the pressure with the TC gauge) and, then, be ready to repeat the same procedure followed with the probe molecule for hydrogen and Ar.
8. After all gases are introduced, the circulation pump is turned on.
9. After 2 min, the 6-way valve is used by moving the handle to the other side. Immediately after, the START button in the GC controller is pushed as well as the start button in the DMM software to start the collection of the data. After the peaks have appeared, leave the system run for additional 10 min in order to be sure that nothing else remains in the GC column and then push the STOP button in the GC controller and in the software. Save the collected data and wait until the system is ready for a new run (showed by the LEDs in the GC). If multiple runs are desired, the

handle can be moved every 12 min without pressing any button in the software and the GC controller.

D. How to turn the system off.

1. Press RESET button.
2. In the Readout Temperature Controller, set the TEMP CONTROL INJ A to 00 (which is 0^{o}C) and the TEMP CONTROL ION DET to 00 (00^{o}C). The temperatures will start to decrease.
3. Turn COL OVEN switch to FAN only position.
4. Set the PID controller from RUN to STOP.
5. Turn off the circulation pump.
6. Pump the gases in the reactor out.
7. Close H_2 and Ar gas cylinders.
8. Wait until the DMM reaches to negative values.
9. Turn COL OVEN Switch off.
10. Close N_2 cylinder.

E. How to make a run using the High-Pressure Cell in the RAIRS chamber.

Under Construction for Shinji.

Working with Vacuum Equipment

A. General

This is not an ultra high vacuum chamber, but nevertheless, careful and correct handling of the equipment parts is a prerequisite to obtain sensitive data.

B. How to find leaks

Try to locate the leak by closing of parts of the gas lines and the reaction chamber etc. In higher pressure ranges, careful spraying of acetone and observation of the pressure also works. This method can also be used to find leaks around the reaction chamber and the gas lines. The latter, however, are easier checked when pressurized, e.g. with Ar and the connector are sprayed with some drops of “Snoop”.

C. Building Gas lines with Swag Lock connections

Although the building of gas lines is not an important concern for ultra high vacuum, it is often necessary in the lab and does require some attention. Refer to the description of the parts and their handling in the Swaglok catalogue. Avoid mixing brass and stainless steel connections, as brass is softer and ferules and threads can be damaged. All nuts have to go smoothly on the thread; do not force a nut on a connection! Clean stainless steel tubing with acetone before assembly. Cut the tubing to the required length,

Installation of fittings:

- Insert the tubing into the fitting (or into a nut and place the ferrule in it, small ring first).
- Turn the nut finger tight.

- Hold the body of the fitting with a back-up wrench, tighten the nut 1-1/4 turns (for all tubing smaller than 3/16’’, only a 3/4 turn is necessary)
- Open the nut again to check if the ferrule is sitting tight and you cannot move the lower ring.

Gas lines can be leak checked with “Snoop” when pressurized. Just put some drops on the fittings, bubbles will show the leak.

D. Start Pumping

1. Check if all valves are closed, particularly the ones to gas supply lines.

2. Turn on the rotary pump and check the pressure with the TC gauge that is connected directly to the dosing line close to the pump.

3. Once the pressure in the dosing line is below the 2 mTorr regime, open the valve that connects the dosing line with the batch reactor loop. The pressure should be close to 2 mTorr. If this is not the case, close the valve and check connections.

E. Shut down

1. Close all valves, in particular the ones to the gas lines.

2. Close the valve connecting the dosing line with the rotary pump.

3. Turn off rotary pump and open the cap in the molecular sieve trap.

If you want to vent, you can use the Ar from the connected gas line. With stepwise opening of the valves you can fill the whole system with Ar until the pressure reading is close to the atmospheric pressure (check the pressure by means of the Baratron gauge). Alternatively, you can connect a nitrogen cylinder to the system and do the same.

F. Maintenance

The rotary pumps require regular oil change, once every half year. As the pump for the gas supply is sometimes pumping a high load of e.g. hydrocarbons or other gases contaminating the oil, and oil change might be necessary in shorter intervals. Together with that, it is recommended to change the molecular sieves. Mechanical pump oil from Kurt Lesker (TK0-19+) is used.