

PYROLYZER OPERATION AND MAINTENANCE MANUAL

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<http://cires.colorado.edu/IIDF/index.html>

PYROLYZER OPERATION AND MAINTENANCE MANUAL

Introduction

The University of Colorado IIDF¹ Pyrolyzer System (Fig. 1) has two major components, a pulsed hyperthermal silicon carbide nozzle and a rack-mountable electronic control unit. The pulsed nozzle is based upon the design conceived by Chen *et. al.*^{2,3} and is installed in a water-cooled housing that attaches to the vacuum shroud of a standard APD Products cryostat. The nozzle consists of a sample inlet tube and a resistively heated SiC tube mounted at the exit of a high-speed valve. Thus, a pyrolyte sample entrained in an inert gas can be fed in short bursts into the hot (300 to 1800 K) SiC tube. Chen has found this pulse mode of operation to be superior to conventional continuous-flow pyrolyzers for the thermal production of reactive intermediates because, in a pulsed system, the residence time is shorter and the pressure is lower in the hot region of the tube. This results in fewer bimolecular reactions and thus fewer byproducts. The second major component, the control unit, regulates both the temperatures of the sample inlet, valve, and SiC tube and the rate and duration of the gas pulses. Careful adjustment of the operating conditions allows the user to optimize the system for the generation of a large range of products.⁴

Figure 1 CU IIDF Pyrolyzer System



¹ The Integrated Instrument Development Facility, University of Colorado, CIRES/Dept. of Chemistry and Biochemistry; <http://cires.colorado.edu/IIDF/index.html>

² P. Chen, in *Unimolecular and Bimolecular Reaction Dynamics*, edited by C. Y. Ng, T. Baer, and I. Powis (John Wiley & Sons, NYC, 1994), Vol. 3, pp. 372.

³ D. W. Kohn, H. Clauberg, and P. Chen, *Rev. Sci. Instrum.* **63**, 4003 (1992).

⁴ X. Zhang, A. V. Friderichsen, S. Nandi, G. B. Ellison, D. E. David, J. T. McKinnon, T. G. Lindeman, D. C. Dayton, and M. R. Nimlos, *Rev. Sci. Instrum.* **74**, 3077-3086 (2003).

Electronic Control Unit

The rack-mountable microprocessor-based control unit consists of three independent auto-tunable digital temperature controllers (Love Control Inc., Series 16) and a pulsed valve controller.

Temperature Controllers – These controllers regulate the temperatures of the pulse valve, sample holder, and the SiC tube. The sample and pulse valve heater controllers have been pre-programmed to accept a temperature range of 20°C to 200°C, while the pyrolyzer controller accepts a temperature range of 20°C to 1500°C. Normally, the only thing the user should have to do to use the Love controllers is to set the desired operating temperatures. This is done by the following series of keystrokes (buttons at the bottom of the controllers):

- 1) Press ◀ (far left key).
- 2) Press ▲ or ▼ to increment or decrement the desired operating temperature.
- 3) Press ▶ (far right key).

If the operating temperature of the pyrolyzer is changed by large amounts or if the SiC tube has been replaced, the temperature stability may deteriorate, and it may be necessary to auto-tune the pyrolyzer controller. After entering the desired operating temperature, this is done by the following series of keystrokes:

- 1) Press ▲ and ▶ simultaneously (keys illuminate).
- 2) Press ◀ repeatedly until **tunE** appears in the lower display.
- 3) Press ▲ repeatedly until **SELF** appears in the upper display.
- 4) Press ▶.
- 5) Press ◀ (**LErn** appears in the lower display).
- 6) Press ▲ (**YES** appears in the upper display).
- 7) Press ▶.
- 8) Press ◀ repeatedly until the normal display appears.

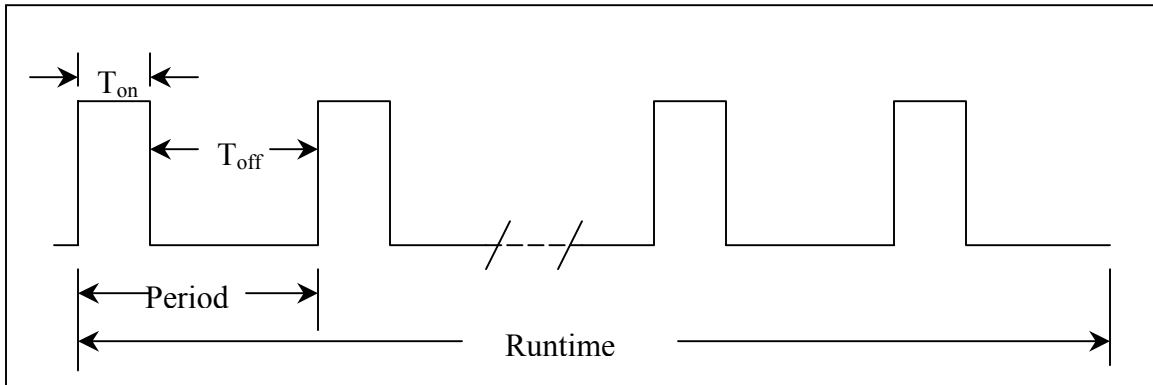
The decimal point in the lower display will flash until tuning is completed and the controller optimized for the new operating temperature. Full details on how to configure and program the Love controllers may be found in the attached “Instructions for the 16A2 & 16A3 Series Microprocessor Based Temperature/Process Control” from Love Controls.

CAUTION

Users should make sure they fully understand the instruction manual before reconfiguring or programming the Love controllers. Incorrect settings could result in poor operation or could even damage the heaters, pulsed valve, or SiC tube. See Appendix 3, “Default Love Controller Settings,” for a list of standard parameter values.

Pulsed Valve Controller – This controller allows the user to set the rate that sample is introduced into the hot nozzle. The user may choose one of ten operating modes that use six parameters. Each mode accomplishes essentially the same thing but allows the user to choose which combinations of the parameters are used to define the sample introduction rate. Not all parameters are used by all modes. Figure 2 illustrates the definition of some of the parameters.

Figure 2 Valve Pulse Waveform Parameters



Parameters

- 1) T_{on} : The length of time the pulse valve is open during each period
Range: 0.1 to 99.9 msec
- 2) T_{off} : The length of time the pulse valve is closed during each period
Range: 0.1 to 99.9 msec
- 3) Duty: The percent time the valve is open ($T_{on}/Period * 100$)
Range: 1 to 99%
- 4) Frequency: The number of times per seconds that the valve is opened
Range: 1 to 200 Hz
- 5) Runtime: The length of time for which the valve will open and close
Range: 1 to 9999 seconds (2.7 hrs)
- 6) Cycles: The number of periods for which the valve will open and close
Range: 1 to 9999 cycles

Operating Modes

In the first nine operating modes, parameter T_{on} is used in combination with the user's choice of a way to define the time that the valve is off during each period (T_{off} , Duty, or Freq) and the length of time that the valve will run (Runtime, Cycle, or Manual). The tenth mode is for test and maintenance and simply allows the user to manually open and close the valve by pressing the Enter (#) key. The operating modes are:

- 1) T_{on} /Duty/Runtime
- 2) T_{on} /Freq/Runtime
- 3) T_{on} / T_{off} /Runtime
- 4) T_{on} /Duty/Cycles
- 5) T_{on} /Freq/Cycles
- 6) T_{on} / T_{off} /Cycles
- 7) T_{on} /Duty/Manual
- 8) T_{on} /Freq/Manual
- 9) T_{on} / T_{off} /Manual
- 10) Manual On/Manual Off

CAUTION

Operating mode 10 (Manual On/Manual Off) is intended for test and maintenance use only. Do not leave the valve on for more than about a minute or the coil may overheat. Monitor the coil temperature with the valve temperature controller to make sure the temperature does not go above 200°C.

To select an operating mode and enter values for the parameters, use the following keystrokes:

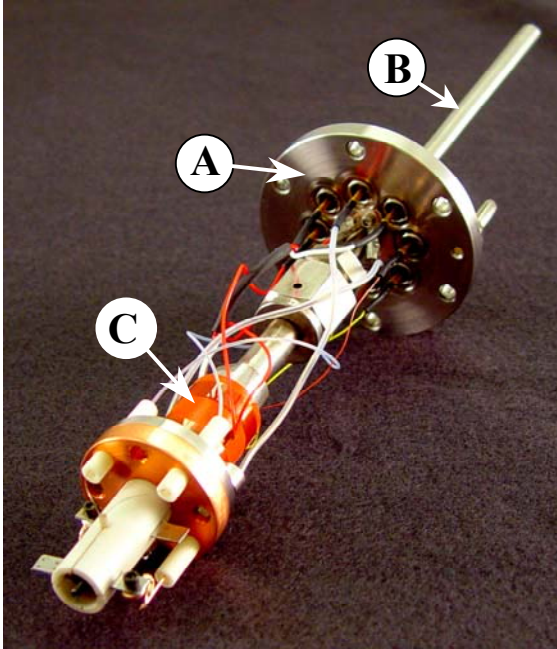
- 1) Press Index (*) to advance to the next operating mode.
- 2) Press Enter (#) to accept the selected operating mode.
- 3) Press the desired number key to change the value of a digit. Index (*) to the next digit.
- 4) Press Enter (#) to accept all values and begin running the valve.

After an operating mode is selected, it will remain in effect with the current parameters until another mode is selected. Pressing Enter (#) twice (steps 2 and 4 above) will repeat operation with the current mode and parameters. The current operating mode and all parameters are retained in microprocessor memory even if the control unit is turned off.

Hyperthermal Nozzle

Photographs of the hyperthermal nozzle with the water-cooled housing removed are shown in Figs. 3 and 4. The components of the nozzle are: (A) vacuum flange with electrical and sample feedthroughs, (B) sample inlet tube, (C) pulsed valve with silicon rubber heater and thermocouple, (D) valve heat sink/mounting flange with (E) locking screw, (F) alumina radiation shield, (G) spring clips, (H) graphite electrical connectors, and (I) SiC tube. While the pulsed valve and a single SiC tube can operate for dozens of hours without attention, they will eventually fail, and disassembly of the nozzle will be required.

Figure 3 Nozzle without Housing

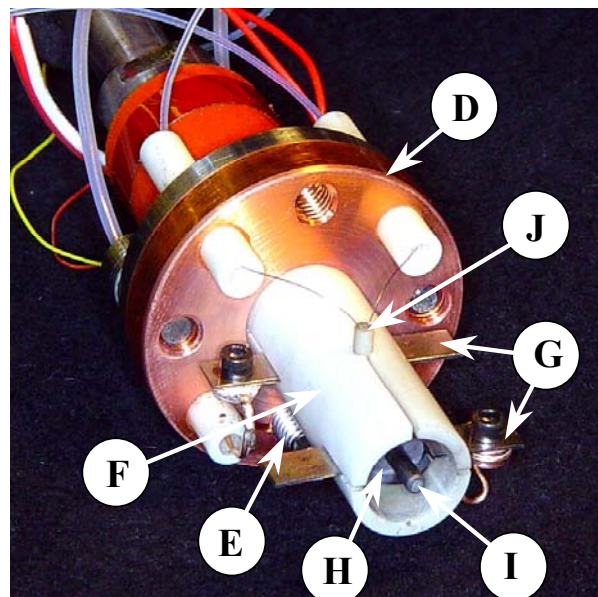


The second common mode of failure, improper SiC tube resistance, occurs slowly with use (rate is temperature dependent) or when the tube is operated in an oxidizing environment (e.g., in air). The indication for this failure is the inability to reach high temperatures if the resistance is too high, or the inability to control at lower temperatures if the resistance is too low. The resistance of the tube can be measured by removing the connector on pin #1 on the vacuum flange and connecting an ohmmeter between pin #1 and the banana plug (or flange). A suitable resistance range for the tube at room temperature (it may take more than ten minutes for the tube to cool if it has been in use and is still in vacuum) is

hours without attention, they will eventually fail, and disassembly of the nozzle will be required.

Nozzle Maintenance – There are two common failure modes for the nozzle: the thermocouple breaks or the resistance of the SiC tube becomes too large or too small. The thermocouple on the SiC tube is a type C (W/5% Re vs. W/26% Re) and is rather brittle, especially after it has been used. After being heated several times, almost any movement of the junction will break it. Thus, the user should be prepared to replace this thermocouple whenever the nozzle is disassembled or occasionally just with use. The indication of a broken junction is a flashing temperature reading on the pyrolyzer temperature controller. The remedy is to disassemble the nozzle and replace the thermocouple.

Figure 4 Nozzle Details



between about 200 and 2000 ohms. If the resistance is found to be greater than this range and the pyrolyzer will not reach the desired temperature, the remedy is to remove the SiC tube and rub its entire exterior surface with a No. 2 graphite pencil until the resistance drops below 2000 ohms. If the resistance is below this range and the controller is having difficulty maintaining the correct temperature, the remedy is to heat the tube to a bright yellow color in a soft gas-oxygen flame, and then rub the surface with a pencil as above. If the resistance cannot be adjusted to a suitable value, the tube should be replaced.

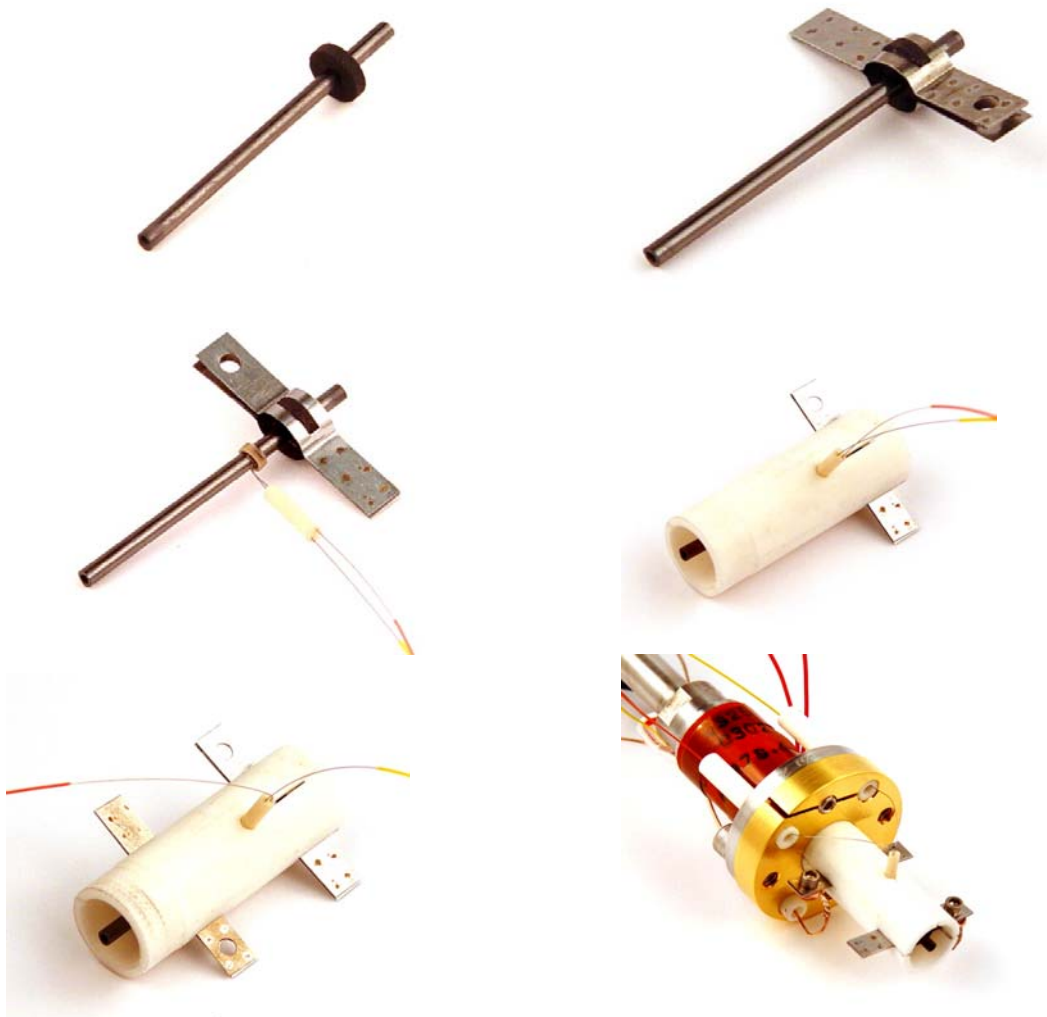
New SiC tubes normally have very high resistance (tens of M Ω) and before they are used need to be rubbed with a pencil as described above and then heated slowly. To condition a new tube proceed as follows:

- 1) Rub the tube with a pencil until the resistance gets as low as possible. Typically, for a new tube this may be only some tens of kilo-ohms.
- 2) Connect a 120 VAC, 500-600 watt (or two 250-300 watt bulbs wired in parallel) in series with the SiC tube and controller. This is easily done by removing the connector on pin #1 and wiring the light bulb(s) between the connector and the pin. The light bulbs are needed because as the tube is heated the first time, the resistance is likely to suddenly decrease very rapidly. This may cause the tube to overheat before the thermocouple/controller has time to respond. The light bulbs limit the current, and thus the temperature, to a safe level.
- 3) Set the controller temperature to 250°C, and begin heating. The temperature should begin rising, but it may be very slow at first, maybe only a few °C/min. When the temperature reaches 250°C, increase the temperature to 500°C and wait until the temperature stabilizes again. Continue increasing the temperature in this way until it reaches 1000°C.
- 4) Remove the light bulbs and use the tube normally.

Nozzle Disassembly – Disassembling the nozzle is not difficult and requires few tools, but it must be done with care to prevent damaging the small and delicate components. After venting the vacuum system, use the following steps:

- 1) Remove connections to the sample inlet tube and electrical vacuum feedthroughs. The electrical connections are the push-on type; pull straight off.
- 2) Remove the nozzle and housing as a unit from the cryostat. Be careful not to drop the copper matrix radiation shield, which is positioned between the housing and cryostat shroud.
- 3) After removing the matrix radiation shield, reach into the open end of the housing with a long 5/64" hex key and loosen the locking screw two or three turns. This screw is in a tapered seat and when tightened expands a portion of the valve heat sink/mounting flange against the inside wall of the water-cooled housing, insuring good thermal contact.
- 4) Remove the six screws from the vacuum flange and withdraw the nozzle from the housing. The valve heat sink/mounting flange is a snug fit inside the housing and some gentle wiggling may be necessary.

- 5) Disconnect the electrical connectors from the vacuum feedthroughs on the vacuum flange.
 - 6) Remove the screws attaching power supply wires to the two spring clips. It may be necessary to gently hold the spring clips with small pliers.
 - 7) Grasp the alumina radiation shield and pull it and all associated parts as a unit straight out from the valve heat sink/mounting flange. Be careful not to snag and damage the thermocouple or power supply wires.
 - 8) Slide the thermocouple insulator up the thermocouple wires until it clears the alumina radiation shield.
 - 9) Holding the exhaust end of the SiC tube with your fingers, slide the opposite (nearest the valve) spring clip and carbon disk out of the alumina tube and off the SiC tube.
 - 10) The other spring clip, carbon disk, SiC tube, and thermocouple, can now be lifted as a unit from the alumina tube.
 - 11) Sliding the carbon disk and thermocouple from the SiC tube completes the disassembly.
- Reassemble the nozzle by reversing these same steps as illustrated below.

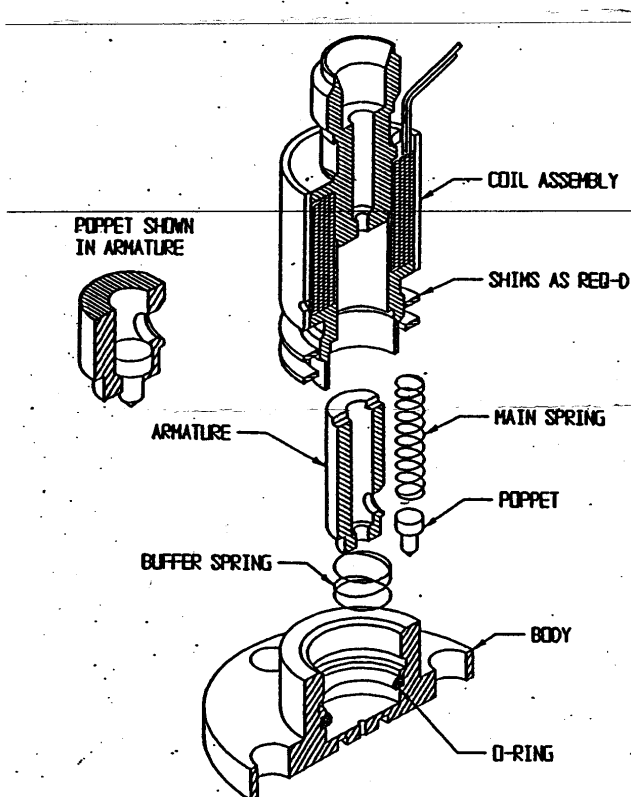


Pulsed Valve Maintenance – The most common problem with the pulsed valve is for the poppet (the active seal) to wear. When this happens, the valve will leak when closed and possibly fail to open completely. With the nozzle disassembled, it is easy to replace the poppet following the steps listed in the one-page instruction sheet (Appendix 1). The valve body should be removed (step 2 in the instruction sheet) from the coil without disturbing the silicon rubber heater. Removing the valve heat sink/mounting flange from the valve body is not necessary. Be especially careful not to lose the shim(s), which will probably remain under the heater and may not be easy to see.

Appendix 1 Pulsed Valve Maintenance Instructions



PARKER HANNIFIN CORPORATION
 GENERAL VALVE DIVISION
 19 GLORIA LANE
 FAIRFIELD, NEW JERSEY 07004
 (973) 575-4844 FAX (973) 575-4011



1) Energize the valve until it opens (a click will be heard). Keep it energized while you dis-assemble the valve. Once open, the valve needs only 5 V DC to keep it open. Reducing the voltage will prevent the coil from heating up quickly.

2) Holding the valve upside down (Flange on top), rotate the body counter-clockwise to separate it from the coil.

3) Remove the body straight up. Remove the buffer spring from the end of the armature. Do not lose the shims surrounding the coil threads.

4) CAUTION: Place your thumb over the end of the armature before de-energizing the valve to prevent the armature, poppet, and main spring from shooting out of the coil. Turn off the power to the valve.

5) Tilt the coil down to remove the armature, poppet and main spring.

6) Remove the main spring from the armature and tap the armature to remove the poppet. Place a new poppet down the armature and make sure the tip protrudes from the end. Replace main spring on top of poppet.

7) Hold coil horizontal and replace the armature into the coil, main spring first.

8) Rotate the coil so the open end is up, replace the shims if they were removed, then energize it (repeat Step 1). Use a finger to push the armature down until it holds. Place the buffer spring on the end of the armature, then screw the body back on (clockwise), tight.

NOTE: the purpose behind energizing the valve during assembly or dis-assembly is to prevent the poppet from rotating in the seat which might damage it, thereby producing leaks.

Appendix 2 Vacuum Flange Pin Connections

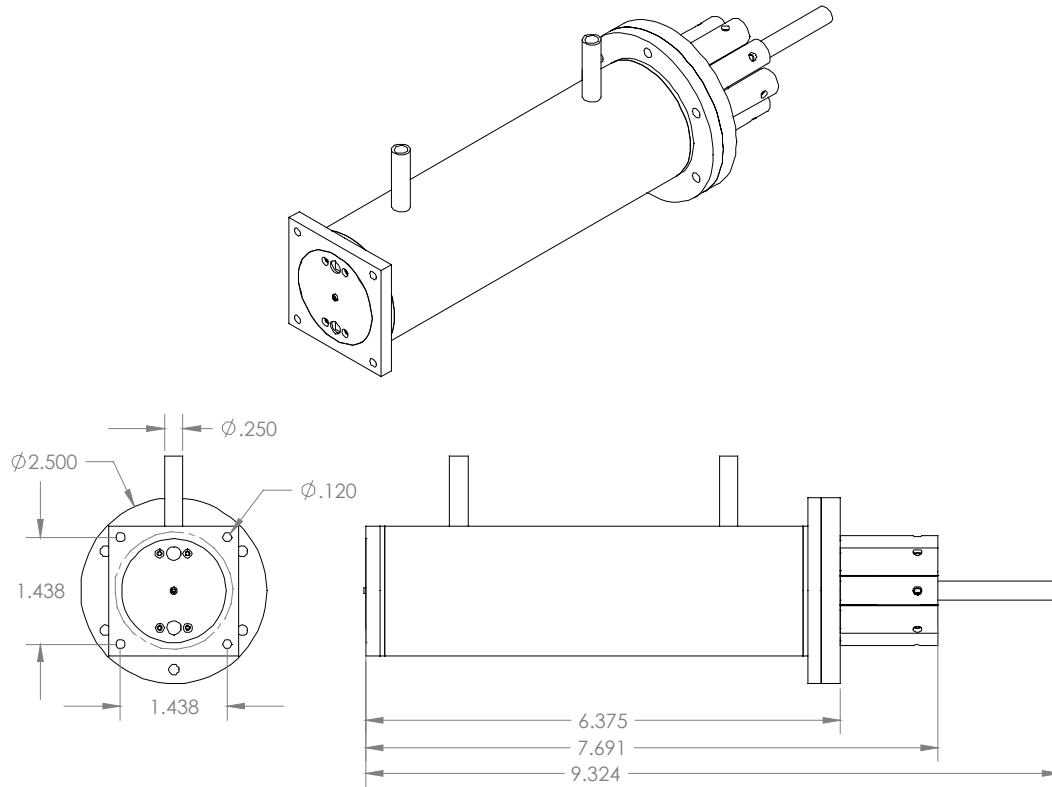
Pin	Wire Color	Function
1)	Red	Nozzle Power (exhaust end spring clip)
2)	Blue	Valve Drive
3)	Orange	Valve Heater
4)	Violet	Nozzle Thermocouple (+)
5)	White	Nozzle Thermocouple (-)
6)	Green	Valve Thermocouple (+)
7)	Yellow	Valve Thermocouple (-)
8)	Brown	Valve Drive
Banana Plug	Black	Nozzle Power & Valve Heater Common

Appendix 3 Default Love Controller Settings

Menu	Parameter ¹	Sample & Valve Heater Controllers	Pyrolyzer Controller
Secondary	Out1	1tP	ProP
	Out2	---	1tP
	tunE	SELF or Pid (see text)	SELF or Pid (see text)
	Pid2	---	OFF
	ArUP	OFF	OFF
	ArtE	OFF	OFF
	Fint	0	0
	Fbnd	Irrelevant	Irrelevant
	FrtE	Irrelevant	Irrelevant
	PEA	Read only	Read only
	UAL	Read only	Read only
	PctO	On	On
	InPC	0	0
	FiLt	1	1
	LPbr	OFF	OFF
Secure	SECr	4	4
	InP	CA	C-
	OSUP	---	OFF
	Unit	C	C
	dPt	0	0
	InPt	OFF	OFF
	InPb	FAIL	FAIL
	SEnC	OFF	OFF
	SCAL	-129	-18
	SCAH	1371	2320
	SPL	20	20
	SPH	200	1500
	SP1O	OutA	OutA
	S1St	rE	rE
	S1OL	0	20
	S1OH	100	47
	S1LP	O on	O on
	S2t	---	dE
	S2St	---	dir
	S2OL	---	0
S2OH	---	100	
S2LP	---	OoFF	

¹ Only parameters that actually appear in the display are listed.

Appendix 4 Housing Dimensions (inches)



Appendix 5 Specifications

Hyperthermal Nozzle Temperature Range: 20 to 1400°C

Length of Hot Zone: 2.0 cm

Nozzle Inside Diameter: 1.0 mm

Pulsed Valve Temperature Range: 20 to 200°C

Solid Sample Probe (optional): 20 to 200°C

Pulsed Valve Open Time (with IIDF controller): 0.1 to 99.9 msec

Pulsed Valve Frequency Range (with IIDF controller): 1 to 200 Hz

Cryostat Mounting: Fits original APD Cryostat Shroud ($1\frac{7}{16} \times 1\frac{7}{16}$ mtg. holes)

Cooling Water: 0.5 L/min. @ 20°C