Report No. FAR-74-019

IMPROVED THERMOELECTRICALLY-COOLED QUARTZ CRYSTAL MICROBALANCE

D. McKeown, W.E. Corbin, Jr. and M.G. Fox

Final Report
(August 27, 1973 - August 26, 1974)

August 26, 1974

Contract NAS5-27579

DCN 1-1-50-[illegible]

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Contract NAS8-27879

DCN 1-1-80-00122

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Marshall Space Flight Center

National Aeronautics and Space Administration

Faraday Laboratories Inc.
La Jolla, California 92037

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FOREWARD

Under Contract NAS8-27879 (October 27, 1971 - August 26, 1974), new instrumentation has been developed to monitor contamination. Work previously reported has been the design and construction of a Precision Quartz Crystal Microbalance[1] for use in the Integrated Real Time Contamination Monitor and the development of a Thermoelectrically-Cooled Quartz Crystal Microbalance[2] to monitor contamination as a function of temperature. This report covers work completed during the final year of the Contract (August 27, 1973 - August 26, 1974) on the further improvement of quartz crystal contamination monitors. The report is divided into two parts.

Part I is entitled "Improved Thermoelectrically-Cooled Quartz Crystal Microbalance" and describes design changes in the microbalance that have extended its temperature range, and increased temperature control, mass sensitivity and cooling power. The mass sensor uses 20-MHz quartz crystals having a sensitivity of 8.8 x 10^{-10} g/cm^2-Hz. The crystals are optically polished, metal plated and overplated with magnesium fluoride to simulate an optical surface. The microbalance temperature circuitry is designed to readout and control surface temperature between +100°C and -59°C to ± 0.5°C and readout only temperature between -60°C and -199°C using auxiliary liquid nitrogen cooling. It is recommended that the microbalance be further modified to give both temperature readout and control down to -199°C to facilitate accurate monitoring with temperature of high-volatile contaminants, such as, water vapor.

Part II is a paper entitled "Thermoelectrically-Cooled Quartz Crystal Microbalance" and was presented at the 7th Space Simulation Conference in Los Angeles, November 12-14, 1973. The paper gives data taken on the measurement of oil contamination of surfaces as a function of temperature in a space simulation chamber.

PART I

IMPROVED THERMOELECTRICALLY-COOLED QUARTZ CRYSTAL MICROBALANCE

D. McKeown, W.E. Corbin, Jr. and M.G. Fox

IMPROVED THERMOELECTRICALLY-COOLED QUARTZ CRYSTAL MICROBALANCE

1.0 INTRODUCTION

The use of a QCM to monitor surface contamination in space simulation chambers is of limited value because a QCM operates several degrees above ambient temperatures. Gaseous contamination in equilibrium with solid materials in the chamber is not readily adsorbed by a QCM because of its higher temperature. Contradicting results are often obtained where a passive optical system shows contamination while a QCM operating nearby does not. To overcome this temperature problem, a thermoelectrically-cooled quartz crystal microbalance (TQCM) was developed in the 1972-73 Contract year for monitoring surface contamination as a function of temperature.[1] During this past year of the Contract, an improved TQCM has been designed with an extended temperature range, precision temperature control, increased mass sensitivity and additional cooling power.

The improved TQCM uses a two-stage thermoelectric device and digital panel meter to automatically control and readout the temperature of the crystal sensor between -59°C and +100°C to ± 0.5°C on a digital panel meter.

An added feature of the improved TQCM is that it can also readout crystal temperature from -59°C to -199°C. This temperature range is used when the heat sink is cooled with liquid nitrogen and permits the measurement of water vapor contamination.

The mass sensor is a precision matched set of 20-MHz quartz crystals for temperature stability having a high mass sensitivity of 8.8×10^{-10} g/cm^{2}Hz. The crystals are 1.27 cm in diameter and optically polished so that in-situ optical measurements can be made.[2]

The TQCM can be set at any particular temperature over its operating range. If the TQCM is set at ambient, the heat generated in the oscillating crystal will be removed so that contamination loading to passive optical systems can be monitored. By increasing temperature to about +100°C the crystal can be cleaned. By periodically dropping the temperature of the TQCM in fixed steps the amount of surface contamination for different equilibrium temperatures can be determined and the background level of contamination in a chamber monitored with time.[3]

The TQCM can be used to generate a calibrated contamination flux so that the contamination sticking coefficients of surfaces can be measured. A TQCM calibrated source is generated as follows. Contamination from an uncalibrated source is directed at a TQCM cooled to -50°C. Contamination is allowed to freeze out on the TQCM. The uncalibrated source is then turned off and the vacuum system allowed to pump down. The TQCM now becomes the calibrated source by simply raising its temperature so that the contamination will desorb at the desired rate. By monitoring the TQCM frequency increase with time, the contamination mass flow rate can be accurately determined.

2.0 TQCM

The TQCM is a precision instrument for measuring surface contamination as a function of temperature in a space simulation chamber. The TQCM uses a quartz crystal oscillator to measure mass loading and the temperature of the crystal is controlled by a thermoelectric device. A drawing of the TQCM instrumentation is shown in Fig. 1.

3.0 OPERATING TEMPERATURE RANGE

The TQCM uses a two-stage thermoelectric device to automatically control the sensor crystal temperature between -50°C and +100°C to ±0.5°C in vacuum. For operation over this range, the heat sink temperature is to be maintained below +40°C. No problem will be encountered in maintaining the heat sink below +40°C by mounting it on a 0.25 inch thick metal bracket. Heat generated by the TQCM is readily dissipated by the bracket at an ambient room temperature of +22°C to +30°C. The sensor is shown in Fig. 2.

The TQCM has been designed with reserve cooling power and will reach a lower temperature limit of -59°C if its heat sink is maintained below +25°C. To maintain a +25°C temperature, the heat sink is to be mounted on a 0.5 inch thick metal bracket capable of removing 3.5 W of power. If the TQCM is to be operated for extended periods at -59°C, it may be necessary to water cool the bracket to keep its temperature from rising above +25°C.

Crystal temperatures to -199°C can be obtained by cooling a special heat sink with liquid nitrogen. Operation in this mode is open loop and not actively controlled.

4.0 VACUUM OPERATION

The TQCM is designed to operate in a space simulation chamber at pressures below 1 x 10^{-4} Torr.

(The TQCM can be operated under ambient room conditions in a heating or cooling mode for short periods between +10°C and +35°C to check-out the instrument.)

5.0 MASS SENSOR

A matched pair of precision 20-MHz quartz crystals are used to measure mass loading. The crystals are designated as a sensor and reference crystal. The crystals are optically-polished, and plated with metal. The sensor crystal is coated with magnesium fluoride for in-situ reflectivity measurements while contamination is collecting on its surface. The crystals can be changed by unloosening two set screws in the TQCM sensor shown in Fig. 2.

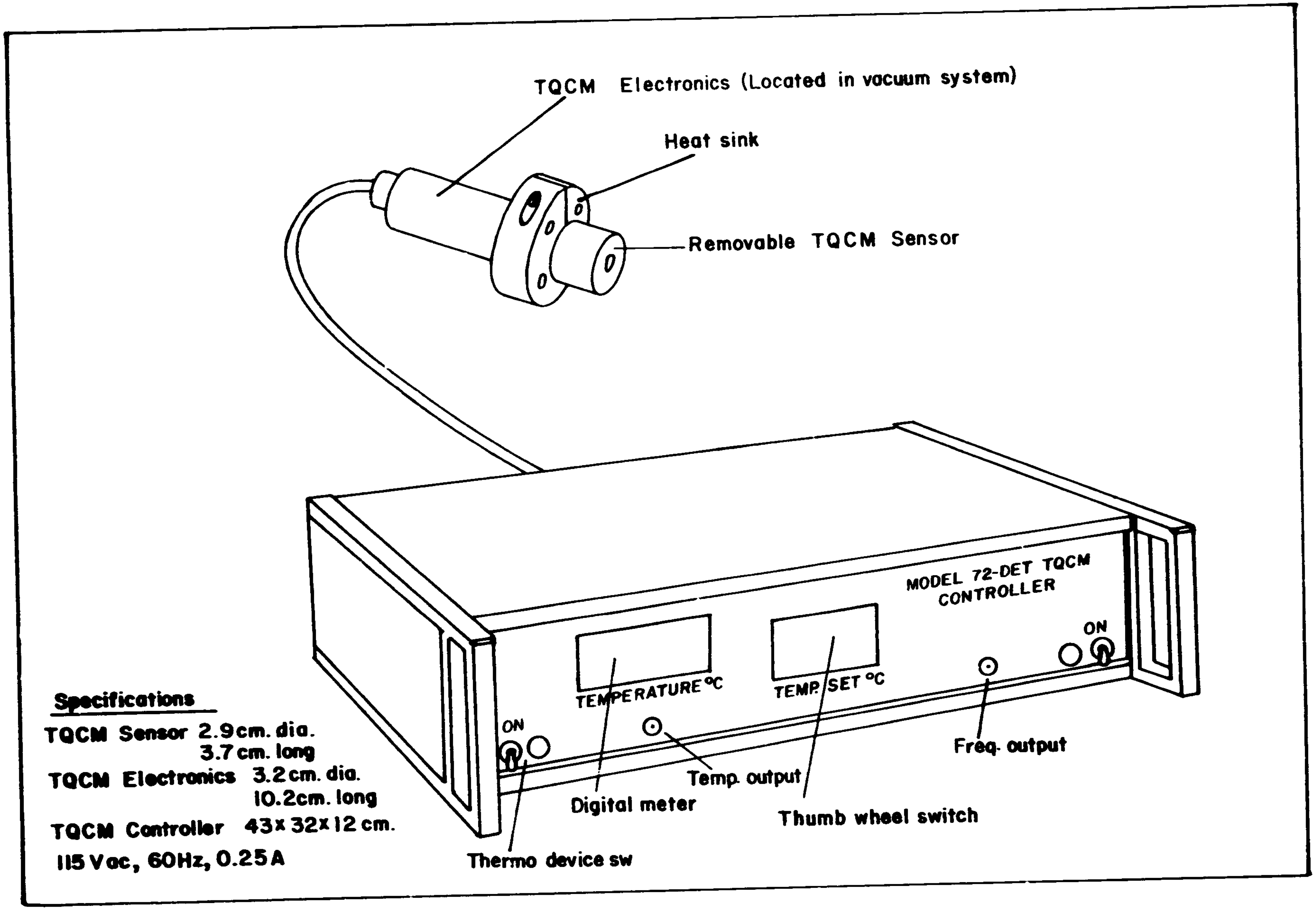

Fig. 1 - Thermoelectrically-Cooled Quartz Crystal Microbalance (TQCM) Instıumentation

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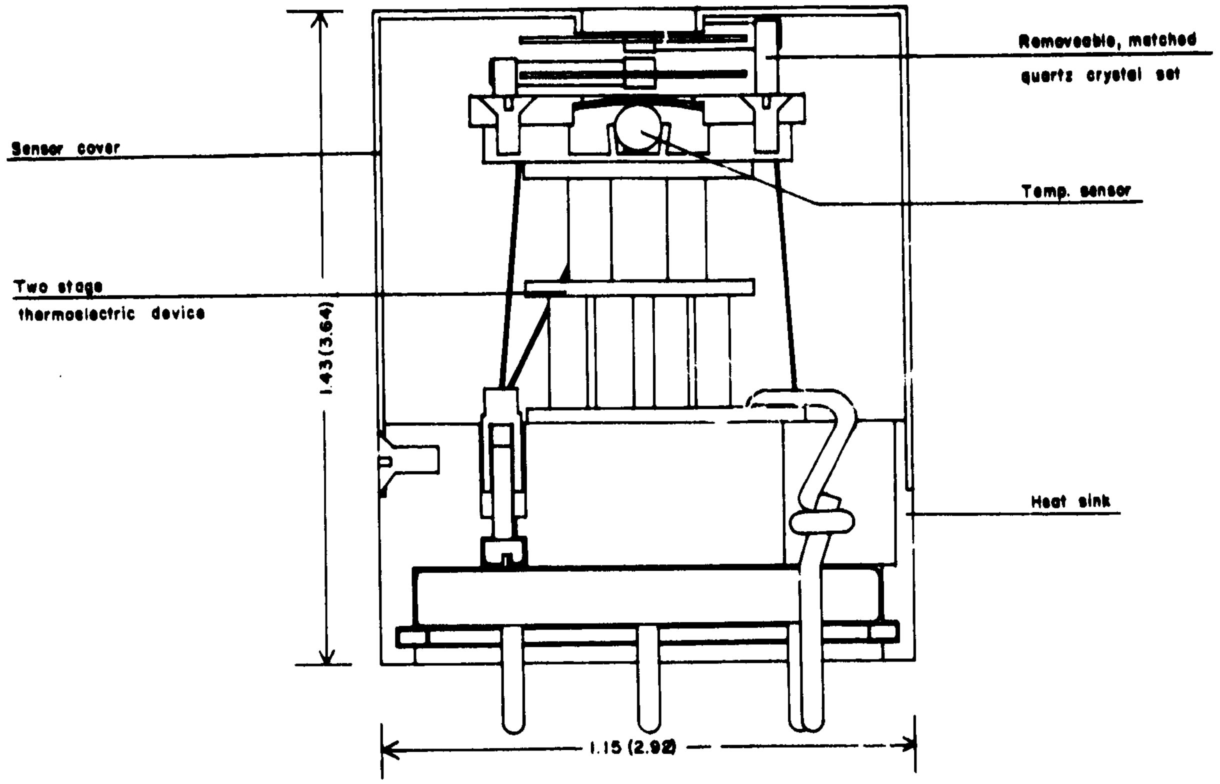


Fig. 2 TQCM Sensor

The output frequency of the TQCM is the beat frequency between the two oscillating crystals. The beat frequency effectively eliminates frequency changes caused by ambient temperature variations. Because only the sensor crystal sees the contamination flux, the TQCM output frequency will increase with mass loading, m, and

$$m = 8.8 \times 10^{-10} \text{ g/cm}^2\text{Hz}$$

The mass calibration curve is shown in Fig. 3.

6.0 TEMPERATURE SET

The TQCM operating temperature is set by positioning the thumb wheel switch on the TQCM Controller between -59°C to +100°C. The TQCM cool-down time from +27°C to -59°C is shown in Fig. 4.

The cooling rate was improved by about 50% by use of the Marlow thermoelectric device instead of a Nuclear Systems device.

7.0 TEMPERATURE OUTPUT

A 3 1/2 digit panel meter is provided on the TQCM Controller for direct readout of crystal temperature between -199°C and +100°C.

A temperature output is provided for remote readout or recording. The TQCM temperature sensor is a precision platinum resistance thermometer linear to ± 0.5%. At 100°C the voltage output is + 1.000 Vdc. At -199°C the voltage output is - 1.990 Vdc. Hence, the TQCM operating temperature in °C equals 100 times the voltage output of the TQCM Controller.

Note that the TQCM actively controls temperature only down to -59°C. A Faraday Laboratories cryogenic cooling adapter for auxiliary cooling with liquid nitrogen must be used to obtain temperatures between -59°C and -199°C.

8.0 FREQUENCY OUTPUT

A frequency output is provided in the TQCM Controller to measure the frequency change of the crystal sensor produced by mass loading. Frequency can be measured by a counter, such as, a Hewlett Packard Model HP5321B. Be sure to use a completely shielded lead from the Controller to the Counter to eliminate noise pick-up that will produce instability in the count.

9.0 INSTALLATION

A cable is provided for connecting the TQCM Electronics to the TQCM Controller for laboratory check out at ambient room temperature

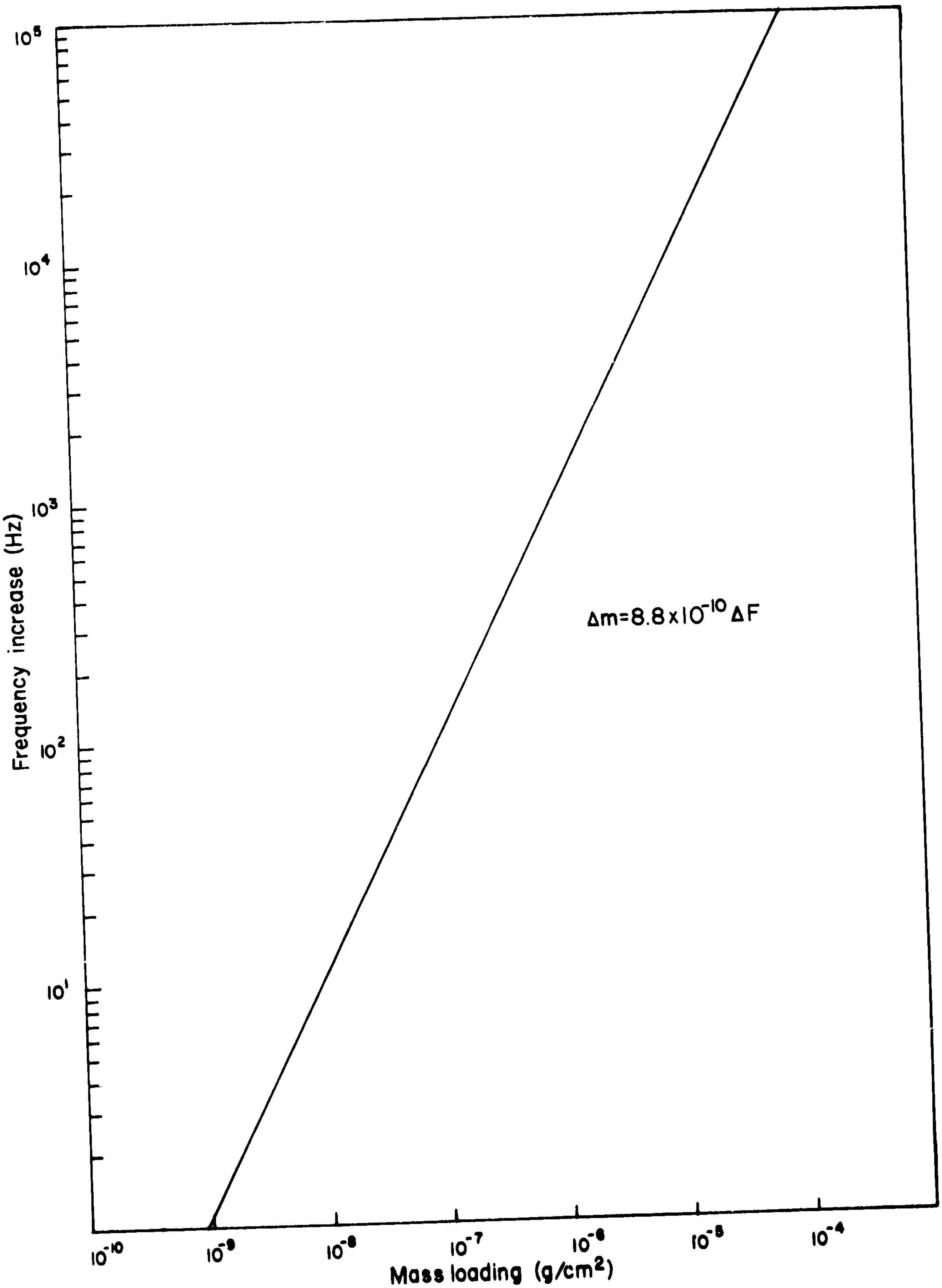


Fig. 3 Calibration Curve for TQCM 20-MHz Mass Sensor

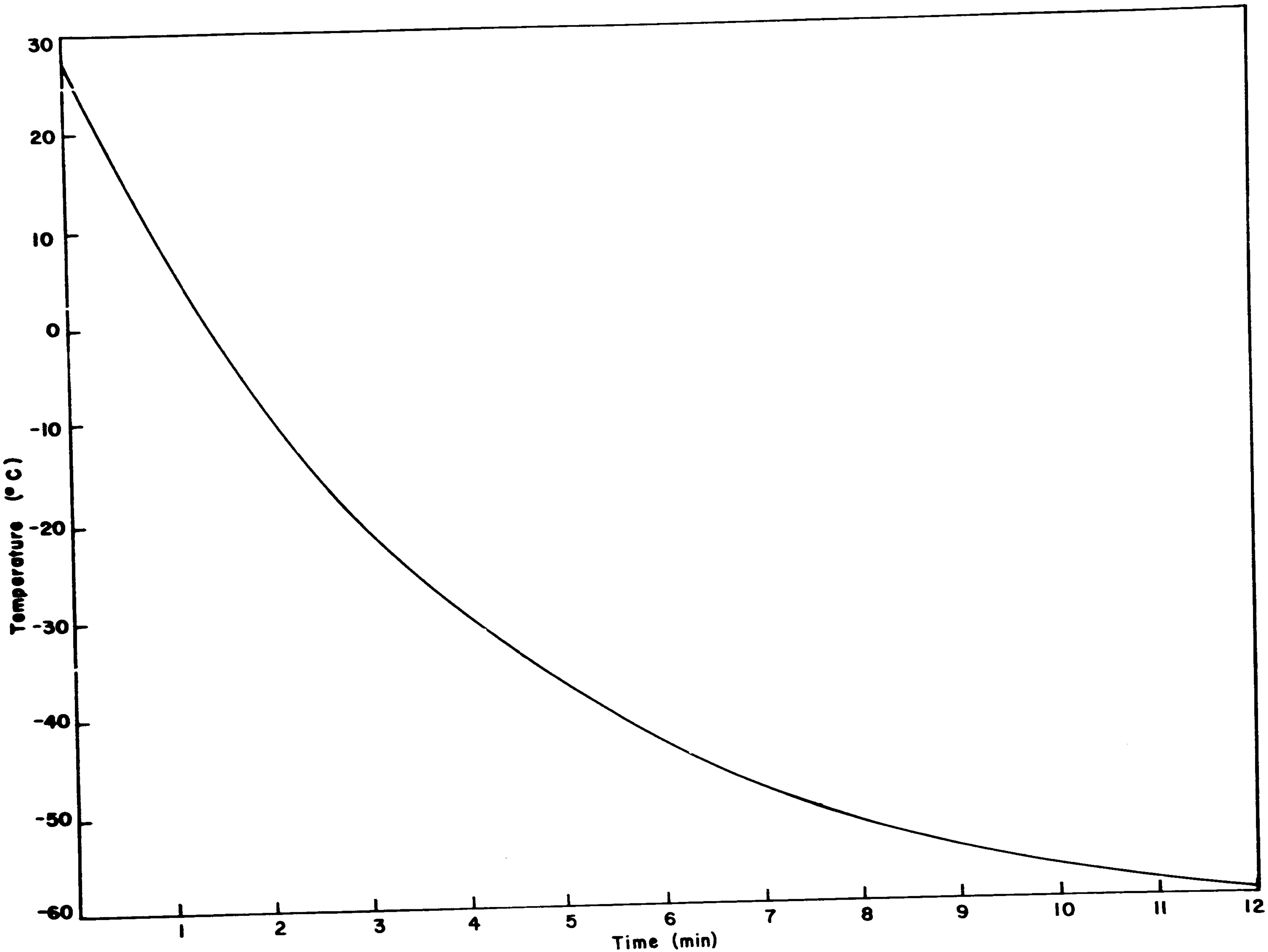


Fig. 4 Cool-Down Time in Vacuum for Marlow Two-Stage TQCM Sensor

and pressure.

For operating in vacuum, cut the cable and wire through an eight pin vacuum feed-thru as follows:

Electronics Input P5 Pin	Nomenclature	Controller Output P4 Pin
A	Shield	No connection
B	Signal Output Frequency (use shielded lead)	E
C	Platinum temp. sensor	D
D	Platinum Temp. sensor	F
E	Power Ground	B
F	Power Input	C
G	Thermoelectric Device (-)	G
H	Thermoelectric Device (+)	A

10.0 LONG TQCM OPERATING CABLE

Some TQCM installations may call for lengthy cables inside and or outside the vacuum chamber. The important fact to remember in such installations is the added resistance in series with the temperature sensing element and the thermoelectric device. Adding resistance in series with the platinum temperature sensing element causes a controlled and indicated temperature error equal to .55°C/ohm. This error may be minimized with heavy gauge wire, calibrated out as indicated in the calibration section or simply ignored. Added resistance in series with the thermoelectric device should be limited to 0.5 ohms. The rather large peak cooling current of 4 amperes causes an excessive voltage drop in the line if resistance exceeds this value and cooling efficiency is decreased. Keep in mind series resistance is the sum of the lead resistance from Controller to TQCM and back in the return line.

11.0 TQCM CALIBRATION

Each TQCM has been accurately calibrated before shipping and under normal conditions the instrument will maintain specifications for at least one year. This calibration was accomplished with the standard eight foot cable and sensor assembly supplied as part of the instrument. Calibration may be considered by the user for one of the following reasons (see TQCM Wiring Diagram Drawing FL-72-318, page 19).

a) Substitution of a cable of significantly different resistance than the supplied cable.

b) Substitution of sensor assembly.

c) Recalibration after operation for a year.

The following factors can be used as a guide in making the decision to recalibrate or accept possible errors. Cable resistance added to the temperature sensor element effects both the displayed and controlled temperatures by an amount equal to .55°C per ohm. Added resistance is considered to be the resistance from P4 pin D to P5 pin C plus the resistance from P4 pin F to P5 pin D, less that which exists in the supplied cable (approximately 0.2 ohms). To better illustrate this effect, assume the instrument is perfectly calibrated and actual sensor temperatures would be 20.0°C. Adding 1 ohm total lead resistance would result in an actual sensor temperature of 19.45°C and a displayed temperature of 20.0°C. While still within specification of ±0.5°C, an error in fact exists and is masked by the fact that the displayed temperature remained unchanged. Substitution of sensor assembly has an effect similar to changing cable resistance. The platinum resistance elements used are specified to be 470 ohms ± .5% at 0°C, although in practice they are better than this.

Examining the extreme case of substituting a + 0.5% element for a - 0.5% element will illustrate the effect in the worst case. A 4.7 ohm element change is equivalent to a temperature change of 2.6°C. Again, if the Controller were then set to +20°C, the actual temperature would stabilize at 17.4°C while the displayed temperature would be 20.0°C.

12.0 CALIBRATION PROCEDURE

Calibration of the TQCM consists of adjusting zero offset currents in three amplifiers, and adjusting the four (4) current sources in the temperature bridge. Only the top cover of the Controller chassis need be removed to make these adjustments.

Adjustments are performed using the seven (7) potentiometers mounted along the top of the circuit board plugged into J2. Looking at the circuit board from the component side, they are potentiometer 1 through 7 from left to right (see Drawing FL-72-318).

13.0 DISPLAY CALIBRATION

1. Turn off Controller and turn off Thermoelectric Device.
2. Remove cable connector P5 from TQCM Electronics.
3. Insert precision decade box in P5 pins C and D. Use complete cable length.
4. Set decade box equal to .4834 ohms.
5. Turn on A.C. power and allow 5 minute warmup.
6. Set Controller switch to +0°C.
7. Measure voltage at J2 pin 30 (accessible on Board Z at left side of third 100K resistor below P6).
8. Voltage should read -.4834V -.5mV +0mV. If it does not, adjust potentiometer 1 to force -.4834 volt reading.
9. Set Controller switch to -0°C.

10. Set voltage to read -.4834 -0mV +.5mV with p2.

11. Move voltmeter connection to read voltage on J2 pin 36 (accessible on Board 2 at left side of the first 54.9K resistor below and to the right of P4).

12. Voltage should read -.4834 ± .1mV. If it does not, then adjust P3 to force reading to be -.4834 volts.

13. Move voltmeter connection to read voltage on J2 pin 34 (accessible on Board 2 at left side of the second 54.9K resistor below and to the right of P4).

14. Voltage should read -.4834 ± .1mV. If it does not, then adjust P4 to force reading to be -.4834 volts.

15. Remove voltmeter.

16. Place short clip on jumper between the left sides of the above 54.9K resistors.

17. Digital Panel Meter (DPM) should read 0.0°C. If it does not, adjust potentiometer 5 to make DPM read 0.0°C.

18. Remove jumper.

19. DPM should read 0.0°C ± .2°C. If it does not, then repeat 7 through 18.

20. If the DPM fails to read 0.0°C ± .2°C a second time but reads 0.0°C ± .5°C, then adjust P3 to force 0.0°C reading.

21. Set the resistance decade box and the digital switch to the indicated values to test linearity. The DPM should read the indicated temperatures ± 1°C.

Resistance	Digital Switch	Indicated Temp
95.3	-199°C	-199.0°C
293.0	-100°C	-100.0°C
389.0	- 50°C	- 50.0°C
483.4	- 0°C	- 0.0°C
483.4	+ 0°C	+ 0.0°C
576.4	+ 50°C	+ 50.0°C
667.9	+100°C	+100.0°C

22. Should the DPM display a temperature other than the desired indicated temperature ± 0.5°C, there exists either a calibration technique error or a hardware failure. It would be best to contact the factory at this point.

23. One final check and adjustment may now be made under certain conditions. If the sensor unit to be used is known to be at a well defined ambient temperature the unit may be matched to the Controller resulting in additional accuracy. Proceed to the temperature control calibration if sensor temperature is not well known.

24. Turn power off.

25. Remove decade resistor from pins C and D of J5 and replace with the TQCM electronics and sensor package.

26 Turn power on.

27. DPM should immediately display the ambient temperature which is also the sensor temperature.

28. Potentiometer 3 should be adjusted to cause a correct DPM display if it differs less than ± 2°C from ambient.

29. Should the DPM initially display a temperature greater than ± 2°C different than ambient the calibration procedure should be redone. A second failure to meet this condition would justify a call to Faraday Laboratories.

30. Continue now with the temperature control calibration.

14.0 TEMPERATURE CONTROL CALIBRATION

1. It is now necessary to balance the two amplifiers that determine thermoelectric device current.

2. Place a short jumper between J2 pins 30 and 36. (As previously mentioned, pin 30 is accessible at left side of 54.9 K resistor below potentiometer 4 and pin 36 is accessible at left side of third 100 K resistor below potentiometer 6).

3. Turn off thermoelectric device switch.

4. Measure the voltage on Board 2 at the left side of the bottom 1.8 K resistor in column of resistors below P6.

5. Use potentiometer 6 to set this voltage as close to 0V as possible. This would usually be less than ± 1mV.

6. Measure the voltage on Board 2 at the upper side of 15 ohm resistor on far right side of circuit board.

7. Use potentiometer to set this voltage as close to 0V as possible. This voltage tends to toggle back and forth between ± .1V when the desired balance is established.

8. Circuit is now balanced as well as it can be statiscally calibrated. While this will cause the instrument to regulate the sensor temperature within the specified ± 1°C, a more precise balance can be obtained by performing the following steps. It is <u>not</u> necessary to perform these steps. The calibration can be considered completed here.

9. If sensor assembly is at atmospheric pressure set digital switch to +10°C. When this is being done in a vacuum, skip to step 14.

10. Remove the jumper between J2 pins 30 and 36.

11. Continue to monitor the voltage at the point described in step 6.

12. Use potentiometer 7 to adjust this voltage to 0 volts coincident with the DPM indicating a sensor temperature of 10.0°C.

13. A more precise balance has now been obtained and the calibration is complete.

14. When the sensor is under vacuum set the digital switch to -0°C or if there is an often used and critical temperature then set the digital switch to this temperature.

15. Remove the jumper between J2 pins 30 and 36.

16. Continue to monitor the voltage at the point described in step 6.

17. Use potentiometer 7 to adjust this voltage to 0 volts coincident with the DPM indicating -0°C or the set critical temperature.

18. Calibration is now complete.

15.0 TROUBLESHOOTING

There are a limited number of failures which can be analyzed and fixed without necessitating return to Faraday Laboratories. This would certainly be true with the assistance of Faraday Laboratories personnel who are available for telephone consultation. Problems existing in the TQCM Controller would normally be customer repairable. Problems existing in the electronics package (sealed and potted) or in the sensor assembly (a delicate assembly) should not be considered to be customer repairable.

16.0 TROUBLESHOOTING PROCEDURES

Symptom	Possible Cause	Test and Fix
No A.C. power indication after plugged in and turned on	Lamp burned out	Turn power off Measure lamp Replace Type 381
	Switch failure	Turn power off Replace switch
	Fuse blown	Change once 1.5 amp slow blow
	Cooler power supply failure	Measure voltage out of 5V cooler power supply
No Thermoelectric Device power indication after turn on	Lamp burned out	Turn power off Measure lamp Replace Type 381
	Switch failure	Turn power off and replace
Minor indicated temp error	Component drift	Use calibration procedure
	Cable resistance change	Use calibration procedure
Temp readout in error or inoperative	Broken cable wire	Check continuity against wiring tables between Controller & electronics - fix wire

Symptom	Possible Cause	Test and Fix
Temp readout in error or inoperative	Broken wire inside electronics or sensor	Measure resistance between J5 pins C and D. Should measure 500 - 525 ohms near room temp.
	Electronics volt power supply failure	Measure I voltages at 15 volt supply Should be 15 V ± 3 volts
	Temp output jack shorted	Check and remove short
	Broken wire inside electronics or sensor	Measure resistance between J5 pins C and D. Should measure 500 to 525 ohms near room temp.
	Heater and DPM power supply failure	Measure voltages at 15 volt supply Should be 15 V
	Temp output jack shorted	Check and remove short
DPM blinking	Exceeding range of -199°C to +100°C	Return to normal temp range
Temp not stabilizing at set temperature	Component drift	Use calibration procedure
	Cable resistance too large	Measure resistance from P4-A to P5-H P4-G to P5-G Both should be less than 0.25 ohm - use larger wire
Temperature control shows major error	Broken wire in cable	Check continuity from P4 to P5
	Broken wire in electronics or sensor	Check for low resistance J4A to J4G - Caution - use only low resistance scale of multimeter

Symptom	Possible Cause	Test and Fix
Temperature control shows major error	Insufficient drive current	Use clip on amp meter on wire from P4G to P5G. Measure 3.5 to 4.0 amps when digital switch set at least 10°C below indicated temperature Measure .8 to 1.2 amp when digital switch set at least 10°C above indicated temperature If these currents are not indicated, measure voltages. 1) +5 volt supply 5.0 V ± .2V 2) -5 volt supply 5.0 V ± 1V 3) voltages under above conditions at common point of power resistors mounted on chassis heat sink.
	Shield short to ground on both ends of cable	Shield should be grounded only on electronics end, NOT the Controller end
	Temperature output jack has been shorted	Power off, measure center conductor to case. If shorted remove short
No output at temp output jack while DPM indicated properly	Open wire from J3-1 to the BNC center conductor	Check continuity with power off - reconnect
No output at frequency BNC	Broken connection inside Controller	Check for continuity BNC center conductor to J4 pin E
	Broken cable wire	Check continuity P4-E to P5-B
	Cable short	Measure resistance from P5-B to P5-A, P5-B to P5-E. With cable disconnected, both should read open

Symptom	Possible Cause	Test and Fix
No output at frequency BNC	Short in Controller	Measure resistance from P5-E to P5-A, P5-B to P5-E. With P4 end connected both should read greater than 10 K ohms
	Electronics package failure	Replace electronics
	Quartz crystals overloaded with contamination or damaged	Replace matched crystal set
TQCM Sensor fails to cool or heat	Thermoelectric device damaged	Measure resistance from P4-G to P4-A. With cable disconnected resistance should be less than 0.5 ohm. If larger, replace sensor
	Platinum temp sensor failed	Measure resistance from P4-D to P4-F. With cable disconnected, resistance should be approximately 530 ohms. If greater than 675 ohms. or less than 80 ohms, replace

If after check out and adjustments, the TQCM instrumentation still fails to operate properly, call Faraday Laboratories, (714) 459-2412, for assistance.

17.0 TEMPERATURE SENSOR CALIBRATION

The operating temperature of the TQCM is monitored by a precision platinum temperature sensor linear to ± 0.5%. Table 1 gives the calibration for the sensor.

T(°C)	R(OHMS)	T(°C)	R(OHMS)	T(°C)	R(OHMS)	T(°C)	R(OHMS)	T(°C)	R(OHMS)	T(°C)	R(OHMS)	T(°C)	R(OHMS)	T(°C)	R(OHMS)
-200	79.88	-160	161.28	-120	240.57	-80	318.24	-40	394.63	0	470.00	40	544.47	80	618.06
-199	81.94	-159	163.29	-119	242.53	-79	320.16	-39	396.52	1	471.87	41	546.39	81	619.89
-198	84.01	-158	165.29	-118	244.49	-78	322.08	-38	398.42	2	473.74	42	548.17	82	621.72
-197	86.07	-157	167.29	-117	246.45	-77	324.00	-37	400.31	3	475.61	43	550.02	83	623.55
-196	88.13	-156	169.29	-116	248.41	-76	325.93	-36	402.21	4	477.48	44	551.87	84	625.38
-195	90.19	-155	171.30	-115	250.36	-75	327.85	-35	404.10	5	479.35	45	553.72	85	627.21
-194	92.25	-154	173.29	-114	252.31	-74	329.77	-34	406.00	6	481.22	46	555.57	86	629.03
-193	94.30	-153	175.29	-113	254.27	-73	331.68	-33	407.89	7	483.09	47	557.42	87	630.85
-192	96.35	-152	177.29	-112	256.22	-72	333.60	-32	409.78	8	484.96	48	559.26	88	632.68
-191	98.41	-151	179.29	-111	258.17	-71	335.52	-31	411.67	9	486.83	49	561.11	89	634.50
-190	100.46	-150	181.28	-110	260.12	-70	337.44	-30	413.56	10	488.70	50	562.96	90	636.32
-189	102.51	-149	183.27	-109	262.07	-69	339.35	-29	415.45	11	490.57	51	564.80	91	638.15
-188	104.56	-148	185.26	-108	264.02	-68	341.27	-28	417.34	12	492.43	52	566.65	92	639.97
-187	106.60	-147	187.25	-107	265.97	-67	343.19	-27	419.23	13	494.30	53	568.49	93	641.79
-186	108.65	-146	189.24	-106	267.91	-66	345.10	-26	421.12	14	496.17	54	570.33	94	643.61
-185	110.69	-145	191.23	-105	269.86	-65	347.02	-25	423.00	15	498.03	55	572.17	95	645.43
-184	112.73	-144	193.22	-104	271.81	-64	348.93	-24	424.89	16	499.90	56	574.02	96	647.25
-183	114.77	-143	195.21	-103	273.75	-63	350.84	-23	426.78	17	501.76	57	575.86	97	649.07
-192	116.81	-142	197.19	-102	275.70	-62	352.75	-22	428.66	18	503.62	58	577.70	98	650.89
-181	118.84	-141	199.17	-101	277.64	-61	354.66	-21	430.55	19	505.49	59	579.54	99	652.71
-180	120.88	-140	201.16	-100	279.58	-60	356.57	-20	432.43	20	507.35	60	581.38	100	654.53
-179	122.91	-139	203.14	-99	281.52	-59	358.48	-19	434.32	21	509.21	61	583.22	101	656.35
-178	124.94	-138	205.12	-98	283.46	-58	360.39	-18	436.20	22	511.07	62	585.06	102	[illegible]
-177	126.98	-137	207.10	-97	285.40	-57	362.29	-17	438.09	23	512.93	63	586.89	103	659.98
-176	129.01	-136	209.07	-96	287.34	-56	364.20	-16	439.97	24	514.79	64	588.73	104	661.79
-175	131.03	-135	211.05	-95	289.28	-55	366.11	-15	441.85	25	516.65	65	590.57	105	663.61
-174	133.06	-134	213.02	-94	291.21	-54	368.02	-14	443.73	26	518.51	66	592.41	106	665.42
-173	135.08	-133	215.00	-93	293.15	-53	369.92	-13	445.61	27	520.37	67	594.25	107	667.24
-172	137.10	-132	216.97	-92	295.08	-52	371.83	-12	[illegible]	28	522.23	68	596.08	108	669.05
-171	139.12	-131	218.94	-91	297.02	-51	373.73	-11	[illegible]	29	524.08	69	597.92	109	670.86
-170	141.15	-130	220.92	-90	298.95	-50	375.63	-10	451.25	30	525.94	70	599.75	110	672.68
-169	143.17	-129	222.89	-89	300.88	-49	377.54	-9	453.13	31	527.80	71	601.58	111	674.49
-168	145.18	-128	224.86	-88	302.81	-48	379.44	-8	455.00	32	529.65	72	603.41	112	676.30
-167	147.20	-127	226.83	-87	304.74	-47	381.34	-7	456.88	33	531.51	73	605.25	113	678.11
-166	149.22	-126	228.79	-86	306.67	-46	383.24	-6	458.75	34	533.36	74	607.08	114	679.92
-165	151.23	-125	230.76	-85	308.60	-45	385.14	-5	460.63	35	535.21	75	608.91	115	681.73
-164	153.24	-124	232.72	-84	310.53	-44	387.04	-4	462.50	36	537.06	76	610.75	116	683.54
-163	155.26	-123	234.69	-83	312.46	-43	388.93	-3	464.38	37	538.92	77	612.58	117	685.35
-162	157.27	-122	236.65	-82	314.38	-42	390.83	-2	466.25	38	540.77	78	614.41	118	687.16
-161	159.27	-121	238.61	-81	316.31	-41	392.73	-1	468.13	39	542.62	79	616.24	119	688.97

Table 1 Calibration of Platinum Resistance Temperature Sensor between -200°C and +119°C

The temperature of the platinum sensor can be determined as follows. Measure resistance between P4-D and P4-F. Then, subtract from this resistance 13.4 ohms (lead resistance in TQCM Sensor) and resistance in TQCM cable (resistance between P4-D and P5-C plus resistance between P4-F and P5-D). The resistance determined after subtraction of lead and cable resistance is used in Table 1 to find the temperature of platinum sensor.

18.0 DESIGN DRAWINGS

In order to extend the temperature readout range from -59°C to -199°C, the TQCM bridge circuit and amplifiers were modified.

The Controller Layout is shown in Drawing No. FL-72-318.

The Controller Wiring Diagram is shown in Drawing No. FL-72-319.

The Temperature Control Bridge is shown in Drawing No. FL-72-321.

The Display Amplifier is shown in Drawing No. FL-72-322.

The Cooler Driver Circuit is shown in Drawing No. FL-72-323.

19.0 RECOMMENDATION FOR TQCM CRYOGENIC TEMPERATURE CONTROL

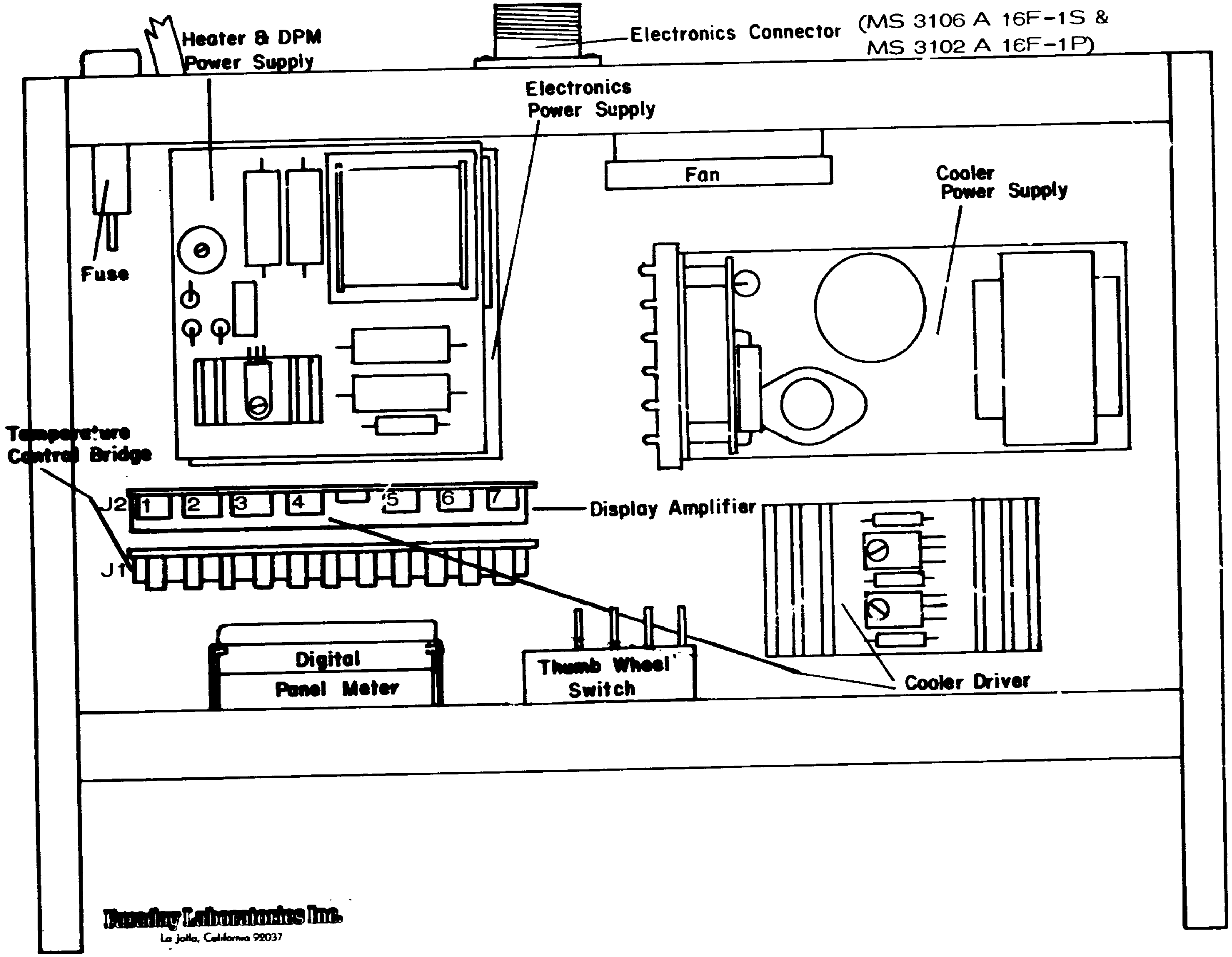
The improved TQCM has been modified to permit readout down to -199°C. The expanded readout was made possible by extension of the temperature bridge resistor network to balance resistance changes in the platinum temperature probe at cryogenic temperatures.

The expanded TQCM readout makes it possible to monitor high-volatile contaminants with temperature, such as, water vapor. Table 2 gives the freezing point of water vapor as a function of vapor pressure.

Temp °C	Pressure Torr
-90	7.45×10^{-2}
-100	1.10×10^{-2}
-110	1.25×10^{-3}
-120	1.13×10^{-4}
-130	6.98×10^{-6}
-140	2.93×10^{-7}
-150	7.4×10^{-12}

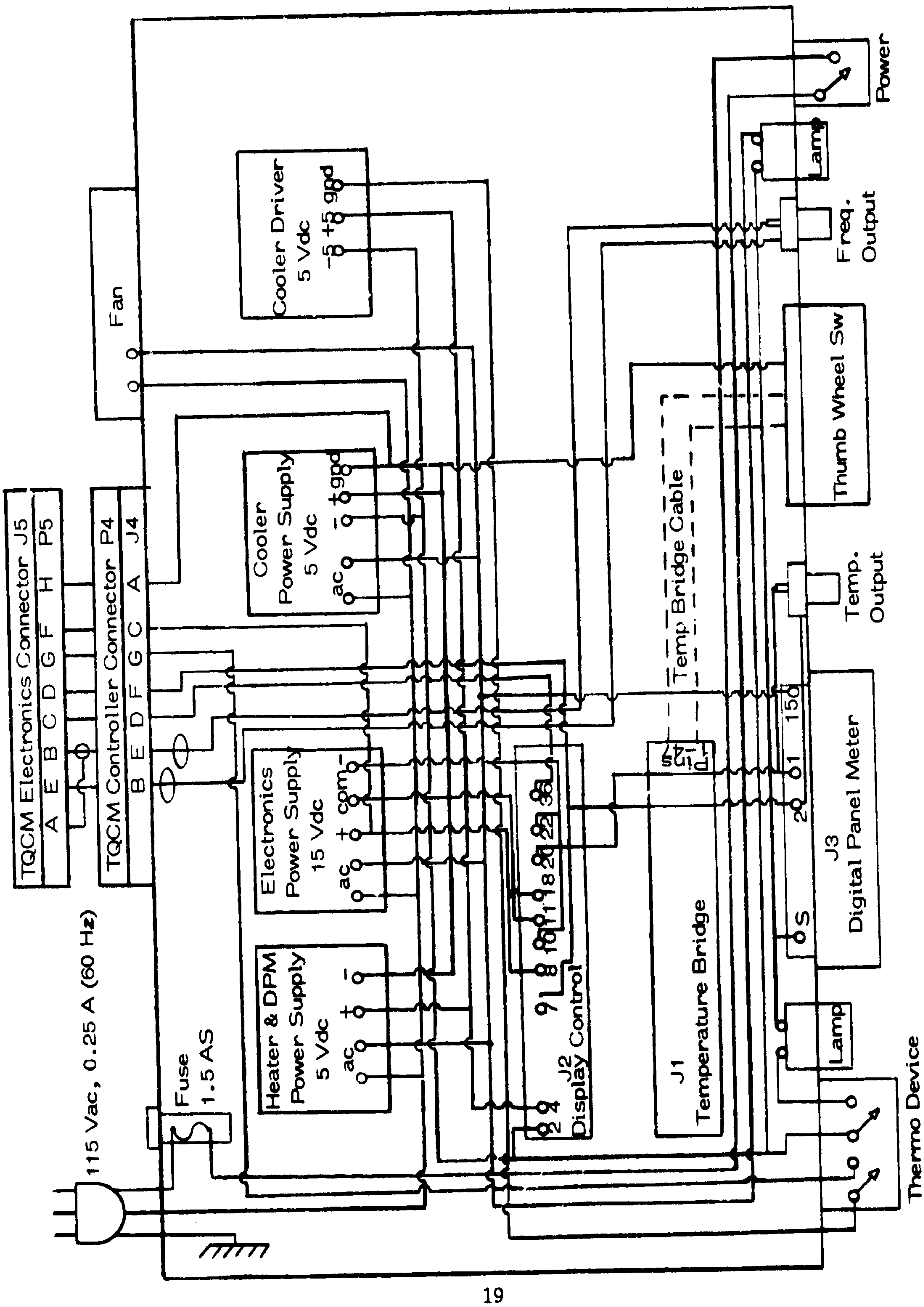
Table 2 Freezing Temperature of Water Vapor for Various Vapor Pressures

As can be seen from Table 2, surface temperatures between -140°C and -150°C are required to freeze out water vapor in a space simulation chamber at pressures below 2.93×10^{-7} Torr. The present TQCM permits the readout of cryogenic temperatures but it does not have the capability to set and control a surface at a particular temperature. It is recommended that the TQCM power control system be modified to control surface temperature to ± 0.5°C between -60°C and -199°C.



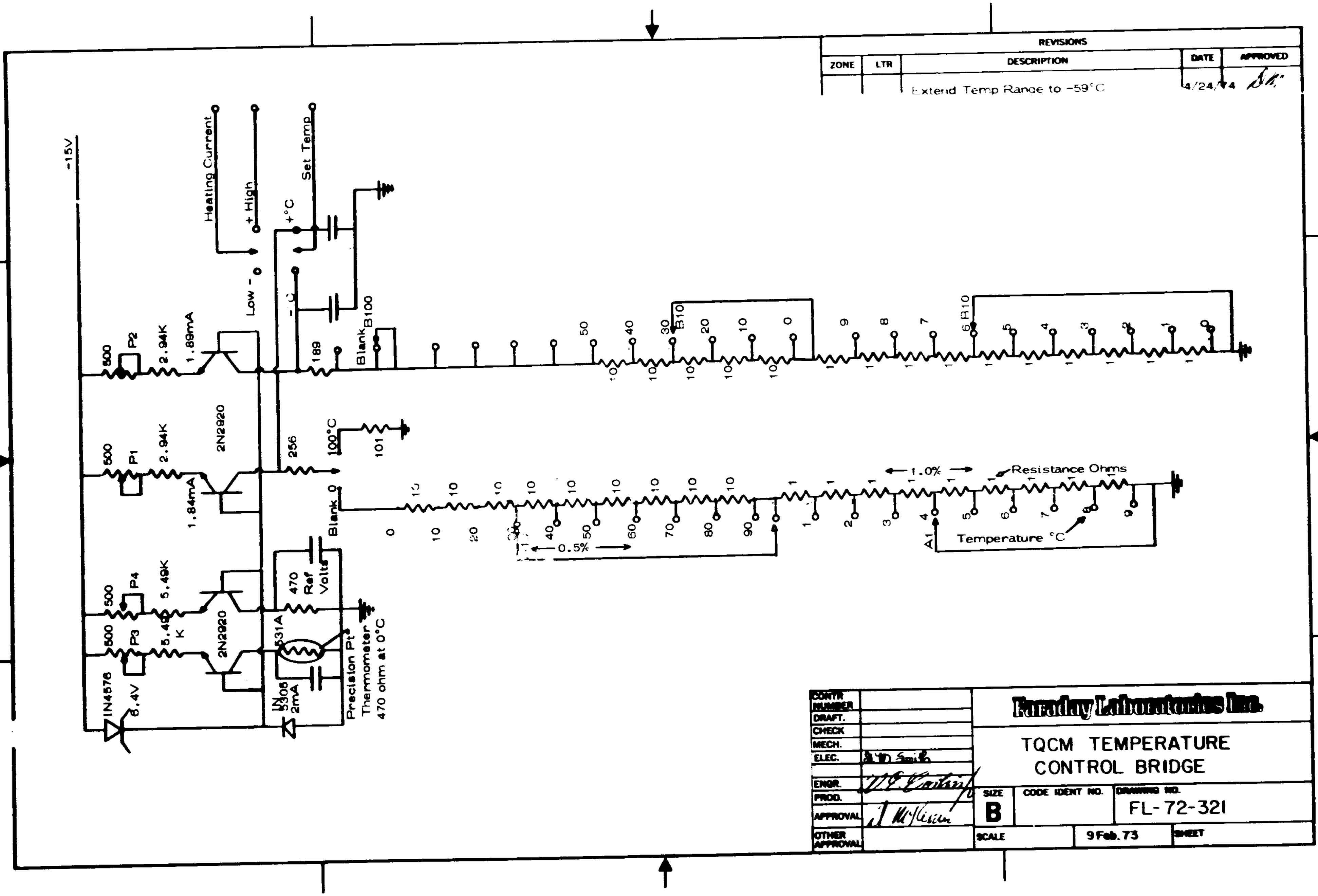
TQCM Controller Layout

Drawing No. FL-72-318



TQCM Controller Wiring Diagram

Drawing No. FL-72-319

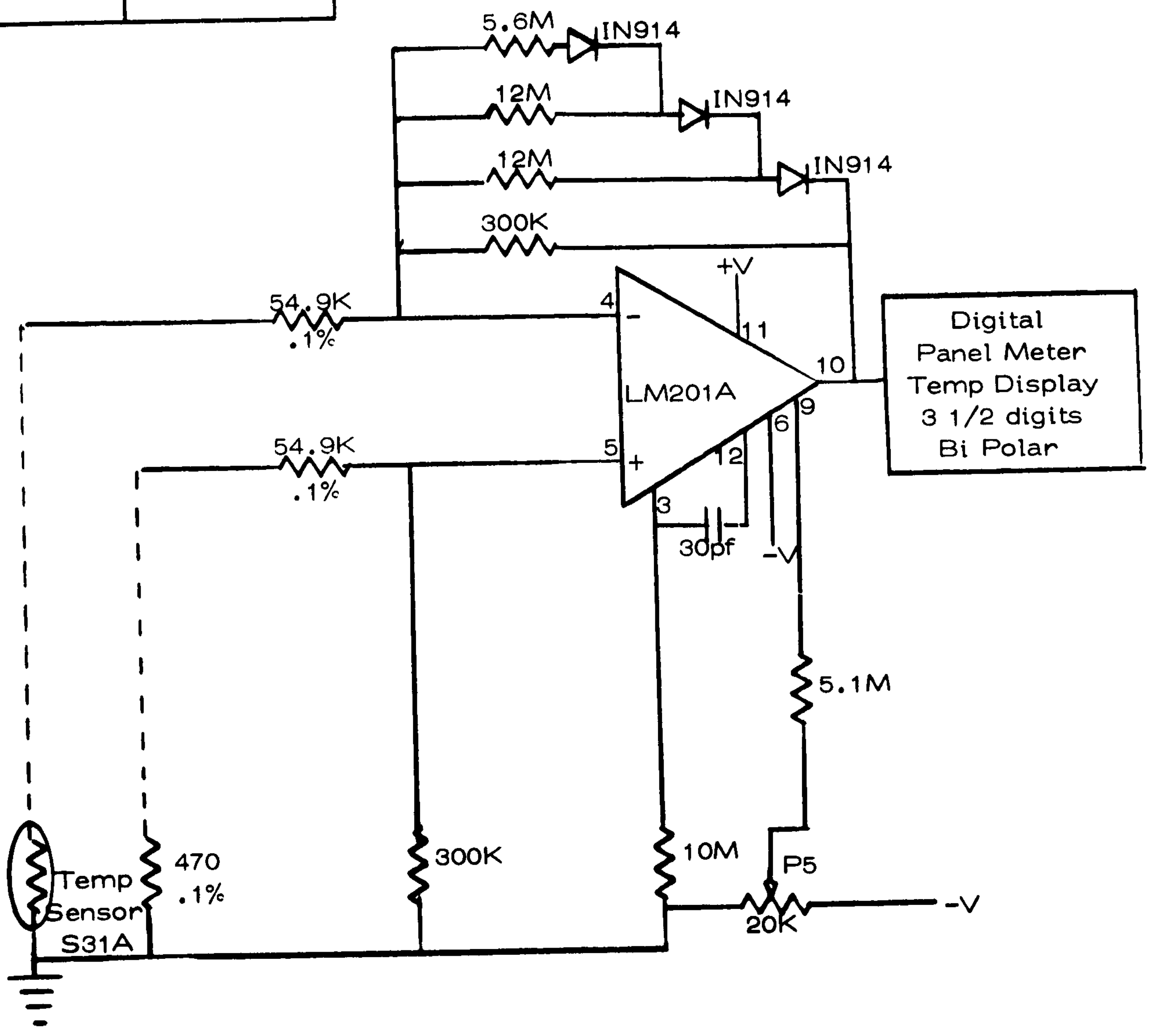


REVISIONS
ZONE
LTR
DESCRIPTION
DATE
APPROVED
Extend Temp Range to -59°C
4/24/74
-15V
Heating Current
+ High
Low -
Set Temp
+°C
-°C
500
P2
2.94K
1.89mA
189
Blank
B100
B10
6 B10
2N2920
P1
1.84mA
256
100°C
101
Blank 0
1.0%
Resistance Ohms
0.5%
Temperature °C
A1
P4
5.49K
P3
470
Ref
Volts
531A
Precision Pt
Thermometer
470 ohm at 0°C
IN4576
6.4V
IN 5305
2mA
CONTR NUMBER
DRAFT.
CHECK
MECH.
ELEC.
D Smith
ENGR.
PROD.
APPROVAL
OTHER APPROVAL
Faraday Laboratories Inc.
TQCM TEMPERATURE
CONTROL BRIDGE
SIZE
B
CODE IDENT NO.
DRAWING NO.
FL-72-321
SCALE
9 Feb. 73
SHEET

APPLICATION	

REVISIONS

LTR.	ECO	DESCRIPTION	DATE	APPROVED
		Increase Display Range to −199°C	4/24/74	DM

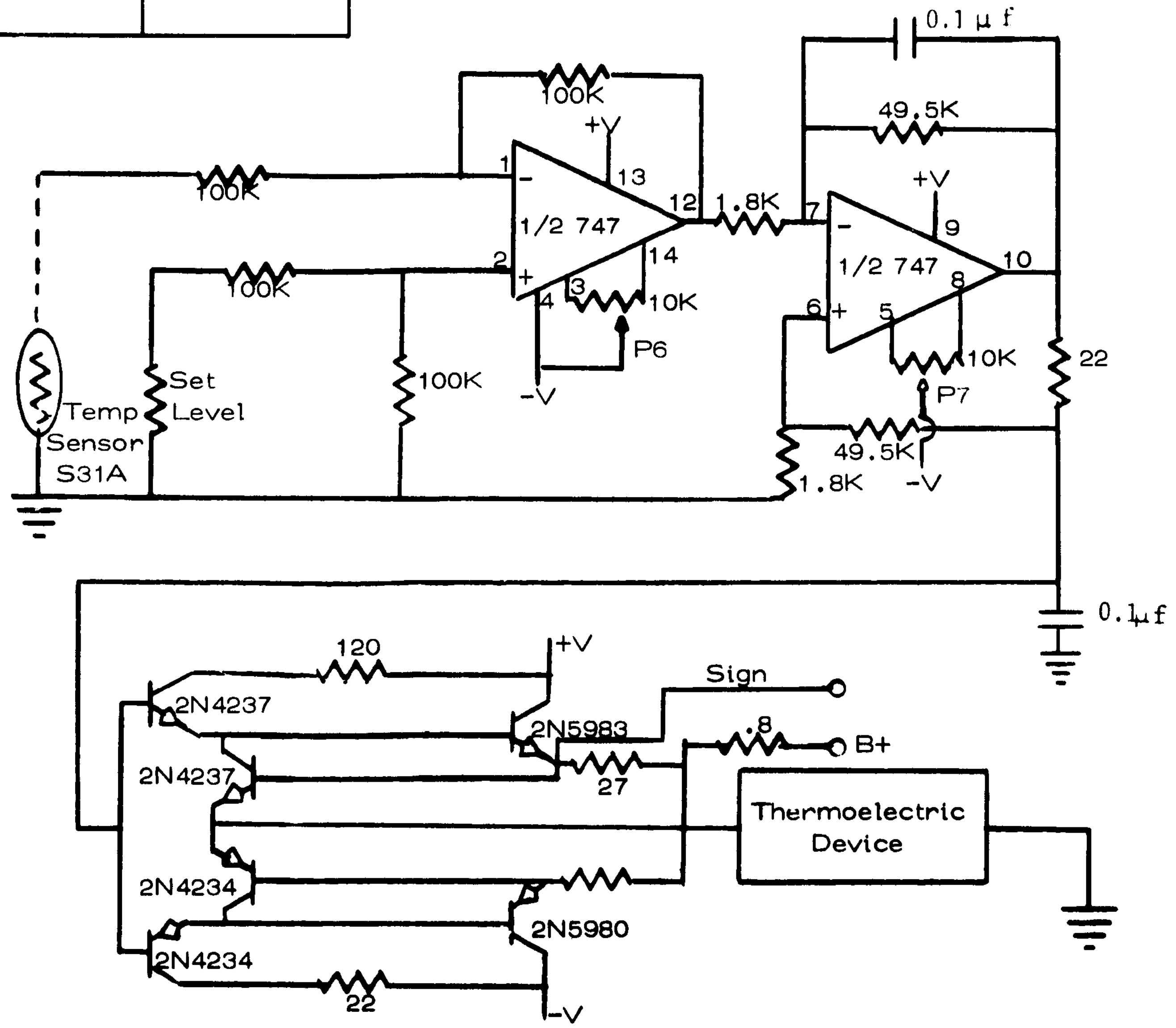


PREPARED		Faraday Laboratories Inc.
CHECK	D. McKenna	TQCM DISPLAY AMPLIFIER
DESIGN	D. M. Smith	
MFG.		
ENG.	W. E. Coorbin	SIZE: A — CODE IDENT. NO.: — DWG. NO.: FL-72-322
RELEASE	9 Feb. 73	SCALE — REV. — SHEET — OF

APPLICATION	

REVISIONS

LTR.	ECO	DESCRIPTION	DATE	APPROVED
		Modify Low Temp Range	4/24/74	



PREPARED	
CHECK	
DESIGN	
MFG.	
ENG.	
RELEASE	9Feb.73

Faraday Laboratories Inc.

TQCM COOLER DRIVER CIRCUIT

SIZE	CODE IDENT. NO.	DWG. NO.
A		FL-72-323

SCALE	REV.	SHEET	OF

Temperature control would be accomplished by modification of the TQCM temperature servo-loop. A cryogenic cooling adapter shown in Fig. 5 would be used to cool the mass sensor down to approximately -199°C by liquid nitrogen cooling.

A helium filled platinum temperature probe in the sensor would be part of the servo-loop. Depending on the temperature set by the thumb-wheel switch in the TQCM Controller, the servo-loop would drive current into a heater in the sensor to reach any desired temperature down to -199°C. The set temperature would be maintained by the TQCM automatically comparing the platinum temperature probe with the desired temperature and correcting temperature errors by varying the heater power.

20.0 REFERENCES

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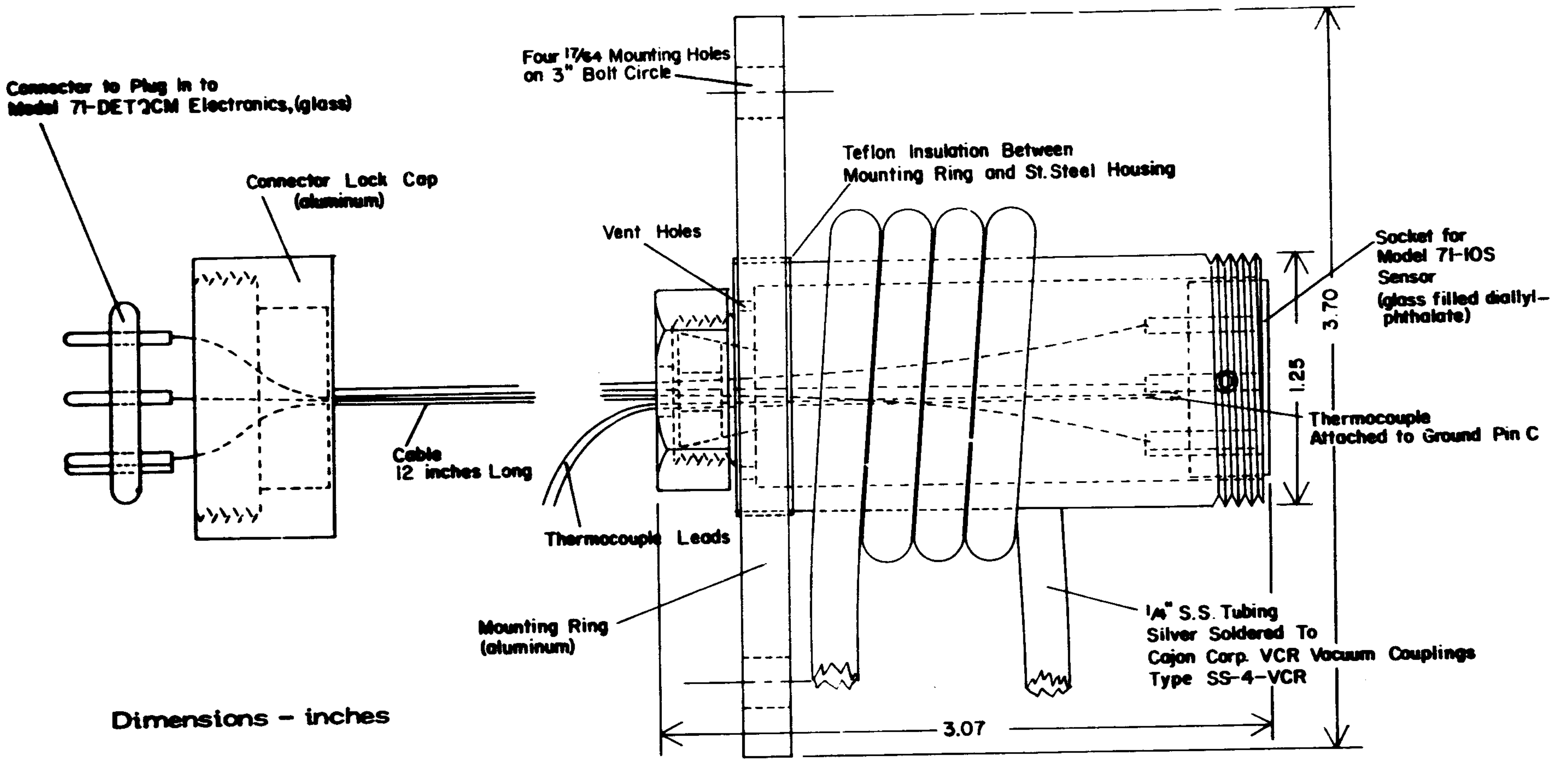

Fig. 5 Cryogenic Cooling Adapter for TQCM Operation between -60°C and -199°C

PART II

THERMOELECTRICALLY-COOLED QUARTZ CRYSTAL MICROBALANCE

D. McKeown, W.E. Corbin, Jr. and R.J. Naumann

THERMOELECTRICALLY-COOLED QUARTZ CRYSTAL MICROBALANCE *

D. McKeown and W.E. Corbin, Jr., Faraday Laboratories Inc., La Jolla, California, and R.J. Naumann, Marshall Space Flight Center, Huntsville, Alabama

ABSTRACT

A quartz crystal microbalance is of limited value in monitoring surface contamination on satellites or in space simulation chambers because it operates several degrees above ambient temperatures. The amount of contamination adsorbed on a surface is highly temperature dependent and the higher temperature of the microbalance will significantly reduce the amount of contamination it adsorbs. Generally, a quartz crystal microbalance will indicate a lower level of contamination than the amount that is actually present. To overcome this problem, a thermoelectrically-cooled quartz crystal microbalance has been developed to monitor surface contamination as a function of temperature.

INTRODUCTION

The use of a quartz crystal microbalance (QCM) is a well established method for weighing thin films of solid materials, down to a fraction of an Angstrom, that are deposited[1] or removed[2] from a surface. Solid films couple strongly into the oscillating QCM and its frequency change is proportional to the mass loading. Direct application of a QCM to monitor a wide range of contamination in space simulation chambers has proven to be a more difficult task because a QCM operates several degrees above ambient temperatures. Gaseous contamination in equilibrium with solid materials in the chamber is not readily adsorbed on a QCM because of its higher temperatures. Contradictory results are often obtained where a passive optical system shows contamination while a QCM operating nearby indicates little is present.

As the study of surface contamination becomes more fundamental in nature, a QCM specifically designed to monitor contamination is

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needed. Not only must the heat generated by the QCM be removed, but a convenient method found to automatically control its operating temperature, so that, surface contamination studies can be made over temperature extremes common to spacecraft. To permit in-situ reflectivity measurements, the crystals should be optically polished. With these objectives in mind, a thermoelectrically-cooled quartz crystal microbalance has been developed for monitoring contamination on optical surfaces as a function of temperature.

QCM LIMITATIONS

A QCM is an active quartz crystal oscillator and power dissipation raises its temperature several degrees above the ambient. Because the amount of contamination adsorbed on a surface is highly temperature dependent, a passive surface at ambient temperature will adsorb a number of contamination monolayers until it reaches an equilibrium with sources in the chamber while a QCM will adsorb a smaller number because of the different equilibrium condition. In some cases, a heavily driven QCM will operate about 10°C above ambient. At this elevated temperature no measureable amount of contamination will be observed.

The amount of contamination adsorbed on a surface is dependent on the residence time, τ, of the contamination molecules[3].

$$\tau = \tau_o \exp(\Delta E/RT)$$

where τ_o is the vibrational period of the contamination lattice, ΔE the desorption activation energy, R the gas constant and T the absolute temperature. Griffith[4] has shown that the desorption rate of contamination with desorption activation energies of less than 25,000 cal/g-mol (oils and epoxies) is highly dependent on temperature. A 10°C temperature rise can result in nearly a ten fold increase in the desorption rate. Use of a QCM to monitor contamination will consistently give lower readings than the actual level present because of its higher temperature.

The strong effect of temperature on the adsorption and desorption of contamination is shown in Fig. 1. Here long-term OGO-6 measurements are shown correlating QCM contamination loading to the eclipse period of the satellite. As has been previously reported, the primary source of contamination on the satellite was the solar panels baking out in the sun[5].

OGO-6 was inserted into a polar orbit with its orbit plane normal to the earth-sun line. This orbit was chosen so that the satellite would

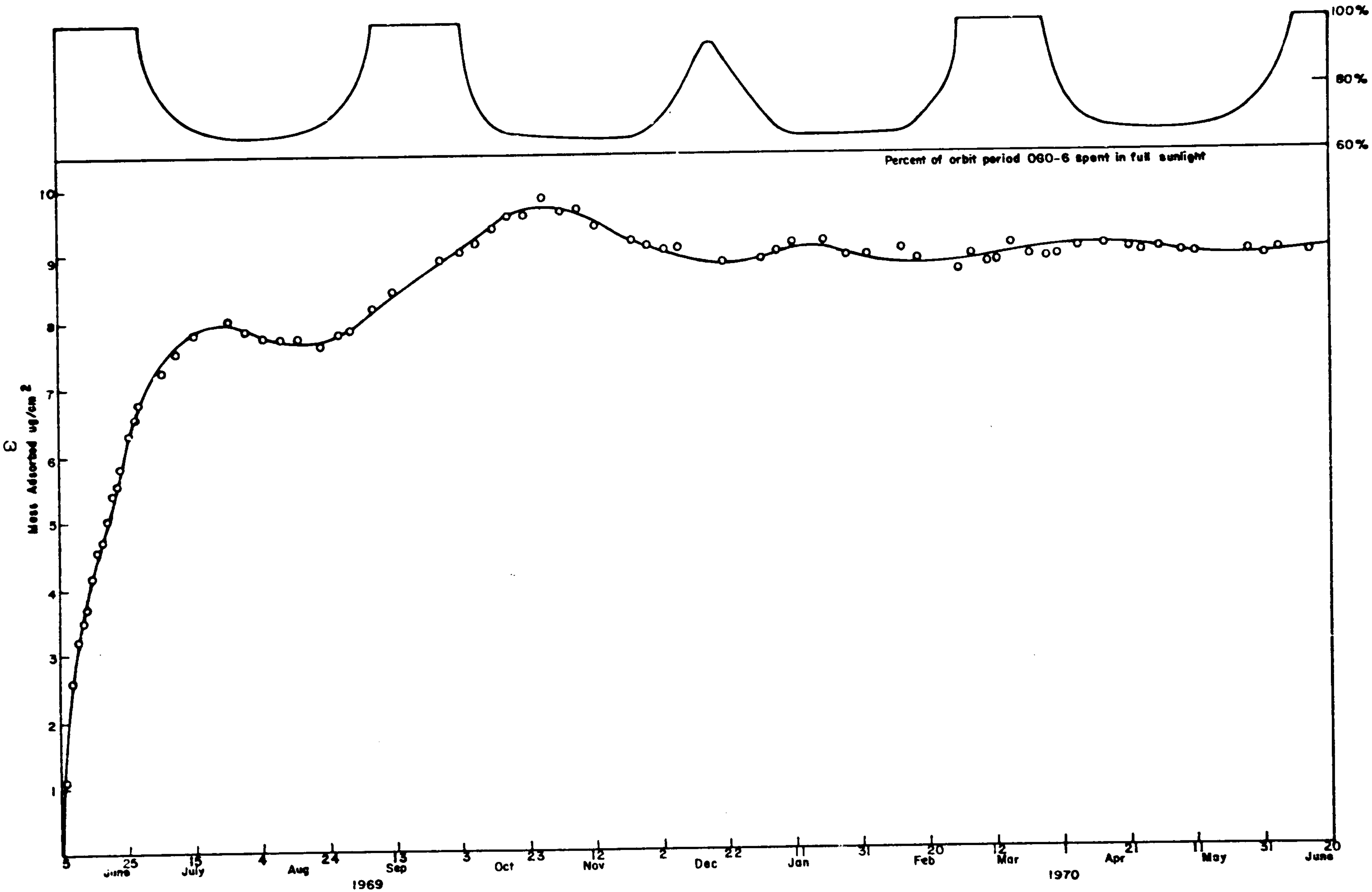

Fig. I Long-term OGO-6 surface contamination measurements correlated to the eclipse periods of the satellite be in full sunlight for the maximum period after launch. During the four week period after launch, the amount of contamination adsorbed onto the QCM steadily increased until the first week in July when it abruptly decreased and finally in August the QCM showed a net loss of contamination and became a contamination source. By correlating the eclipse periods of the satellite to the QCM measurements, the reason for the fluctuation in the contamination adsorption and desorption rates became apparent.

In full sunlight the temperature of the solar panels was 72°C and a wide range of high and low volatile contamination outgassed from the panels onto the QCM. During maximum eclipse, when OGO-6 was in the earth shadow 30% of the time, the average temperature of the solar panels dropped to 60°C and the contamination flux from the panels decreased significantly. The QCM lost contamination during the eclipse period because the lower flux rate from the panels did not balance out contamination desorbing from the QCM. The QCM desorbed contamination into space and onto adjacent surfaces that were at a lower temperature than the QCM.

Although the QCM indicated a loss of contamination during eclipse, contamination was present. Reber's Neutral Mass Spectrometer, located next to the QCM, showed that a strong flux of contamination continued to outgas from the panels.

THERMOELECTRICALLY-COOLED QCM

In order to conduct contamination experiments as a function of temperature, a new instrument called a thermoelectrically-cooled QCM (TQCM) was developed. A thermoelectric device was picked to control temperature because it offers several advantages over other methods. It uses only a series of solid-state bismuth telluride junctions, through which electrical current is passed, to pump heat to or from a load by the Peltier effect. It is small in size and can be remotely operated with a signal pair of electrical leads. It has no moving parts and is highly reliable. There are no requirements for pumping a refrigerant or for supplying a coolant, such as, liquid nitrogen. These features result in greatly reduced operating and maintenance costs in controlling the temperature of a QCM with a thermoelectric device.

The design of the TQCM has been previously reported[6] and only its operation will be described here. The TQCM instrumentation operating under ambient conditions is shown in Fig. 2. The TQCM Controller operates on 115 Vac, 60 Hz at 0.25 A and provides the various voltage outputs to operate the crystal oscillators, temperature bridge,

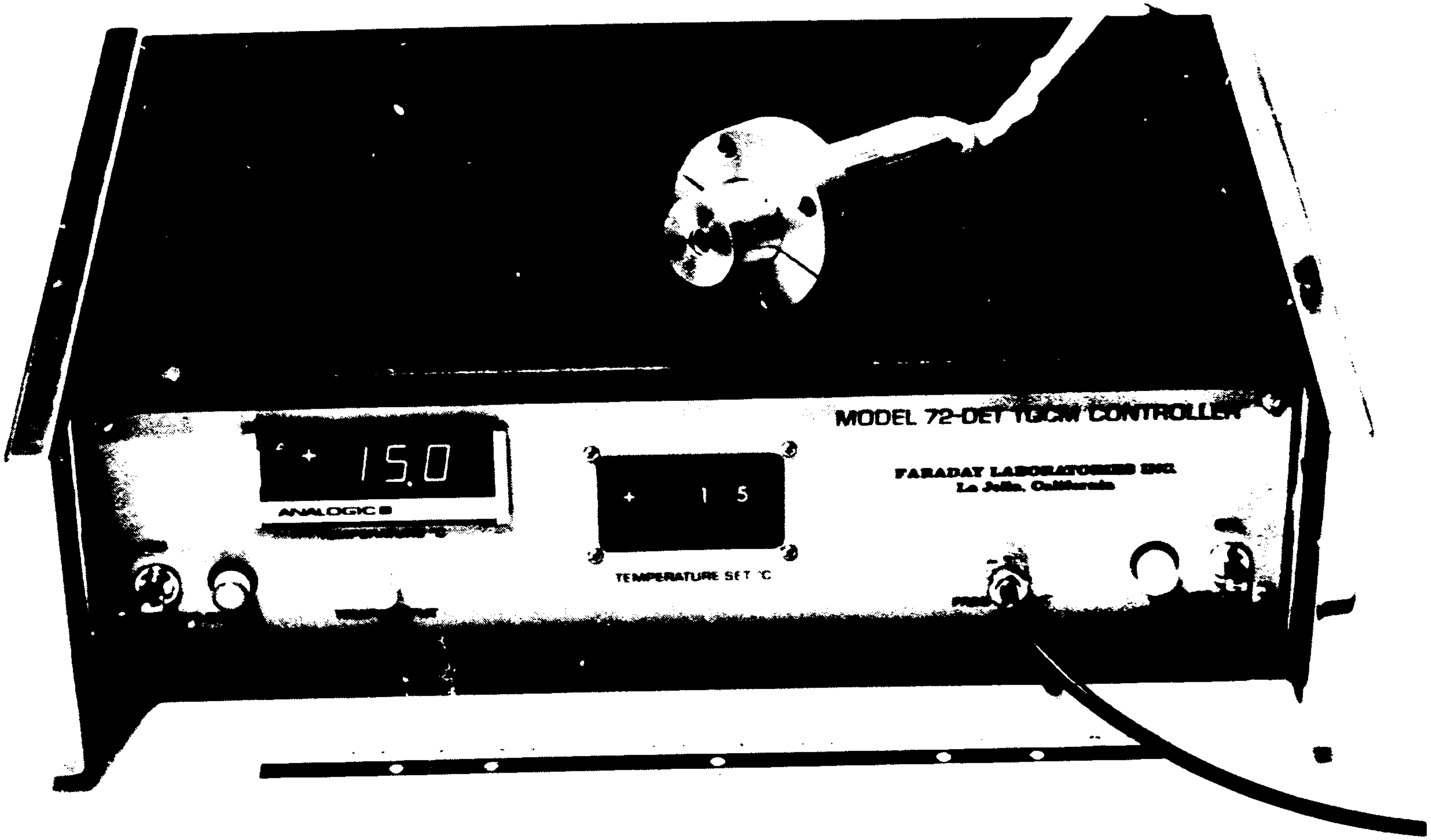

Fig.2 TQCM Operating at +15°C under Ambient Room Conditions

thermoelectric device and readouts of temperature and frequency.

The TQCM Electronics, Heat Sink, and Sensor are shown in Fig. 3. The TQCM uses a two-stage thermoelectric device to automatically control the sensor crystal temperature between -50°C and +100°C to ± 1°C in vacuum. For operation over this range, the heat sink temperature is to be maintained below +40°C. No problem will be encountered in maintaining the heat sink below +40°C by mounting it on a 0.6 cm thick metal bracket. Heat generated by the TQCM is readily dissipated by the bracket at ambient room temperatures.

The TQCM has been designed with an extended temperature bridge circuit and reserve power and will reach a lower temperature limit of -59°C if its heat sink is maintained below +25°C. To maintain a +25°C temperature, the heat sink is to be mounted on a 1.2 cm thick metal bracket capable of removing a maximum 2.8 W when the TQCM is at -59°C. The TQCM cool-down time in vacuum is shown in Fig. 4.

The TQCM operating temperature is set by positioning the thumb wheel switch on the Controller. A 3 1/2 digit panel meter is provided in the Controller for direct readout of temperature.

A temperature output is provided for remote readout or recording. The TQCM temperature sensor is a precision platinum resistance thermometer linear to -.5%. At 100°C the voltage output is 1.00 Vdc. At -59°C the voltage output is - 0.59 Vdc. The TQCM operating temperature in °C equals 100 times the voltage output of the Controller.

A matched pair of precision 10-MHz quartz crystals is used to measure mass loading. The crystals are designated as a sensor and reference crystal. The crystals are optically-polished and plated with Al. The sensor crystal is coated with magnesium fluoride for in-situ reflectivity measurements while contamination is collecting on its surface. The crystals can be changed by unloosening two set screws in the TQCM Sensor.

The output frequency of the TQCM is the beat frequency between the two oscillating crystals. The beat frequency effectively eliminates frequency changes caused by ambient temperature variations. By carefully matching sets of crystals in vacuum, frequency change with temperature of less than ± 50 Hz between -59°C and +100°C is attained. Because only the sensor crystal sees the contamination flux, the TQCM output frequency will increase with mass loading. The crystal sensor is optically polished and full plated on one side. This technique produces a more active crystal whose mass sensitivity is greater by about 20% than semi-polished crystals. The TQCM mass sensitivity, m, is

$$m = 3.5 \times 10^{-9}\ g/cm^2\text{-Hz}$$

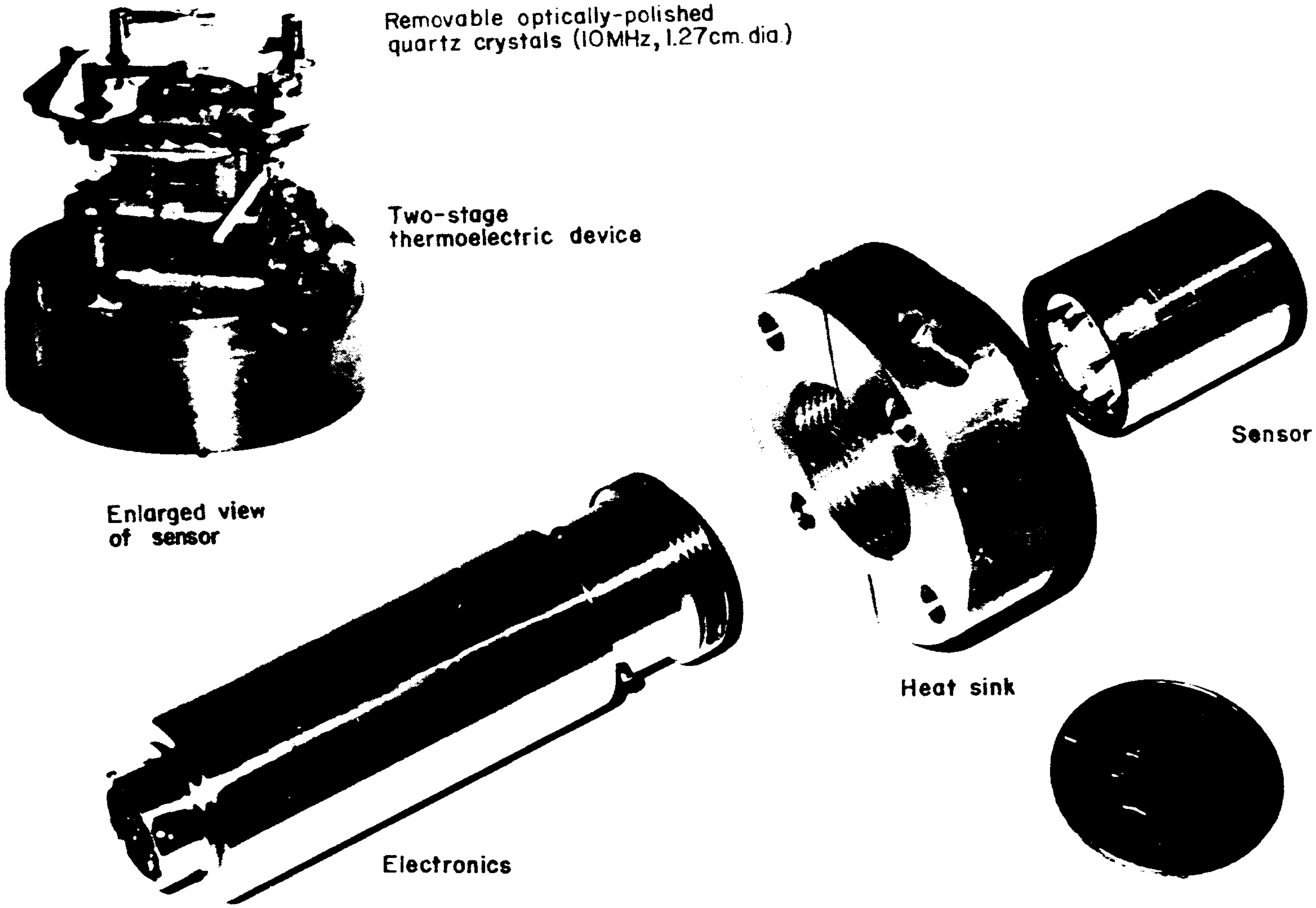

Fig. 3 TQCM Electronics, Heat Sink and Sensor

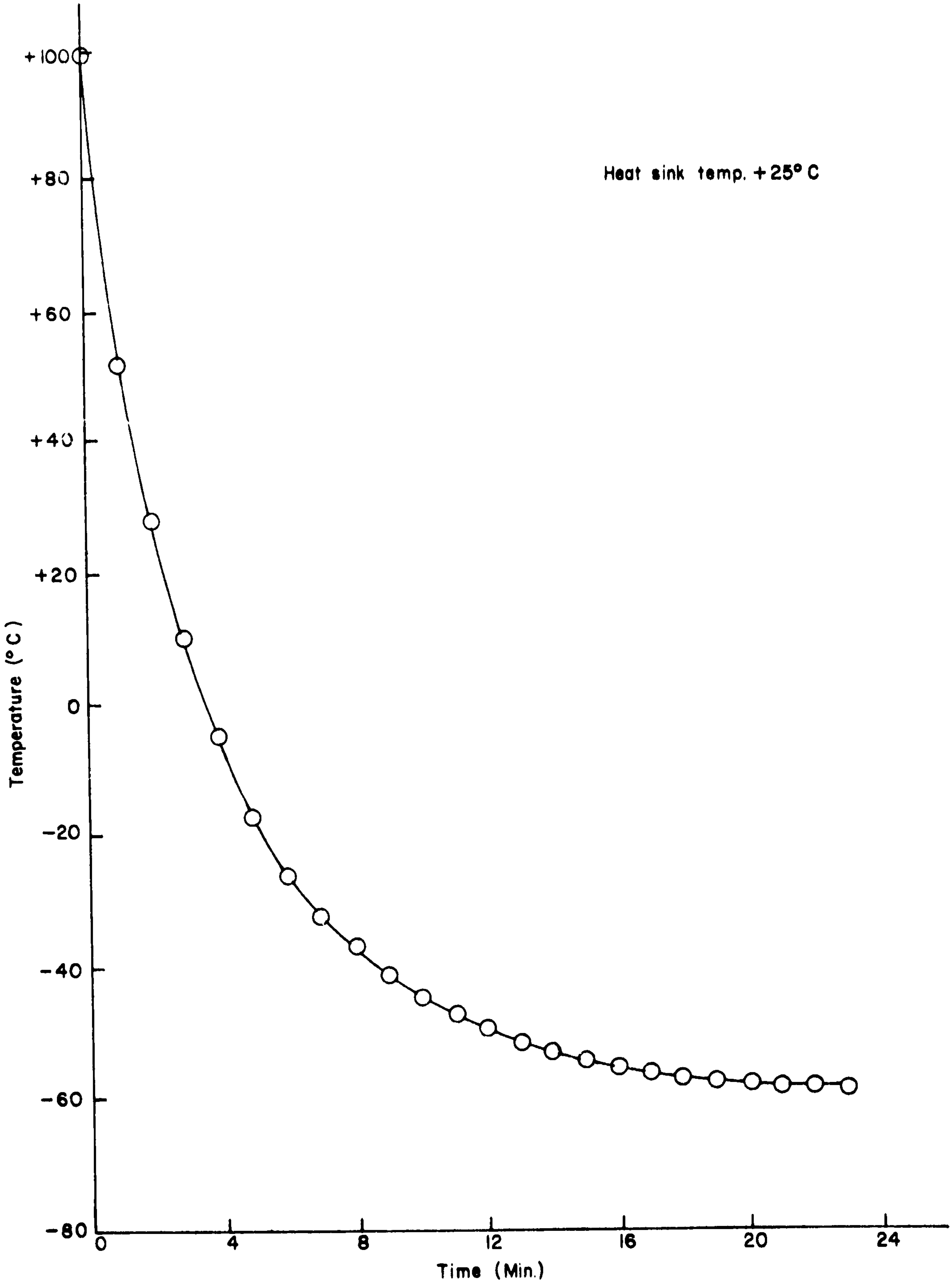

Fig. 4 TQCM cool-down time in vacuum from +100° C to -59° C

A frequency output is provided in the TQCM Controller to measure the frequency change of the crystal sensor produced by mass loading. Frequency is measured by a counter, such as, a Hewlett Packard Model HP5321B.

The TQCM can be set at any particular temperature over its operating range. If the TQCM is set at ambient, the heat generated in the oscillating crystal will be removed so that contamination loading to passive optical systems can be monitored. By increasing temperature to about +100°C the crystal can be cleaned. By periodically dropping the temperature of the TQCM in fixed steps, the amount of surface contamination for different equilibrium temperatures can be determined and the background level of contamination in a space simulation chamber monitored with time.

The TQCM can be used to generate a calibrated contamination flux so that the contamination sticking coefficients of surfaces can be measured. A TQCM calibrated source is generated as follows. Contamination from an uncalibrated source is directed at a TQCM cooled to -50°C. Contamination is allowed to freeze out on the TQCM. The uncalibrated source is then turned off and the vacuum system allowed to pump down. The TQCM now becomes the calibrated source by simply raising its temperature so that the contamination will desorb at the desired rate. By monitoring the TQCM frequency increase with time, the contamination mass flow rate can be accurately determined.

The TQCM can also be used to calibrate the mass loading of viscous films on the quartz crystal sensor that do not couple well into the oscillating mass of the crystal. As a contamination film grows to several hundred monolayers, its top layers will slip relative to the oscillating crystal. The simple relationship between mass loading and frequency change will not hold true. Calibration is achieved by dropping the sensor temperature to freeze the contamination and provide rigid mass coupling to the crystal.

CONTAMINATION MEASUREMENTS

Studies of background contamination in a vacuum chamber were made to show the capability of the TQCM to measure surface contamination under equilibrium conditions. A 150 l/sec Vac-Ion pump was used to evacuate the chamber to the 10^{-9} Torr range. Just prior to the measurements, the chamber was contaminated with Welsh Duo-Seal roughing pump oil that raised its pressure into the 10^{-7} Torr range.

The net mass gain or loss for an aluminum surface from the adsorption and desorption of background contamination present in the chamber at 7×10^{-7} Torr is shown in Fig. 5. Below -30°C adsorption predominated and contamination collected on the surface. Above -30°C desorption predominated. The break in the curve at about -10°C where the rate of desorption increased abruptly is significant.

The break shows a phase change occuring in the contamination from a solid to a liquid. The phase change caused a large increase in its vapor pressure and the higher desorption rate. We were unable to make a measurement at +20°C because the desorption rate became so large that by the time the surface reached +20°C the contamination was nearly completely desorbed.

Fig. 6 shows the desorption rate of roughing pump oil as a function of the number of monolayers on the surface for a contamination background pressure of 4×10^{-7} Torr. When the number of contamination layers reaches 200, the increase in the desorption rate starts to level off indicating the bulk properties of the oil predominate and the properties of the surface have little effect on the desorption. At 0°C the leveling off of the desorption rate is quite evident.

The desorption rate decreases rapidly as the number of layers present is reduced because of the higher bonding energy holding contamination layers near to the surface. The higher bonding energy results from contamination molecules filling cracks and crevices in the polycrystalline aluminum surface.

The number of monolayers of contamination on a surface in equilibrium with the contamination on the walls of the vacuum chamber as a function of temperature is shown in Fig. 7. The ambient temperature of the chamber was 23°C. The measurements were made by raising the TQCM temperature to +80°C to bake off surface contamination and then dropping its temperature to -50°C to adsorb a film of contamination. The TQCM temperature was then increased to a particular equilibrium temperature shown in the figure to determine the number of contamination monolayers. From the figure it can be seen that there was always oil contamination on the surface even at 4×10^{-7} Torr for temperatures below +30°C. It would have been impossible to make the measurements with a QCM because there are no net mass changes at equilibrium.

CONCLUSIONS

Most contamination is adsorbed on a surface in the gaseous

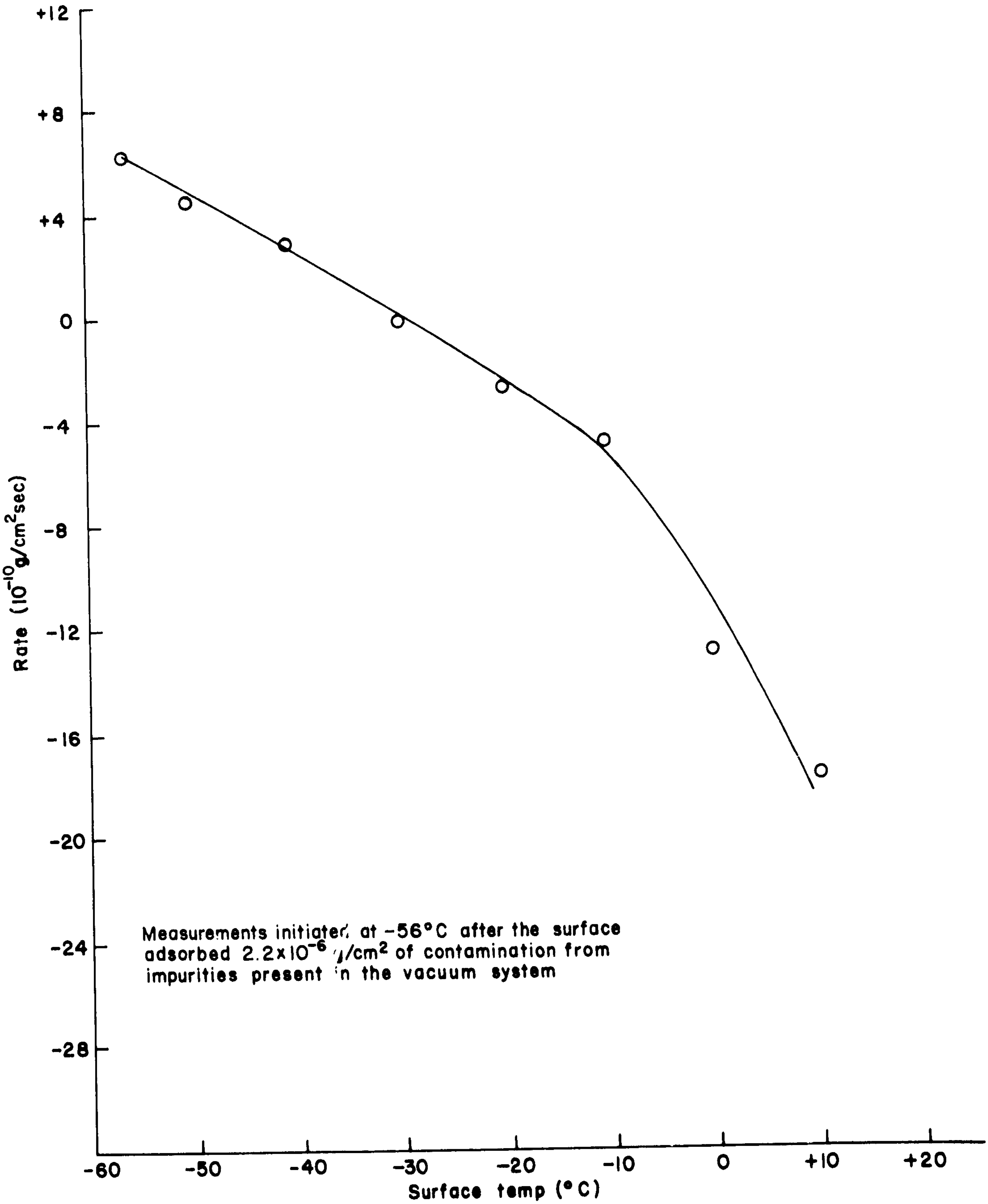

Fig.5 Contamination adsorption and desorption rates for an Al surface with temperature in a 7×10^{-7} Torr vacuum

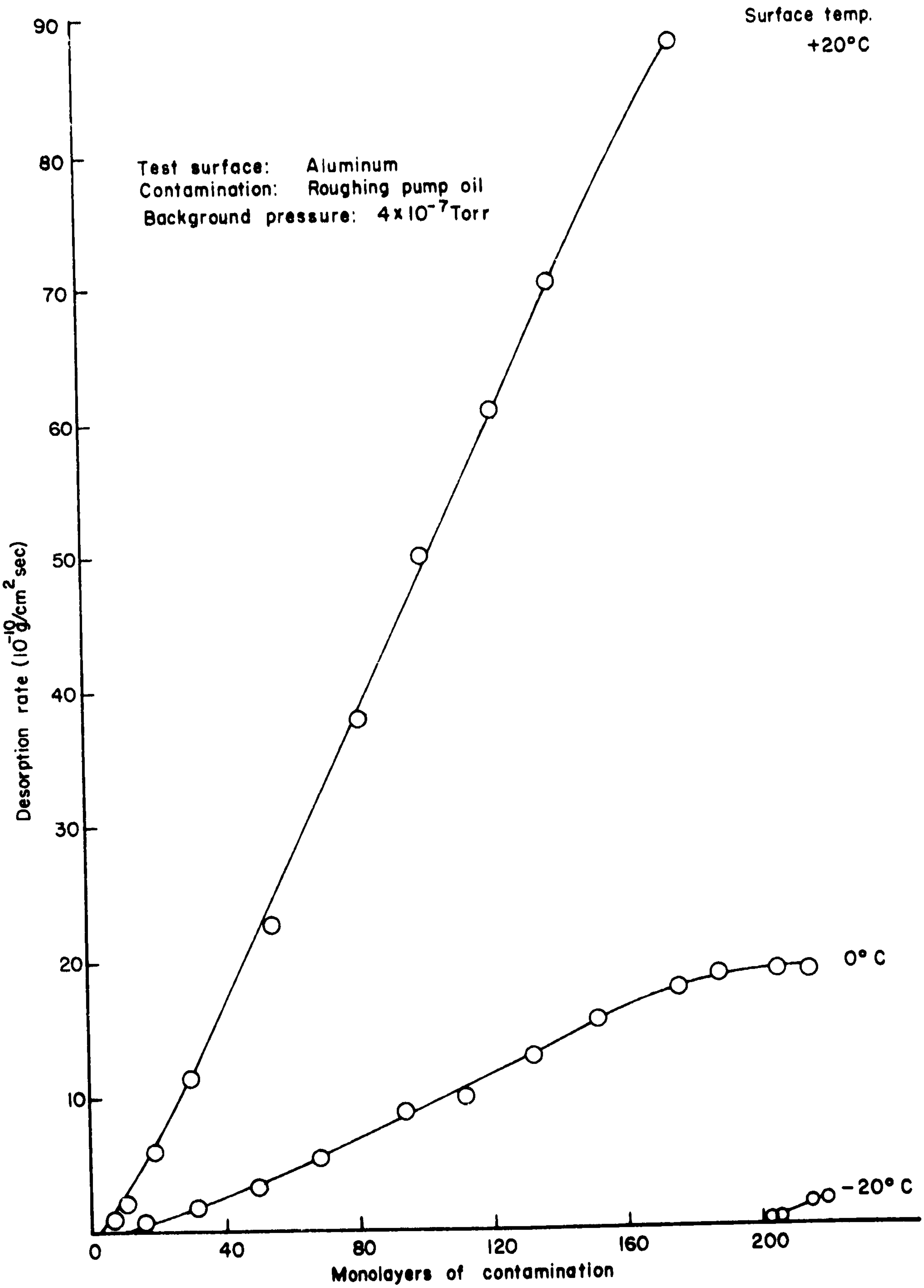

Fig. 6 Contamination desorption rate as a function of monolayers on the surface

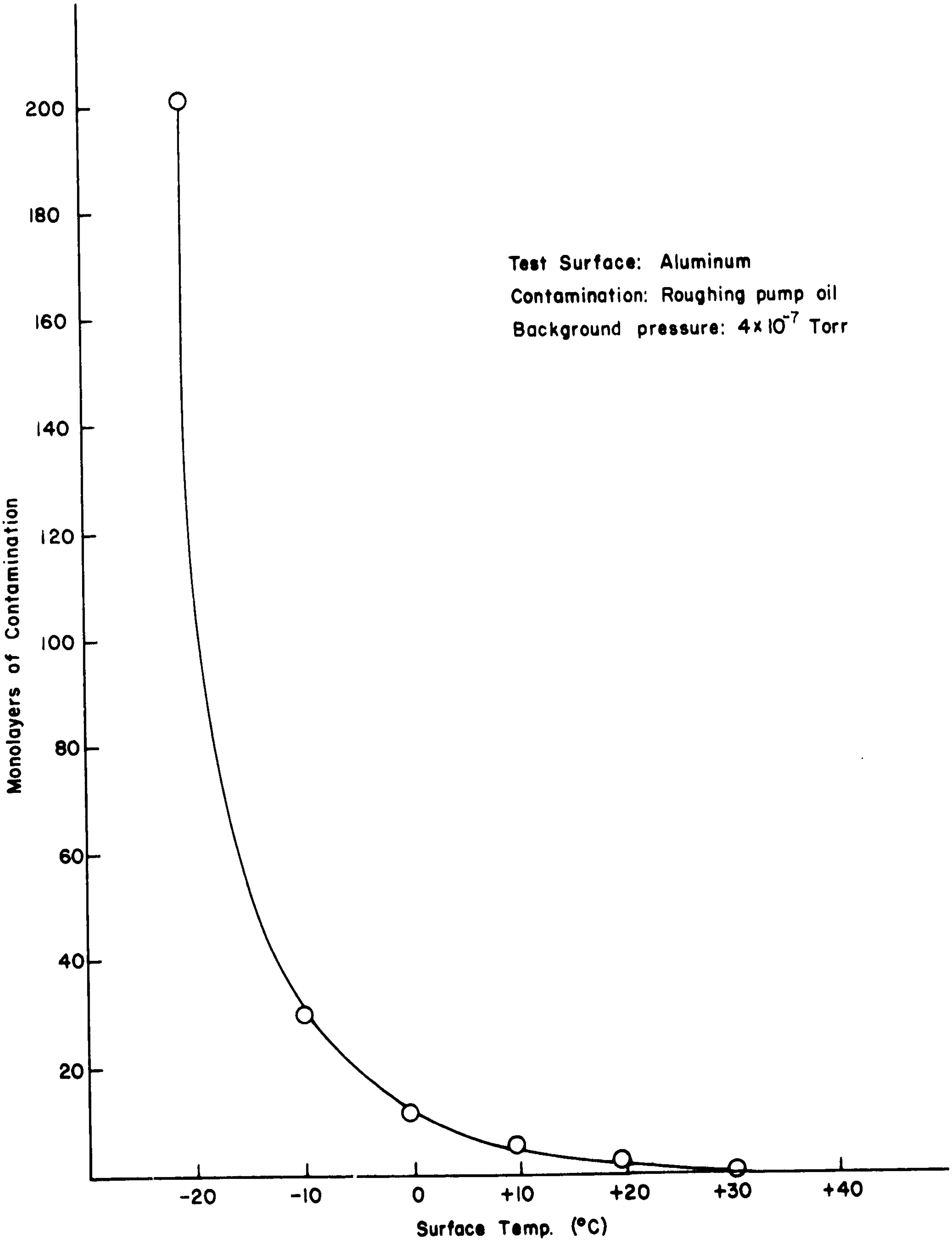

Fig. 7 Number of contamination monolayers on a surface at equilibrium

or liquid state and the adsorption rate is highly temperature dependent. A QCM is of limited value in monitoring contamination because it operates several degrees above ambient temperatures and does not readily adsorb contamination. For accurate measurements, a temperature controlled QCM should be used.

If a QCM is used to monitor contamination, measurements should be made from a directed source. The source temperature should be much higher than the QCM operating temperature to insure that the contamination sticking coefficient is greater than zero.

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