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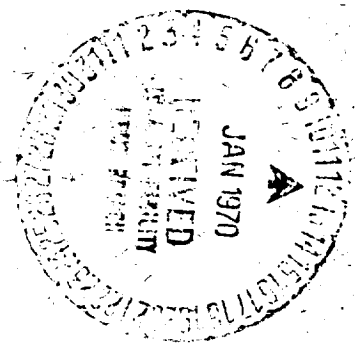
GSFC MICRO-VOLATILE CONDENSABLE MATERIALS SYSTEM FOR POLYMER OUTGASSING STUDIES

OCTOBER 1969



GSFC

GODDARD SPACE FLIGHT CENTER

GREENBELT, MARYLAND

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GSFC MICRO-VOLATILE CONDENSABLE MATERIALS SYSTEM FOR POLYMER OUTGASSING STUDIES

Aaron Fisher and Benjamin Mermelstein
Materials Research and Development Branch
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ABSTRACT

This document comprehensively describes instruments and techniques used by the Polymer Section for rapid quantitative screening of gases and condensables evolved from polymeric materials heated in vacuum at 125°C. The GSFC volatile-condensable-materials (VCM) system is adapted from the basic Stanford Research Institute (SRI) system, with specialized GSFC instrumental and operational modifications.

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ILLUSTRATIONS

GSFC MICRO-VOLATILE CONDENSABLE MATERIALS SYSTEM FOR POLYMER OUTGASSING STUDIES

INTRODUCTION

It has been recognized since early in the space-operations program that the use of polymers in an extraterrestrial environment has inherent disadvantages not normally found in the use of ceramics and metals. Although polymers have been employed extensively in spacecraft for their many unique and specialized properties, they can be susceptible to particulate radiation. In addition, at certain temperatures, various components or ingredients of a normally useful polymer may be driven off or outgassed as volatile materials in vacuum. The radiation of polymers could cause potentially volatile materials to develop as degradative end products or low-molecular-weight fractions. Initially, only weight-loss values resulting from thermal-vacuum environments were used as criteria for spacecraft suitability. Later the concept developed that although outgassing is undesirable, the formation of condensable volatiles has the more detrimental effect on a spacecraft's vulnerable thermal-control coatings and optical surfaces. Condensables can collect on cold optics, affect light transmission and reflectivity, and change the critical a/e ratio of coatings. Excessive outgassing can contribute to lower voltage corona inception and multipacting[1], and can also modify the initial physical properties of the polymer. The VCM[2] was developed to permit screening of various polymers through evaluation of their volatile and condensable material contents and on that basis allow the selection of those polymers with the lowest VCM's for particular applications.

Dr. Muraca of the Stanford Research Institute, under contract to the NASA Jet Propulsion Laboratory, developed the initial equipment required for measuring condensables. The SRI staff performed extensive testing on polymer materials[2] from June 1964 to August 1967 when the contract terminated. The GSFC Polymer Section, because of its own outgassing information requirements relative to Goddard cognizant spacecraft, has been deeply involved in this field for 3 years. This continuing effort has been found necessary since requests for material evaluation from contractors on OAO, OSO, and ATS-F and G have continually increased. The Polymer Section has tried to improve techniques and instrumentation and to develop new use concepts for obtaining the maximum capability from the basic VCM apparatus. The measuring instrumentation and conditioning techniques described in this document are GSFC initiated.

MICRO-VCM OPERATIONAL CRITERIA

Basically, the GSFC MR&D VCM system is a rapid-screening technique to evaluate the weight loss of polymeric materials being subjected to 125°C at 1×10^{-6} to 1×10^{-7} torr for 24 hours. The overall weight loss can be classified into noncondensables, or true gases, and hot vaporous condensables. The latter are further characterized as capable of depositing out on a relatively cool surface, 23°C ±2°C, in the above vacuum.

The micro-VCM was developed at SRI from an earlier system of macro-VCM determination which required larger samples and a longer time period for weight loss to reach equilibrium. In general, the case for micro-VCM states that if much smaller samples are used, the representative total weight loss should occur in a much shorter period of time.

In addition, on the basis of physical property change in outgassed material[2] and optical criteria, it was believed that 1 percent total outgassing and 0.1 percent volatile condensables should be the outer limits on material acceptable for spacecraft use, especially for long-term missions. These criteria set high standards for material acceptance, yet still allow the use of many available polymers for most required applications.

DESCRIPTION

The VCM screening apparatus consists of two resistance-heated vertically mounted copper bars (Figure 1). Each bar is 25.5 inches long with a 1-inch square cross section, and contains 12 horizontally oriented sample chambers. The open rear cross section of each chamber "sees" or projects through a perforated barrier plate, onto a removable chrome-plated cold collector plate (Figure 2) maintained at ambient temperature throughout the 125°C test period. A total of 18 outgassing chambers are used for testing during a 24-hour run. Four additional compartments are set up as controls. The VCM system is mounted on the base plate of the Veeco 775[3], within a narrow 10-inch diameter pyrex vacuum bell that rests on a specially adapted feed-through collar, also supported by the base plate.

The test vacuum system operation and pyrex bell-raising mechanism are automatically controlled. In addition, an extended table top provides for adequate instrumentation-mounting space. Power to the Xactoglow heating element mounted in the copper bar is at first manually controlled by variac powerstat transformers. The Leeds and Northrop fail-safe temperature controllers then take over this critical input. Honeywell-Electronik 19 recorders, with electronic ice-point reference-junction feedback, monitor heater-bar temperatures. A Haake heat exchanger using Dow-Corning 200 silicone fluid maintains the collector plate at ambient temperature during the test.

Figures 1 - 16 show GSFC's complete VCM system as it is adapted to the Veeco 775. These figures may be used as a guide to construct an identical system. This present setup has been operating with no breakdowns after many months of continuous testing.

APPLICATION OF THE VCM SYSTEM

Many types of organic and polymer materials can be tested. These include polymer potting compounds, foams, elastomers, films, tapes (magnetic, electrical, reflecting), insulations, shrink tubing, adhesives, coatings, fabrics, tie cords, and greases. The materials may be tested in the as-received condition, or prepared to varied specifications for curing.

The VCM was originally conceived as, and still basically is, a fast screening test. However, the VCM has also been developed into a test procedure for evaluating the effect of various post cures or temperature treatments on polymer outgassing. It was also found possible to analyze condensables with infrared. The GSFC method deposits condensables directly onto KBr salt flats (Figures 19 and 20) adapted to immediate infrared analysis, with no interposed steps.

The Polymer Section has used the VCM to develop or analyze known-composition low-outgassing potting materials, paints, sealants, and useful concentrations of fluorescent materials in polymers. Optical filters are now being considered as condensing surfaces in studies on the effectiveness of such filters in an outgassing environment. Plans are underway to study reflectivity, and also to evaluate the efficiency of interposed barriers between an outgassing source and an optical surface.

General VCM Procedure and Calculations for Total Weight Loss and Condensables

The material to be tested is put in a preformed degreased weighed aluminum foil boat for 24 hours storage at 50-percent relative humidity. At the end of this period, boat and sample are reweighed and put into one of the 12 compartments of the copper bar. The bar heater raises the compartment temperature uniformly to a prescribed controllable 125°C ± 2°C. Under vacuum conditions, the heated material evolves true gases and vapors. The vapors stream from a hole in the rear of the chamber, move toward and condense on a previously weighed and independently cooled chrome-plated aluminum disc. After 24 hours the entire system is cooled down with ultra high purity gaseous nitrogen having low moisture content. Sample boats and collector plates are weighed. Differences are obtained from pre-run weighings. Total percentage material loss in conjunction

with percentage condensable deposition is ascertained. Final values are an average of results from three samples. Several empty chambers and collector plates at the bottom of the heater bar are run as controls to ensure that uniform cleaning procedures have been followed from run to run. This operational method permits examination of six individual type samples each time the two-bar system is run. Normal runs from bulk materials, requiring no preparation, require 3.5 to 4 days.

Calculations for Obtaining Total Weight Loss and Condensables

	Initial Wt. gms.	Final Wt. gms.
Sample and Boat	$S_I + B_I$	$S_F + B_I$
Boat	B_I	B_I
Sample alone	$(S_I + B_I) - B_I = S_I$	$(S_F + B_I) - B_I = S_F$

Difference or weight loss $L = S_I - S_F$

$$\frac{L}{S_I} \times 100 = \text{percent total outgassing weight loss}$$

Final weight (gms), collector plate and condensables C_F
Initial weight (gms), collector plate (no condensables) $-C_I$
Weight (gms), condensables C_0

$$\frac{\text{Condensable weight (gms)}}{\text{Initial sample weight (gms)}} \left[\frac{C_0 \times 100}{S_I} = \text{percent total VCM of original sample}\right]$$

Infrared Analysis of Condensables

This important capability has been designed into the GSFC system to permit rapid analysis. Infrared tests for polymer condensables can be run alone or in conjunction with weight-loss tests for specific polymers; when the tests are run together, weight loss and corresponding condensables can be determined immediately and completely. If weighing aspects are not involved and only infrared analysis is desired, comparatively large amounts of material can be used in the heater bar to ensure adequate deposition of film condensate onto the KBr salt flats. The flats, 1-inch in diameter by 0.125-inch thick, are supported edgewise in a metal holder which fits into the collector-plate receptacle (Figures 8 and 9). On test completion, the flats can be released immediately and placed into the Perkin Elmer infrared unit adapter for examination.

Thermal - Vacuum Fractionation of Condensables

Infrared analysis of condensables is normally part of the conventional 125°C operation. However, because heater-bar temperatures are controllable, the system may be used as a potential fractionator, where outgassing compounds may be separated at specific heater-bar temperatures as a function of their vapor pressures. In this way, condensables produced with a 75°C heater bar were examined, using the system as a potential fractionator. This enabled clarification of the infrared trace of the same material made from condensables evolved at 125°C.

REFERENCES

1. The Study of Multipactor Breakdown in Space Electronic Systems. Hughes Aircraft Co. NASA CR-448. July 1966

2. R. F. Muraca, J. S. Whittick, and SRI project ASD-5046. Polymers for Spacecraft Application. Prepared by SRI for JPL under JPL contract 950745, NAS-7-100. June 1964 to August 1967

3. Veeco-775 Series High Vacuum Systems, Stations and Evaporators, Operation and Maintenance Manual

APPENDIX A

VCM OPERATIONAL CYCLE

a. Weigh the precleaned aluminum foil boat and return it to its storage beaker in a glass desiccator.

b. Add the test sample (100 to 300 mg) to the boat and condition the sample at 50-percent relative humidity for 24 hours.

c. Quickly weigh the sample and boat in a conditioned 40-50-percent RH environment, using the Mettler-Micro-Grammatic M-5 optical balance. (This unit has a 20-g capacity and a ± 0.001-mg sensitivity.)

d. Place the sample and boat into a compartment of the micro-VCM test bar.*

e. Weigh a clean collector disc and mount it into its cooling-plate receptacle.

f. Mount and screw down respective cover plates onto the entry end of each compartment.

g. Lower the glass bell which encloses the system during testing onto the feed-through collar. Evacuate the system (see Veeco Manual 775).

h. Begin cooling the baffles with liquid nitrogen while the system is being evacuated. Begin cooling the collector plates, using the Haake heat exchanger.

i. Activate the bar heater temperature regulating "powerstat" variacs when the system attains a vacuum of 1×10^{-5} torr. This input (40 on the variac dial) raises the copper-bar temperature to 125°C in 25 minutes.** At that temperature, cut back the dialed input to 20. These steps allow the Leeds and Northrop temperature controllers to maintain bar temperatures at 125°C ± 2°C.

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*At the beginning of step d, the copper compartment bar, separator, and cooling plate are all clean, in position, and awaiting the sample boats and collector plates. The separator plate minimizes cross-contamination between samples.

**Powerstat variacs rated at 1 kva, 7.5 amps and 140 volts

j. Maintain collector-plate temperatures at 23°C ± 2°C with the Haake thermal exchanger.

k. Continue heating for 24 hours, then start the cooling cycle.

l. Turn off the hi-vac valve to the Veeco pump system and the heater current.

m. Open the vent valves so that 2 psi of clean dry nitrogen is bled into the system to cool the bars rapidly.

n. Raise the bell 1.5 to 2 hours after the start of the cooling cycle. By this time, the heater-bar temperature should be down to 50°C.

o. Store aluminum boats with samples and respective collector plates in desiccators immediately. After the samples have been conditioned for half an hour, quickly weigh them. This simulates the dry condition of the sample within the VCM at the end of testing.

This test sequence applies to bulk samples, as received. Various polymer forms require some modification in sample support during testing. Adhesive tapes are normally tested while rolled around a smooth glass rod with the adhesive surface facing the rod. They may also be wrapped around a stainless-steel rolled screen, to allow maximum adhesive-surface areas to be exposed during testing. Paints are normally applied to stainless-steel mesh screening by dipping, then cured before testing. Some adhesives or sealants may be cured in the aluminum boats; other cured polymers may be powdered before testing.

APPENDIX B
PREPARING AND CLEANING ACCESSORIES

Aluminum Boats

Fabrication. Use Alcoa aluminum foil 5182, 0.001-inch thick, to make 1/2-inch by 1/4-inch sample boats. Contour the boats to fit the heater compartments by pressing the flat foil into a 1-lb density flexible urethane foam (Figure 17) with an appropriate die.

Degreasing. Vapor-degrease the boats for 15 minutes with a 1:1:1 by volume, c.p. chloroform-benezene-methanol blend and dry at 125°C for another 15 minutes.

Storage. Place boats in 10-cc beakers with designated compartment numbers, then store in a desiccator containing indicating silica gel. Seal the unit with Dow-Corning high-vacuum grease.

Condensor or Collector Plates

Fabrication. Prepare plates with a highly polished chrome face (Figure 14) to assist in visual observation of condensables.

Degreasing. Vapor-degrease and dry plates according to the procedure for degreasing and drying boats.

Storage. Mount plates on a circular plate rack (Figure 18) and store in a desiccator containing indicating silica gel. Seal the unit with Dow-Corning high-vacuum grease.

Compartmentalized Copper Heater Bar

Fabrication. The Mount Vernon Research Company of Alexandria, Virginia, machined the heater bar according to Figure 6. The Claude S. Gordon Company of Cleveland, Ohio manufactured the hair-pin-shaped resistance heater, Xactoglow 601-1107-007 (see Xactoglow Bulletin 1-600). The Walt Colmoney Company of Morrisville, Pennsylvania, brazed the Xactoglow heater to the copper bar, using a silver-copper composition of 72 and 28 percent, respectively. A hydrogen atmosphere furnace maintained at 1900°F was required for this operation.

Degreasing. Take special care with the bar between runs to avoid subsequent test contamination. Abrade all cavities and flat surfaces clean with a heavy-duty A4 medium-grit rubber-bonded abrasive rotating wheel (Fordome Electric Company, Bethel, Connecticut). Then wash the bar cavities and surfaces with a 1:1 volume certified ACS acetone-ethyl alcohol blend; dry the bar with Freon 12 clean gas. Mount the bar into the bell without sample specimens. Evacuate the system to 10^{-6} torr and outgas the bar at 130°C for 5 hours. This is 25°C above normal test temperature. Then shut down the system and allow the bar to cool over night.

Storage. Keep the heater-compartment bar under the bell until it is ready to be loaded with test samples.

Separator Plate

Fabrication. This aluminum plate is 25-7/8 inches long with 3/8-inch-diameter holes, interposed directly between the outgassing cavity and condensor plate. Each hole is opposite the exit hole of the heater-bar chamber (Figure 4).

Degreasing. Wash the separator plate with a 1:1 certified ACS acetone-ethyl alcohol blend, then dry the plate with compressed Freon 12 gas.

Storage. Keep the plate clean and cover it during preliminary bar outgassing.

Cooling-Plate Support

Fabrication. See Figure 2.

Degreasing. Wash the cooling plate with C.P. ethyl alcohol, then dry it with compressed Freon 12 gas.

Bell Jar

Fabrication. The Corning Glass Company manufactured the pyrex vacuum bell jar. This unit is 10-1/4 inches in diameter, 30 inches tall, and has an L-shaped Viton A gasket seal.

Degreasing. Inefficient vacuum development often indicates that material is outgassing from the internal bell-chamber surface. Wipe down the bell interior with C.P. ethyl alcohol to restore the system's operating efficiency.

Collar

Fabrication. The Mount Vernon Research Company manufactured the feed-through collar according to Figure 15.

Degreasing. Wipe the collar clean with C.P. ethyl alcohol before a vacuum run.

Veeco Vacuum System

Fabrication. See Veeco catalog 775.

Maintenance. Maintain the bell as indicated, and change the Dow-Corning 704 silicone oil every 6 months. Check O-rings every 6 months. Replace filters for the cooling water on the diffusion pumps every 3 weeks.

APPENDIX C

GSFC VCM INSTRUMENTATION MODIFICATIONS FOR SYSTEM RELIABILITY

The Leeds and Northrop Milli-Temp Controller, model 7122-1129 (Figure 21), provides fail-safe temperature control of the heater bars. The copper-constantan sensor is tightly clamped at the bar's center point with a screw arrangement.

The Honeywell Electronik-19 two-pen recorder (Figure 21) continuously monitors bar temperature throughout the run and indicates any unusual temperature fluctuations during the night. The copper-constantan sensor is clamped to the top of the bar.

The ice-point reference system 2150 series 6 copper-constantan temperature control (Figure 21), supplied by the Joseph Kaye Co. of Cambridge, Mass., has a six-junction capacity and is used with the recorders.

The Haake heat exchanger, model KT-62, provides sensitive control of the collector-plate temperature, 23°C ± 2°C, using Dow Corning 200 silicone oil as the heat-transfer medium. The sensor is tightly clamped on the cooling collector support plate, right next to the collector stem.

The Veeco 775 vacuum system (Figure 21) with automatic controls provides an ultimate 1×10^{-7} torr vacuum environment when liquid nitrogen is used to cool its chevron baffles. Rated capacity is 2000 liters per second, maximum.

The modified feed-through collar Mount Vernon Research, Alexandria, Virginia shown in Figure 15 allows the use of maximum sensor inputs and rapid nitrogen cooling.

The Tenney environmental humidity test chamber, model TH-1R20-200 (Figure 22), provides continuous reliable sample conditioning of 50 percent relative humidity at 23°C ± 2°C.

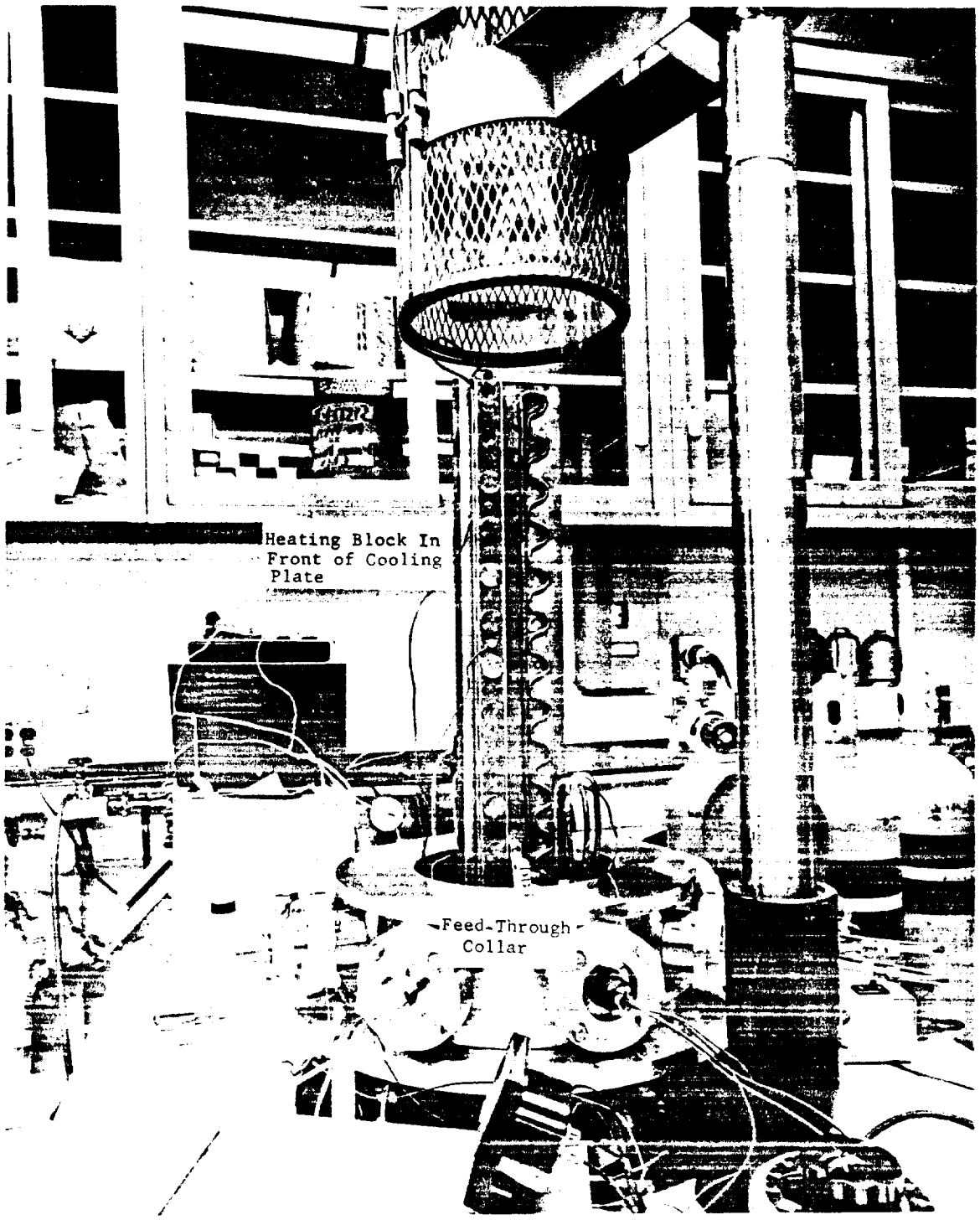


Figure 1. Mounted VCM Apparatus Showing Copper Heater Block and Cooling Plate

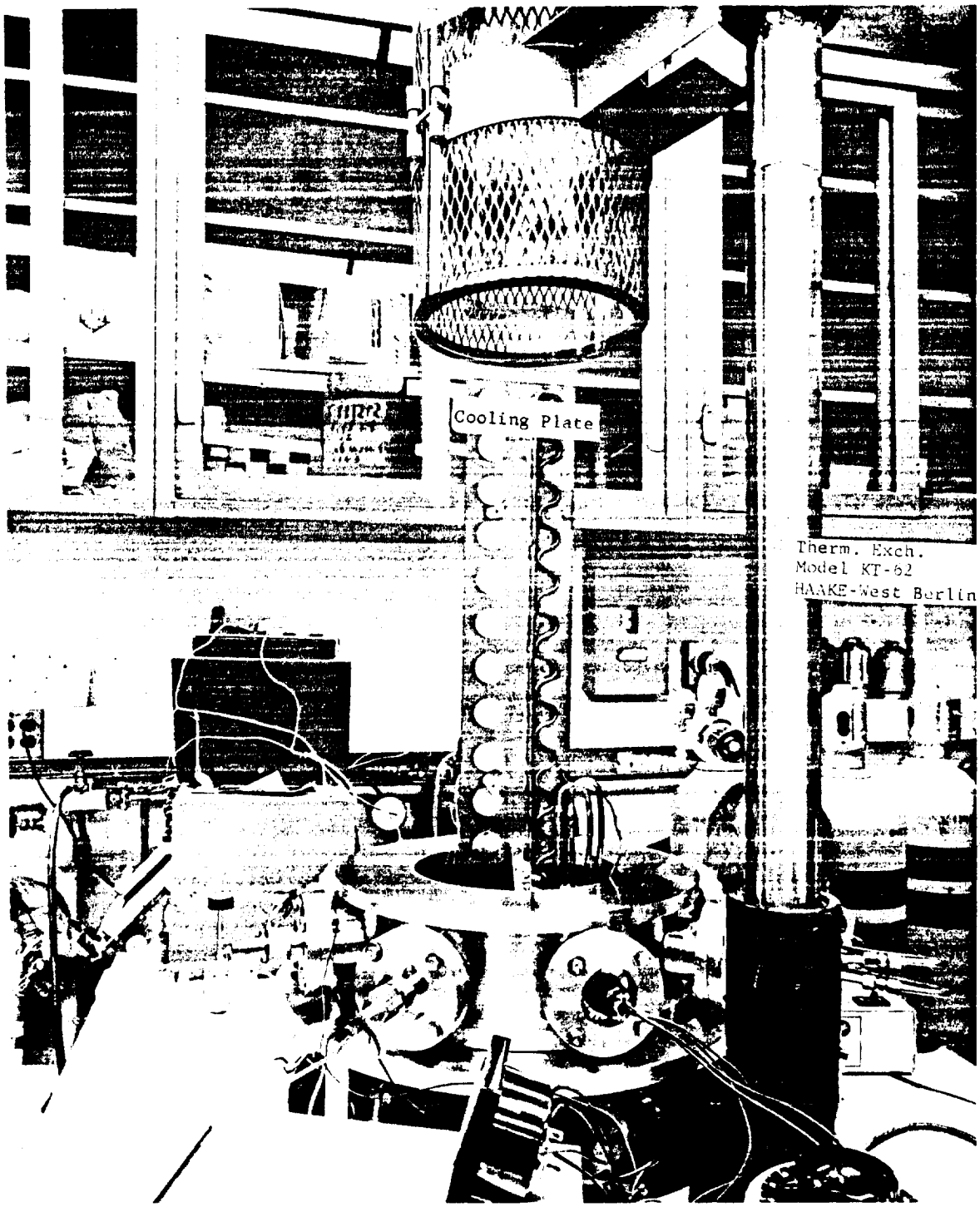
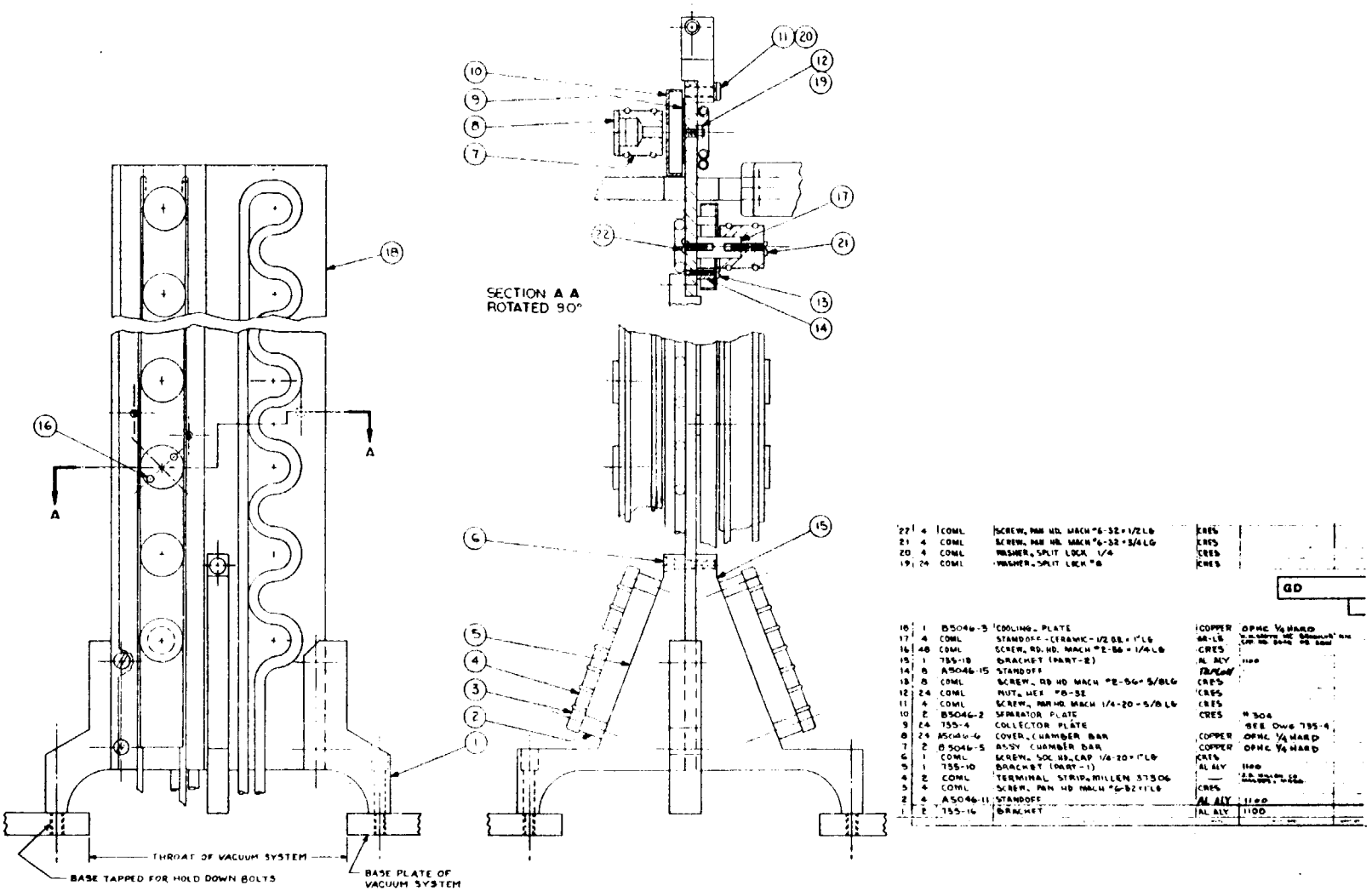


Figure 2. VCM Apparatus Heater Block Removed, Showing Chrome–Plated Removable Collector Plates



22	4	COML	SCREW, PAN HD. MACH 6-32 × 1/2 LG	CRES	
21	4	COML	SCREW, PAN HD. MACH 6-32 × 3/4 LG	CRES	
20	4	COML	WASHER, SPLIT LOCK 1/4	CRES	
19	24	COML	WASHER, SPLIT LOCK #8	CRES	
18	1	B5046-3	COOLING PLATE	COPPER	OFHC 1/8 HARD
17	4	COML	STANDOFF - CERAMIC - 1/2 OD × 1" LG	66-LG	
16	48	COML	SCREW, RD. HD. MACH #2-56 × 1/4 LG	CRES	
15	1	735-18	BRACKET (PART-2)	AL ALY	1100
14	8	A5046-15	STANDOFF		
13	8	COML	SCREW, RD HD MACH #2-56 × 5/8 LG	CRES	
12	24	COML	NUT, HEX #8-32	CRES	
11	4	COML	SCREW, PAN HD. MACH 1/4-20 × 5/8 LG	CRES	
10	2	B5046-2	SEPARATOR PLATE	CRES	#304
9	24	735-4	COLLECTOR PLATE		SEE DWG 735-4
8	24	A5046-6	COVER, CHAMBER BAR	COPPER	OFHC 1/4 HARD
7	2	B5046-5	ASSY. CHAMBER BAR	COPPER	OFHC 1/4 HARD
6	1	COML	SCREW, SOC HD. CAP 1/4-20 × 1" LG	CRES	
5	1	735-10	BRACKET (PART-1)	AL ALY	1100
4	2	COML	TERMINAL STRIP, MILLEN 37306	—	
3	4	COML	SCREW, PAN HD MACH #6-32 1" LG	CRES	
2	4	A5046-11	STANDOFF	AL ALY	1100
1	2	735-16	BRACKET	AL ALY	1100

Figure 3. Micro-VCM Test System Assembly
SRI Modified

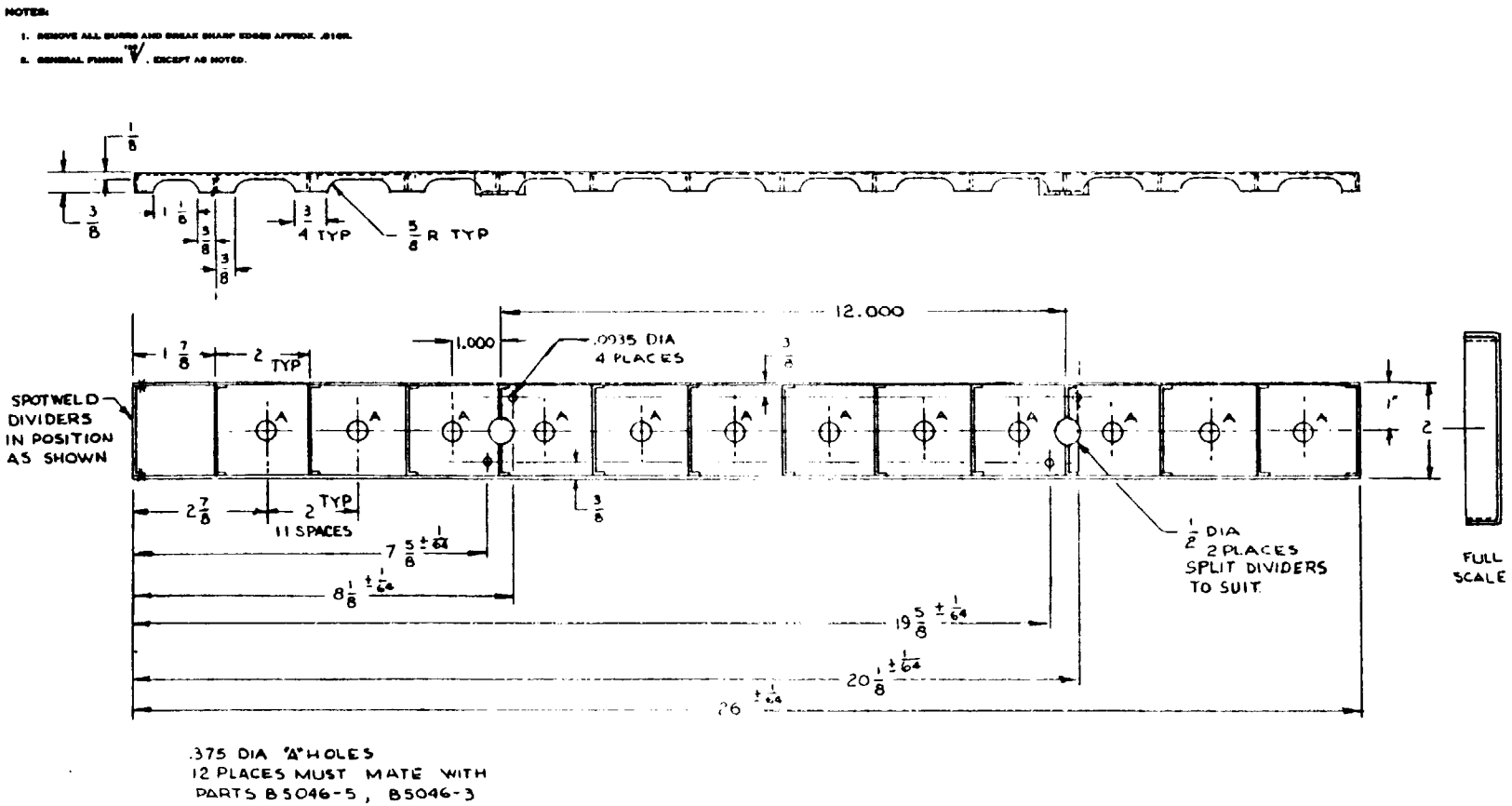
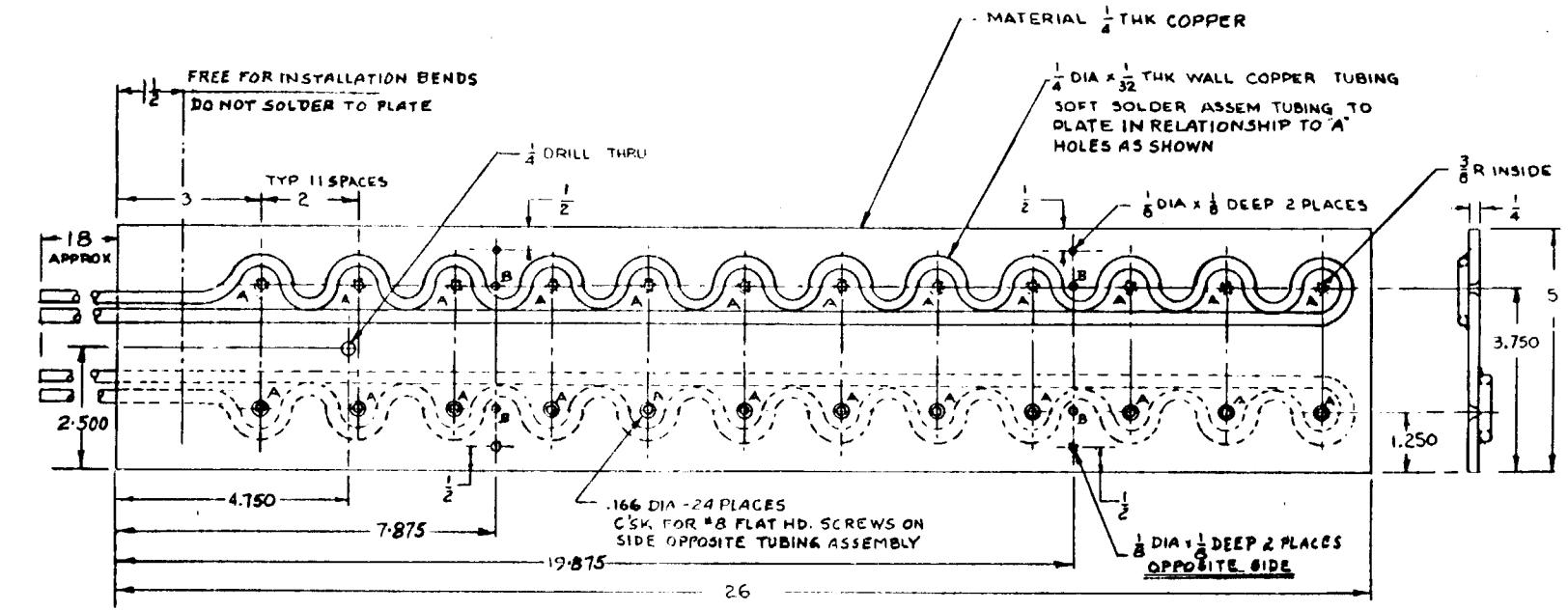


Figure 4 Separator Plate
SRI Drawing



NOTES:- "A" HOLES MUST MATE WITH PARTS B5046-2, B5046-5

4 "B" HOLES .149 DIA.

Figure 5 Cooling–Plate Assembly
SRI Drawing

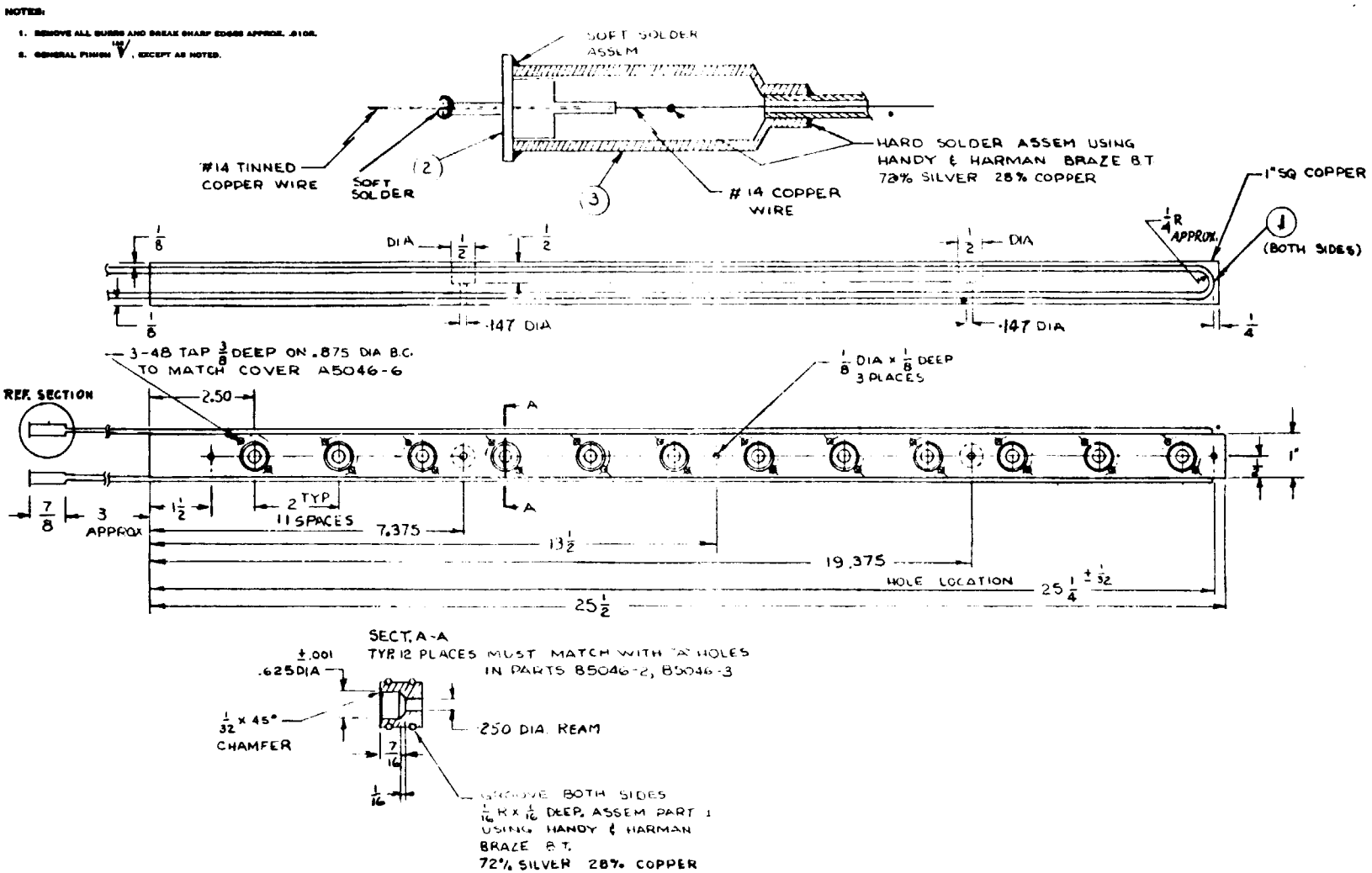


Figure 6. Chamber-Bar Assembly
SRI Drawing

NOTES:

1. REMOVE ALL BURRS AND BREAK SHARP EDGES APPROX. .010R.
2. GENERAL FINISH 125 V, EXCEPT AS NOTED.

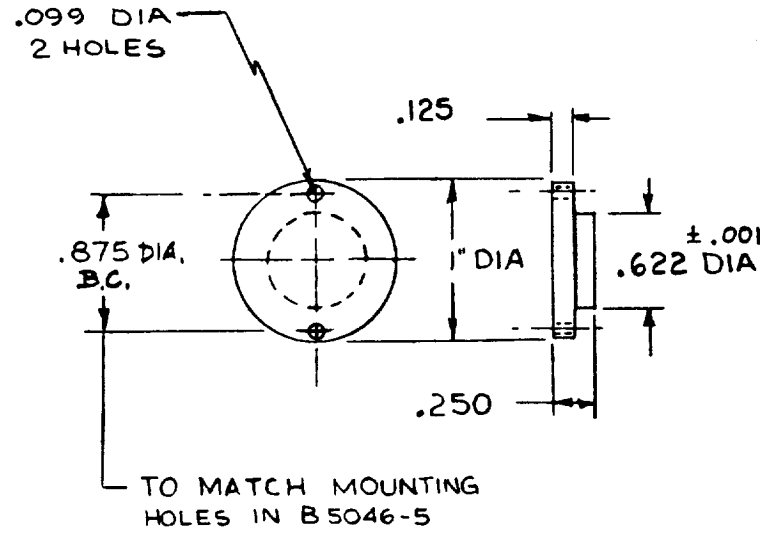


Figure 7. Chamber-Bar Cover
SRI Drawing

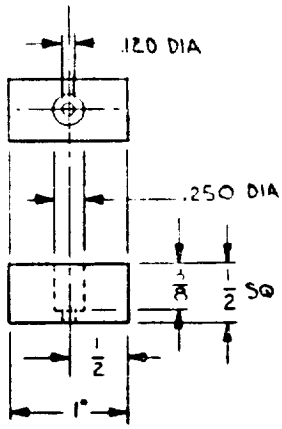


Figure 8. Insulator
SRI Drawing

NOTES:

1. REMOVE ALL BURRS AND BREAK SHARP EDGES APPROX. .01CR.
2. GENERAL FINISH 125 V, EXCEPT AS NOTED.

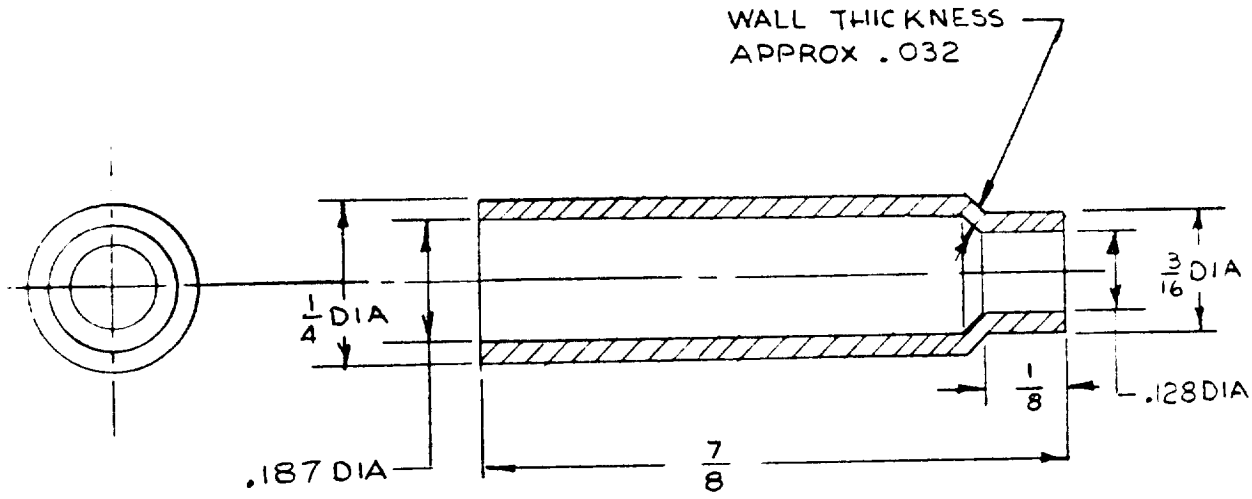


Figure 9. Heating–Element Terminal
SRI Drawing

BRACKETS

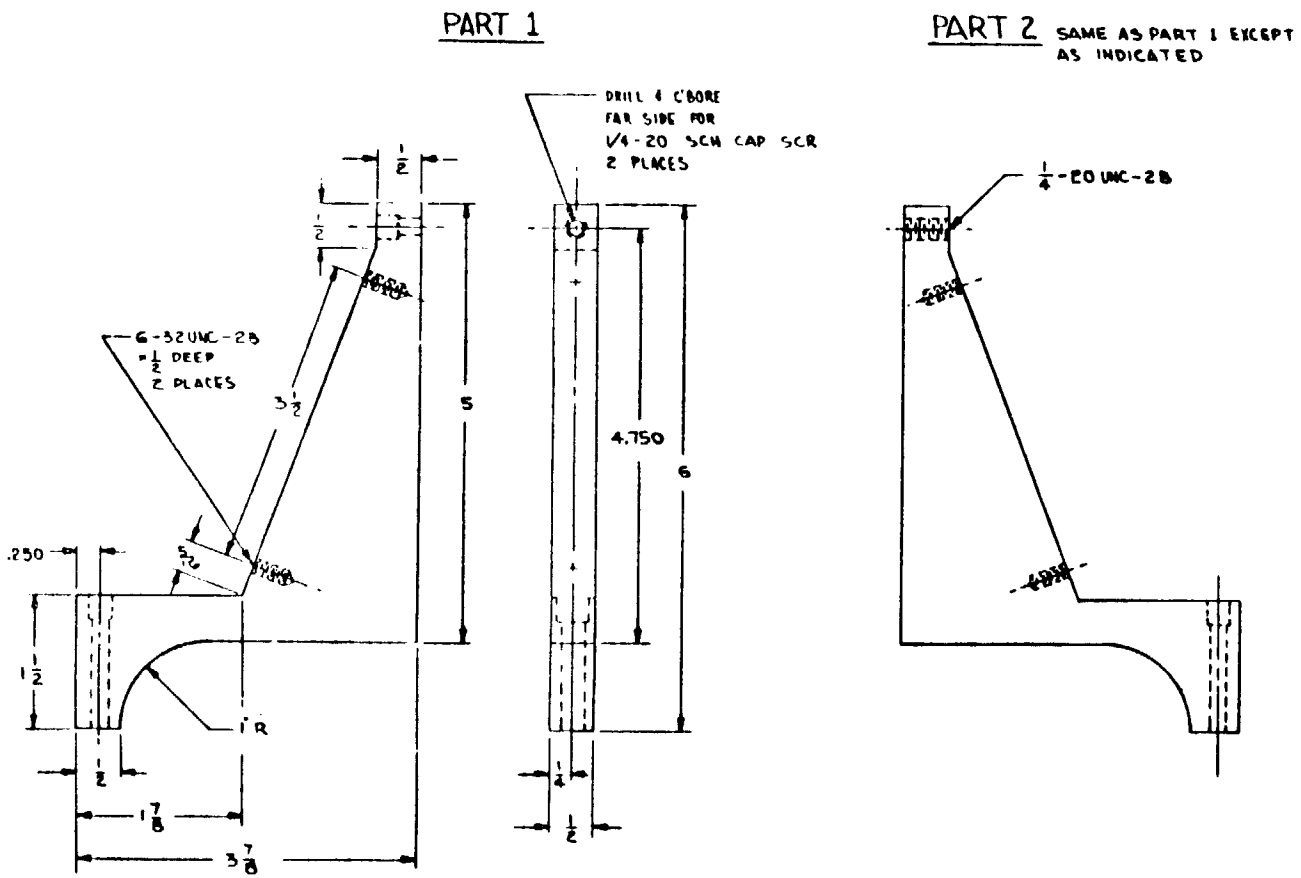


Figure 10. Cooling-Plate and Terminal-Strip Support Brackets

NOTES:

1. REMOVE ALL BURRS AND BREAK SHARP EDGES APPROX. .010R.
2. GENERAL FINISH $\sqrt{}^{125}$, EXCEPT AS NOTED.

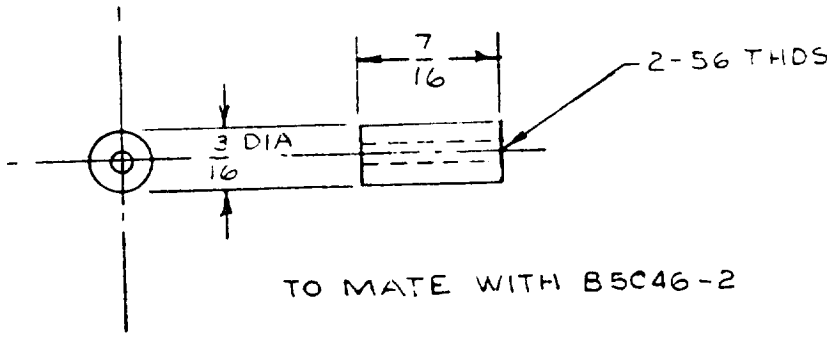


Figure 11. Standoff
SRI Drawing

NOTES:

1. REMOVE ALL BURRS AND BREAK SHARP EDGES APPROX. .010R.
2. GENERAL FINISH $\sqrt{}^{125}$ EXCEPT AS NOTED.

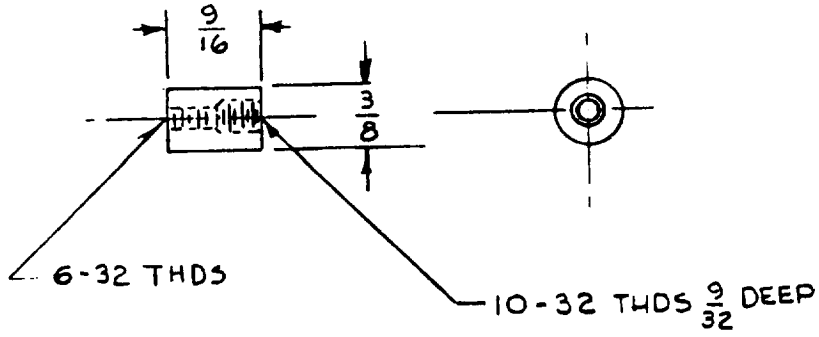


Figure 12. Standoff Insulator
SRI Drawing

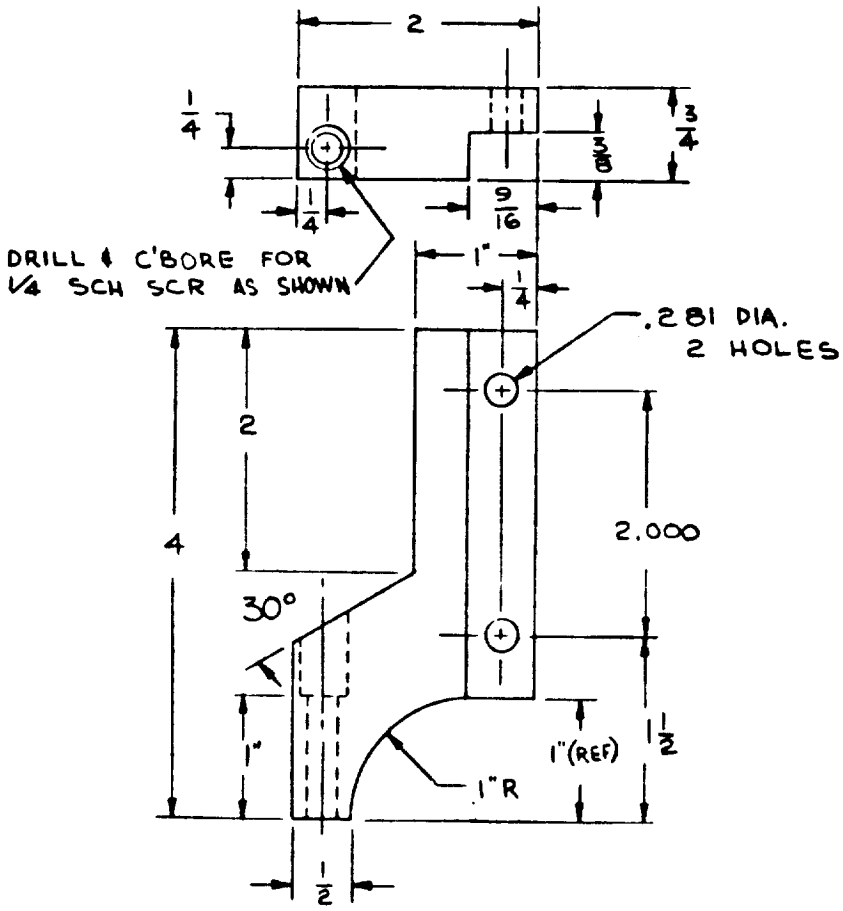


Figure 13. Cooling-Plate Support Bracket

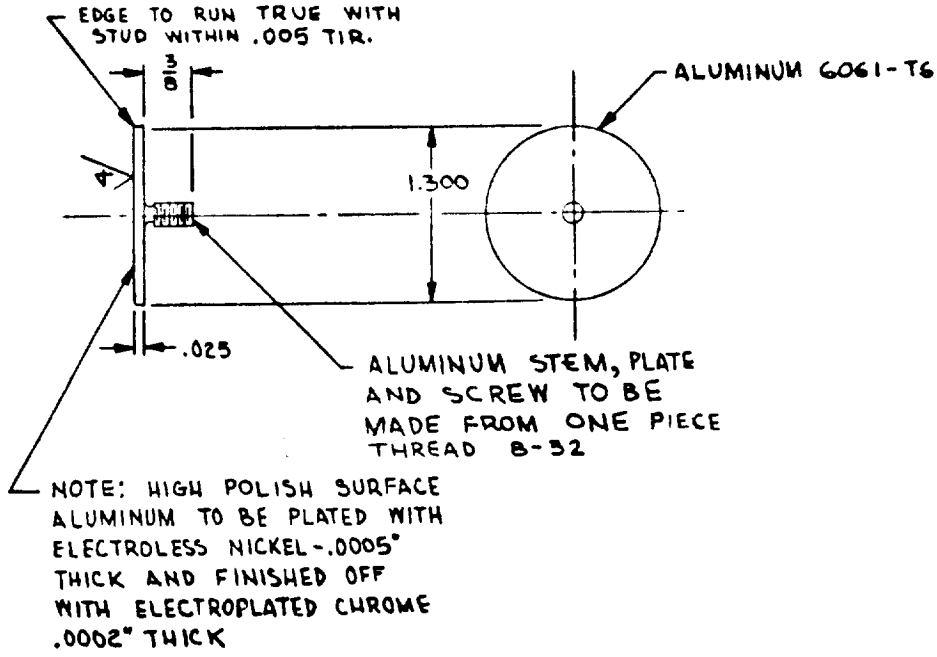
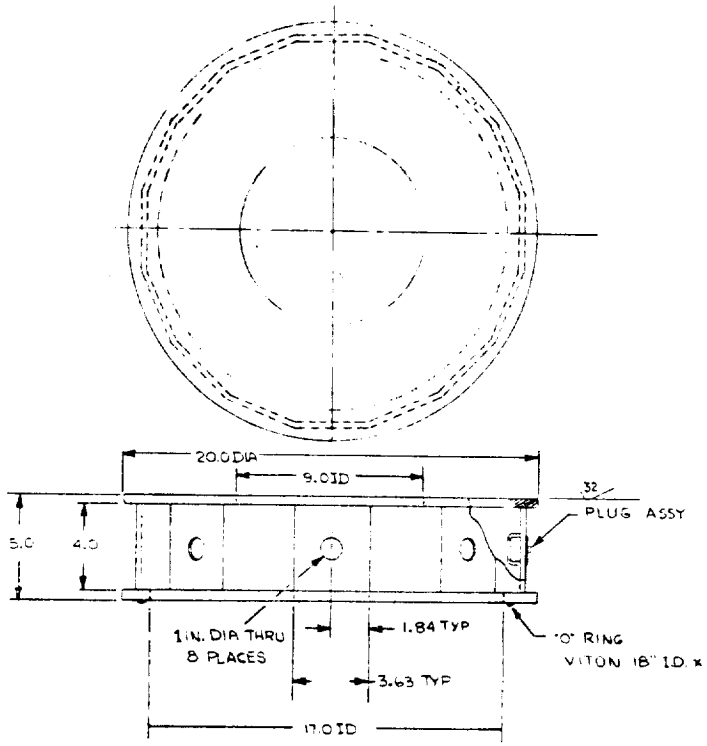


Figure 14. Collector Plate



NOTES:

1. FURNISHED WITH O-RINGS & BLANK OFF PLUGS
2. LEAK RATE: $< 1 \times 10^{-9}$ cm³/sec
   He MASS SPECTROMETER TESTED
3. MTL: S.S. TYPE 304

Figure 15. Feed-Through Collar

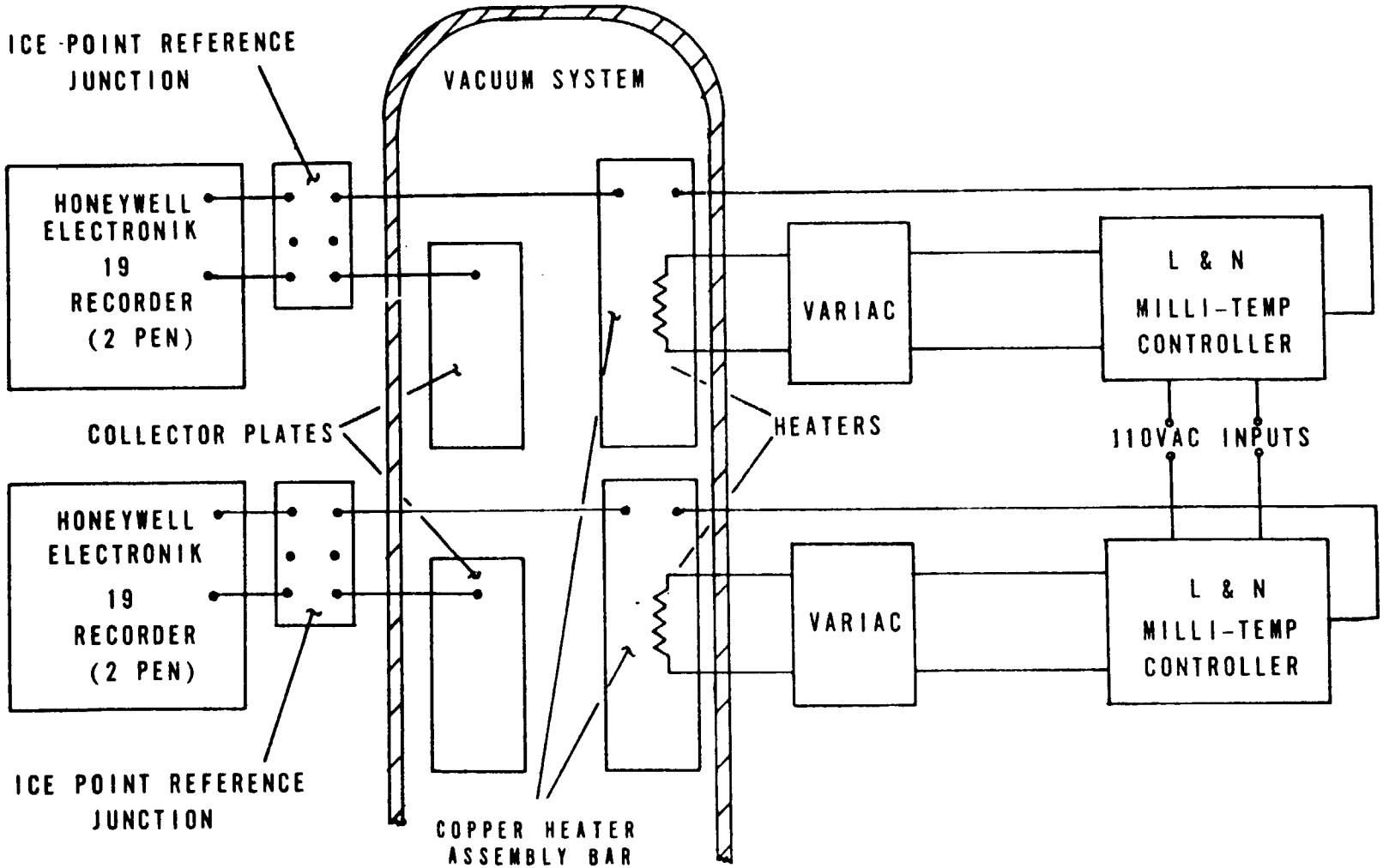


Figure 16. GSFC VCM Apparatus, Electrical Block Diagram

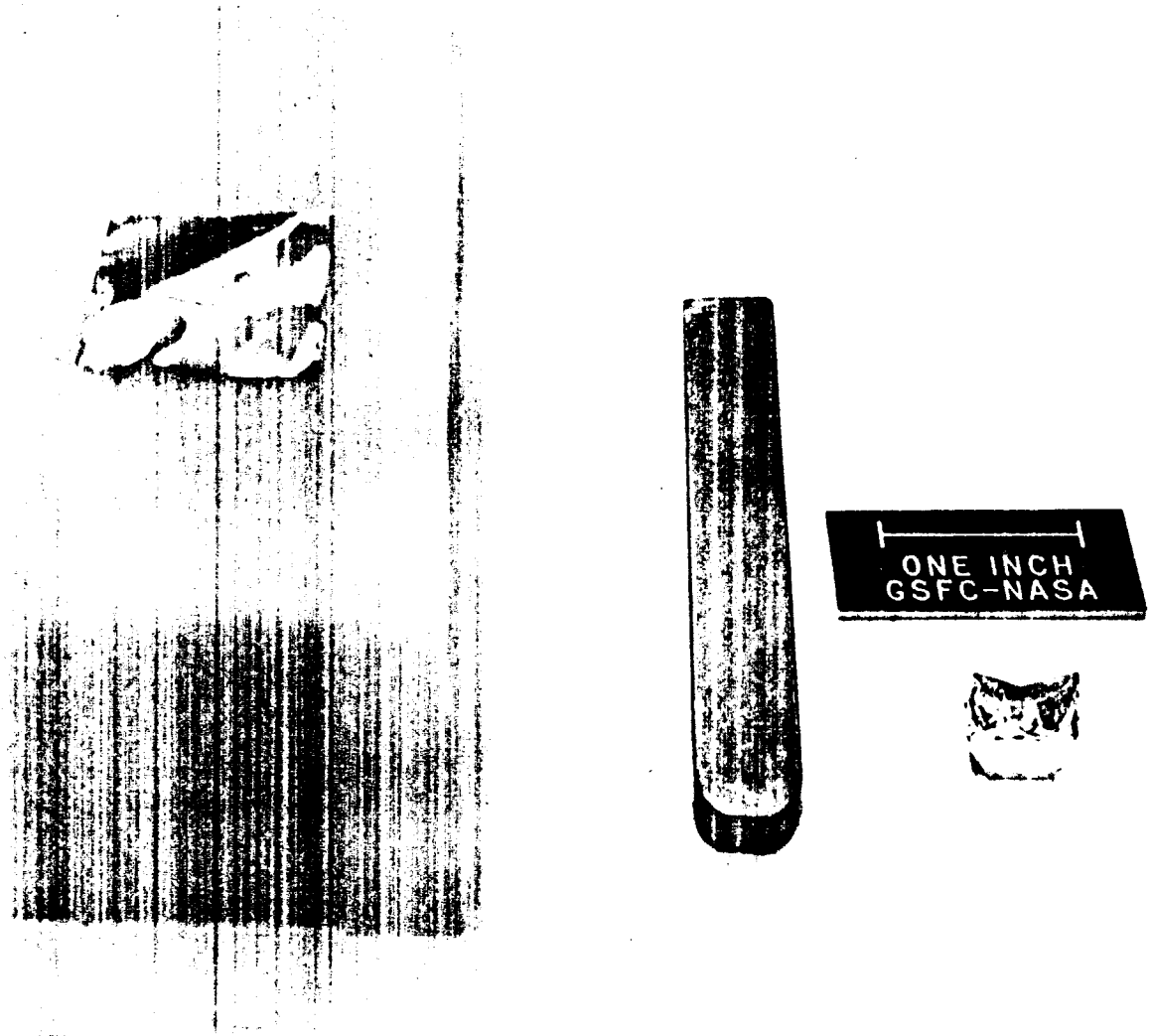


Figure 17. Materials for Preforming Sample Boats

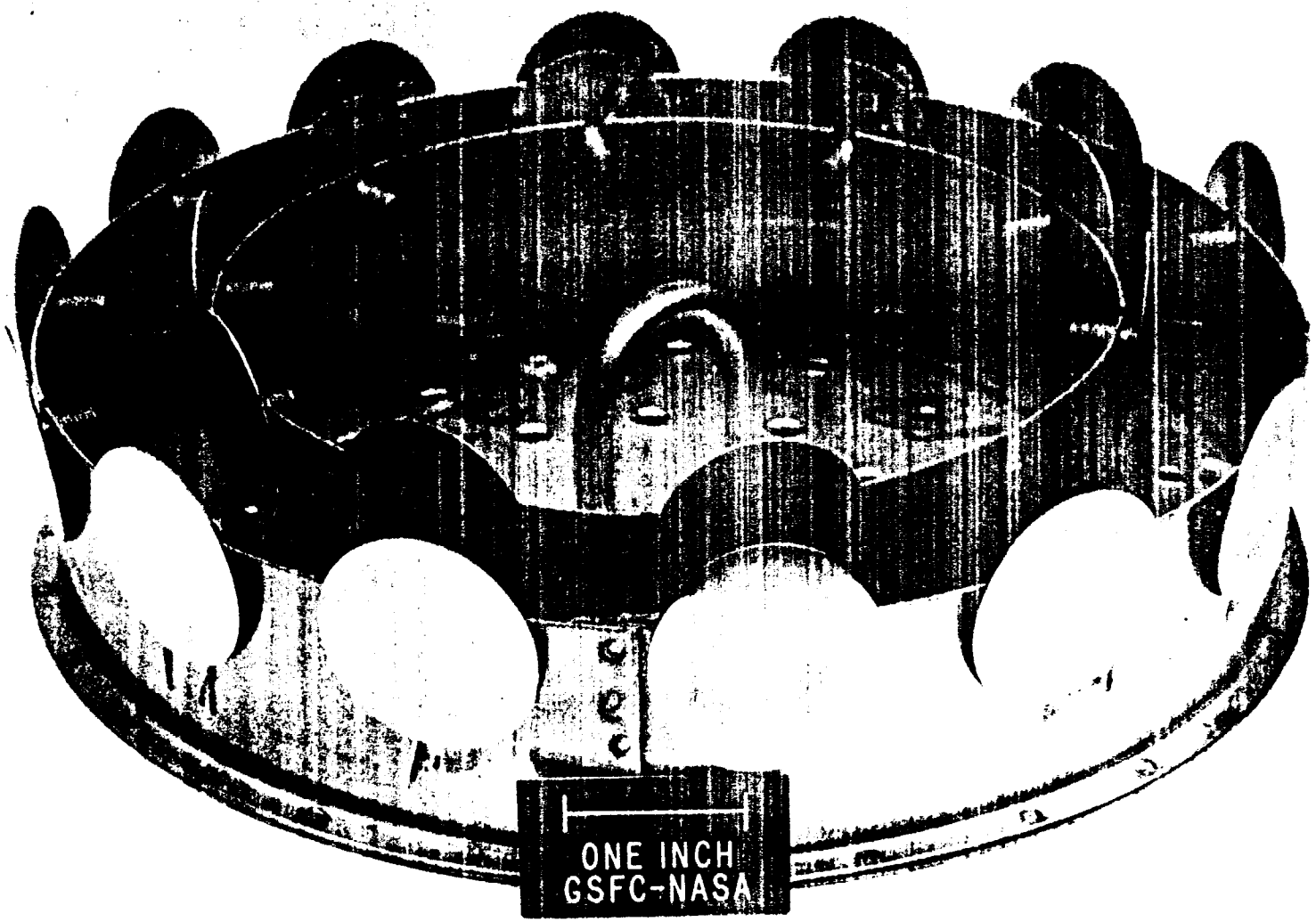


Figure 18. Collector-Plate Storage Rock

* INSERT THREADED STUD INTO TAPPED HOLE AND SILVER SOLDER, GRIND FLUSH WITH INSIDE FACE OF RETAINER.

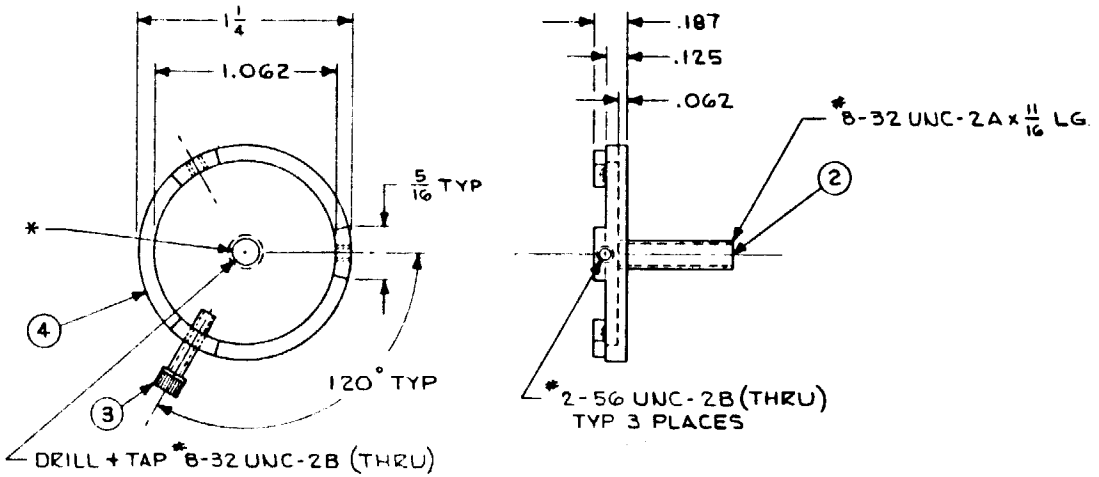


Figure 19. Salt-Flat Retainer

Figure 20. KBr Salt Flat and Retainer

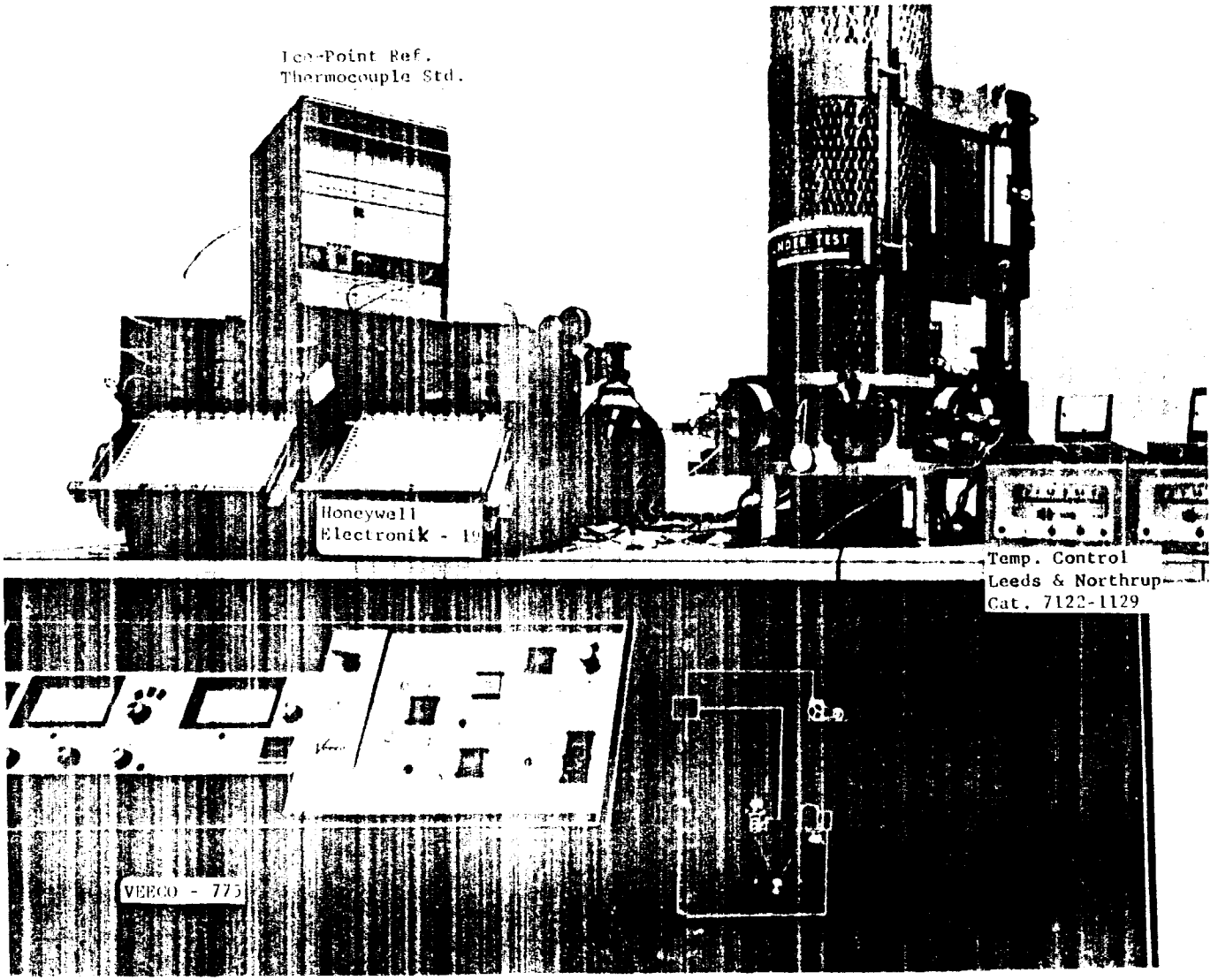


Figure 21. GSFC Operational VCM Apparatus

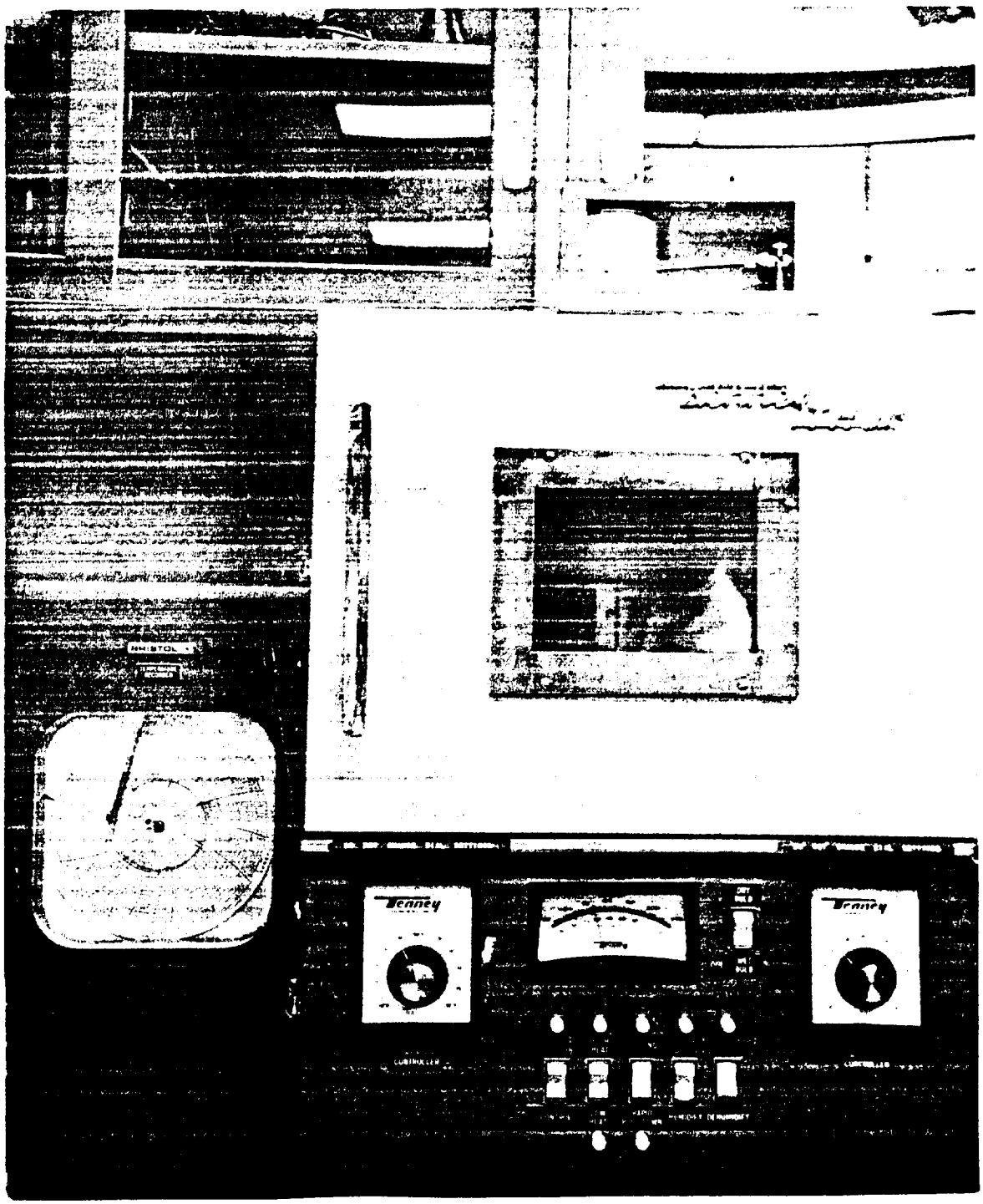


Figure 22. Tenney Conditioning Chamber