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# PROGRESS REPORT NO. 38
# FOR A PROGRAM OF
# THERMOELECTRIC GENERATOR TESTING
# AND
# RTG DEGRADATION MECHANISMS EVALUATION

MASTER

Submitted to

The US Department of Energy
Division of Advanced Nuclear Systems and Projects
Washington D.C.

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

November 1980

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Prepared by

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by

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CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

November 1980

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# FOREWORD

This report is submitted to the Department of Energy covering work conducted under Interagency Agreement No. E(04-3)-959 by the Jet Propulsion Laboratory and documents all activities covering the period of September-October 1980 performed under the technical direction of Mr. Patrick O'Riordan Power Systems Branch, Space and Terrestrial Systems Division of the DOE Office of Advanced Nuclear Systems and Projects.

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# SECTION I

## SUMMARY

The n-type gadolinium selenide legs after 17,500 hours continue to show reasonable agreement with the 3M Co. published thermal conductivity data.

Weight loss for both coated and uncoated Si-Ge material produced by G.E. are reported. No significant discrepancies with the results previously obtained on R.C.A. material from the MHW program have been found. Thermal conductivity measurements are also in agreement.

The remaining MHW generator on test, Q1-A, has accumulated 26,800 hours and performance remains stable. The performance of the 18 couple modules S/N-1, S/N-2, and S/N-3 to date is summarized in this report.

Telemetry data indicate no changes in the trends of degradation of LES 8 and 9 and the Voyager RTGs.

# SECTION II

# SELENIDE TECHNOLOGY EVALUATION

## A. THERMAL CONDUCTIVITY TESTS

The long-term testing of the gadolinium selenide n-type legs has been continued with $T_H = 800^oC$ and a maximum $T_C = 250^oC$ (see reports No. 26, 5/78 and No. 27, 8/78 for experimental details). Approximately 17,500 hours of operation have accrued. The thermal conductivity values for the four legs are shown in Figure 1 and normalized to the original value ($K_o$ = 20 hours) in Figure 2, as a function of operating time. The thermal conductivity values for three of the four legs has remained relatively stable. The change to neodymium selenide makes this test obsolete. Data for this test will not be reported again.

## B. INGRADIENT TESTING

Testing of gadolinium selenide n-type thermocouple legs is discontinued. Two neodymium selenide n-type legs will be put on test during the next reporting period. The ingradient test station will be taken down to remove the gadolinium selenide legs and to refurbish the p-leg instrumentation. Instrumentation and contact problems make recent data difficult to interpret.

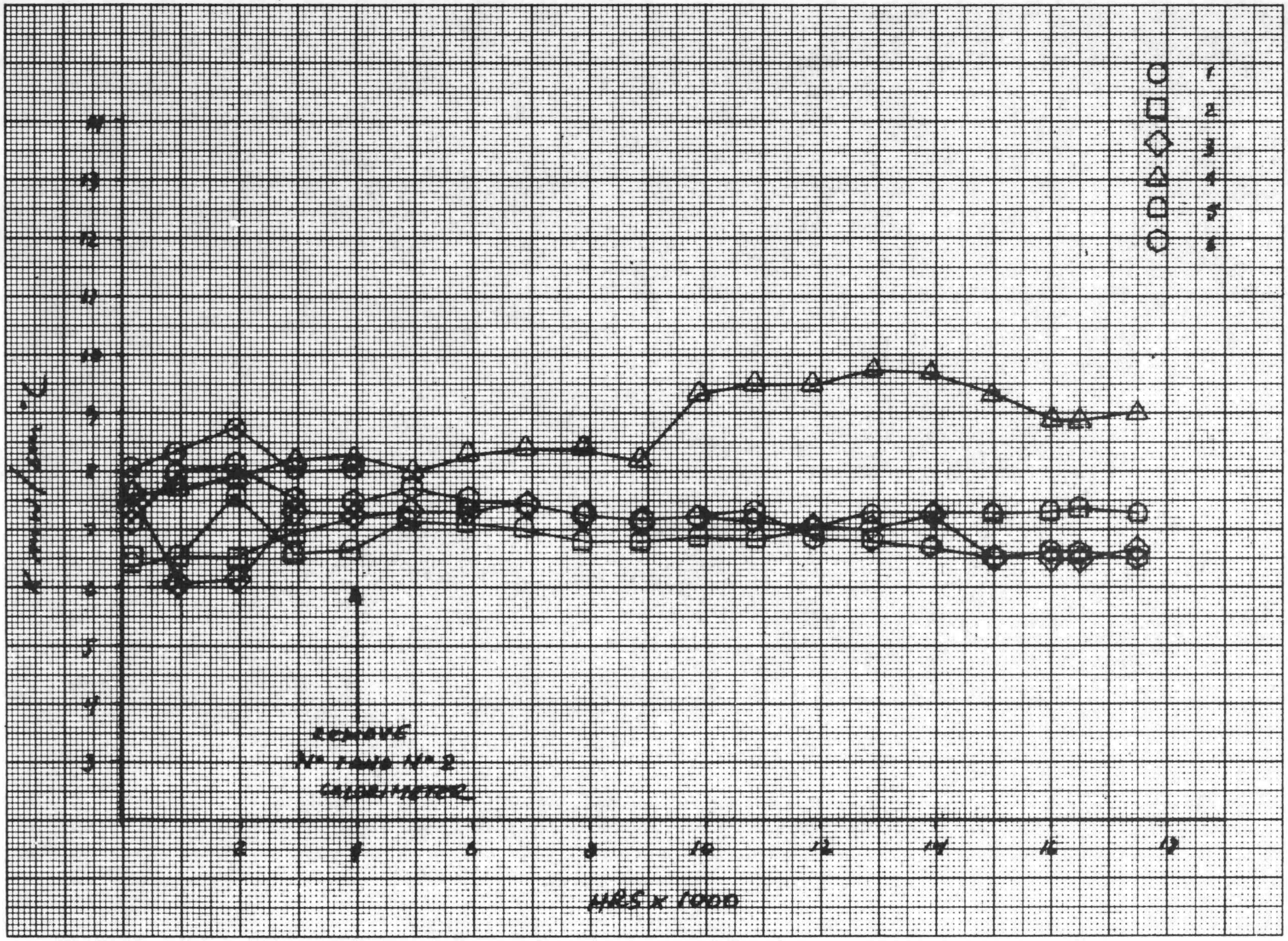


Figure 1. Thermal Conductivity Test N-Type

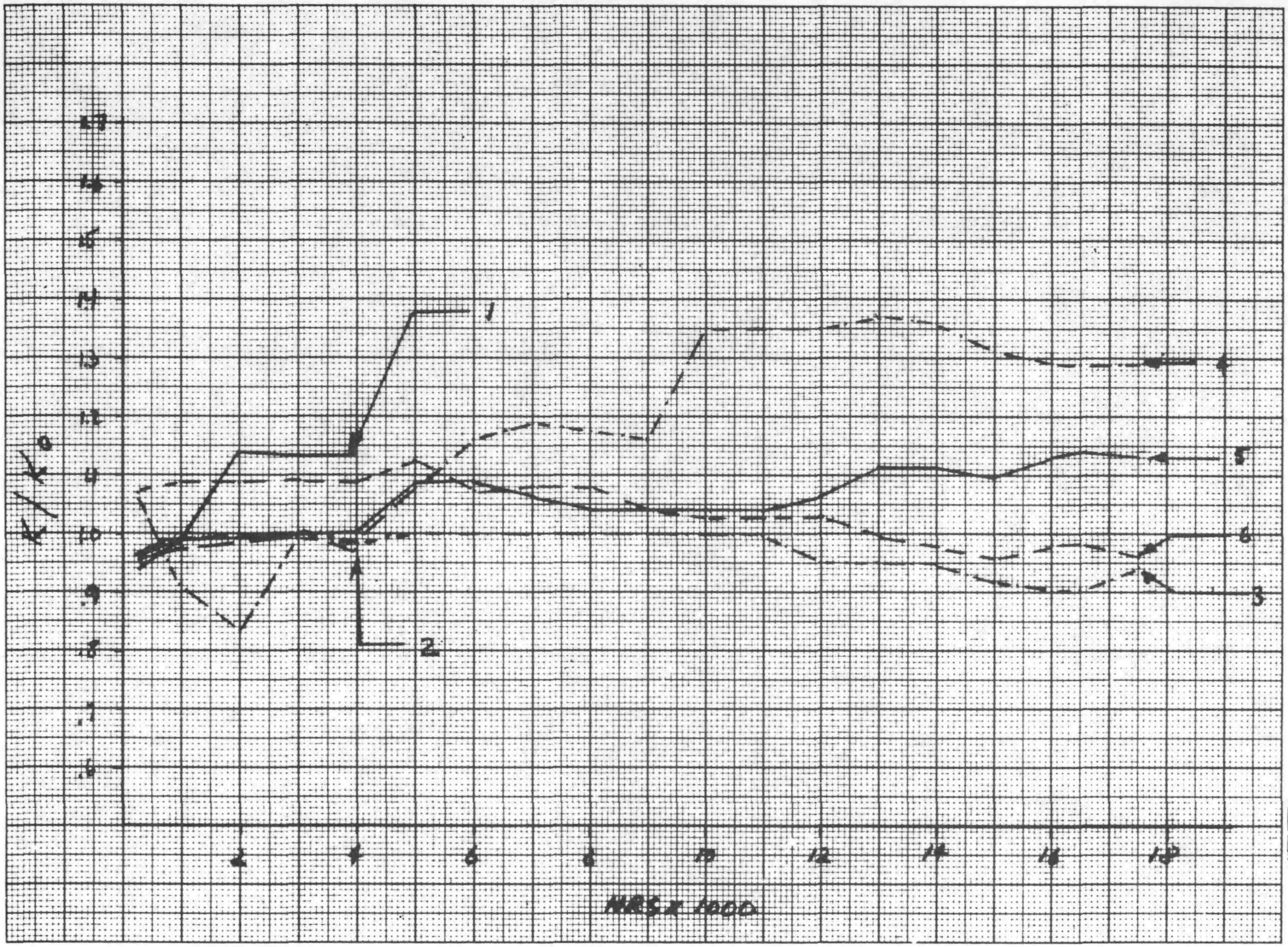


Figure 2. Thermal Conductivity Test N-Type, Normalized

# SECTION III

# SILICON GERMANIUM MATERIALS TECHNOLOGY

## A. PROPERTIES OF Si-Ge PRODUCED BY GE

The samples of early silicon-germanium production submitted by GE are continuing under test for verification of their thermoelectric and physical properties. Sublimation data are presented for both coated and uncoated components. Figure 3 shows weight loss results for uncoated 78% silicon legs at 1150°C, both n- and p-type. The loss rate over the last 600 hours is approximately $1.0 \times 10^{-4}$ g/cm$^2$-h for the n-type material. This is about 1.4 times that for the RCA n-type material. The corresponding loss rate for the p-type material over the same period is approximately $4.7 \times 10^{-5}$ g/cm$^2$-h. This is about 0.9 times that for the RCA p-type material. The average over 1350 hours is about 2.0 times the RCA average for the n-type material and about 1.8 times for the p-type material. Because of the difference in accuracy between investigators, produced by the inherent difficulty of these measurements, the agreement of the data is considered good.

The losses for coated n- and p-legs over 1350 hours are shown in Figure 4. After the first 250 hours the rates are $2.1 \times 10^{-7}$ g/cm$^2$-h for n-type and $\sim 1.5 \times 10^{-8}$ for p-type at 1000°C. Losses of $1.4 \times 10^{-6}$, $1.3 \times 10^{-5}$, and $1.4 \times 10^{-5}$ g/cm$^2$-h were observed (Figure 5) for the Si-Mo hot shoes at temperatures which were 1000°C, 1150°C, and 1200°C respectively. The Si-Mo hot shoes under test are standard design with n and p sections bonded together before coating. Comperative data for RCA coated legs and coated hot shoes is not available for presentation in this report. This data will be included at a later date if found to exist.

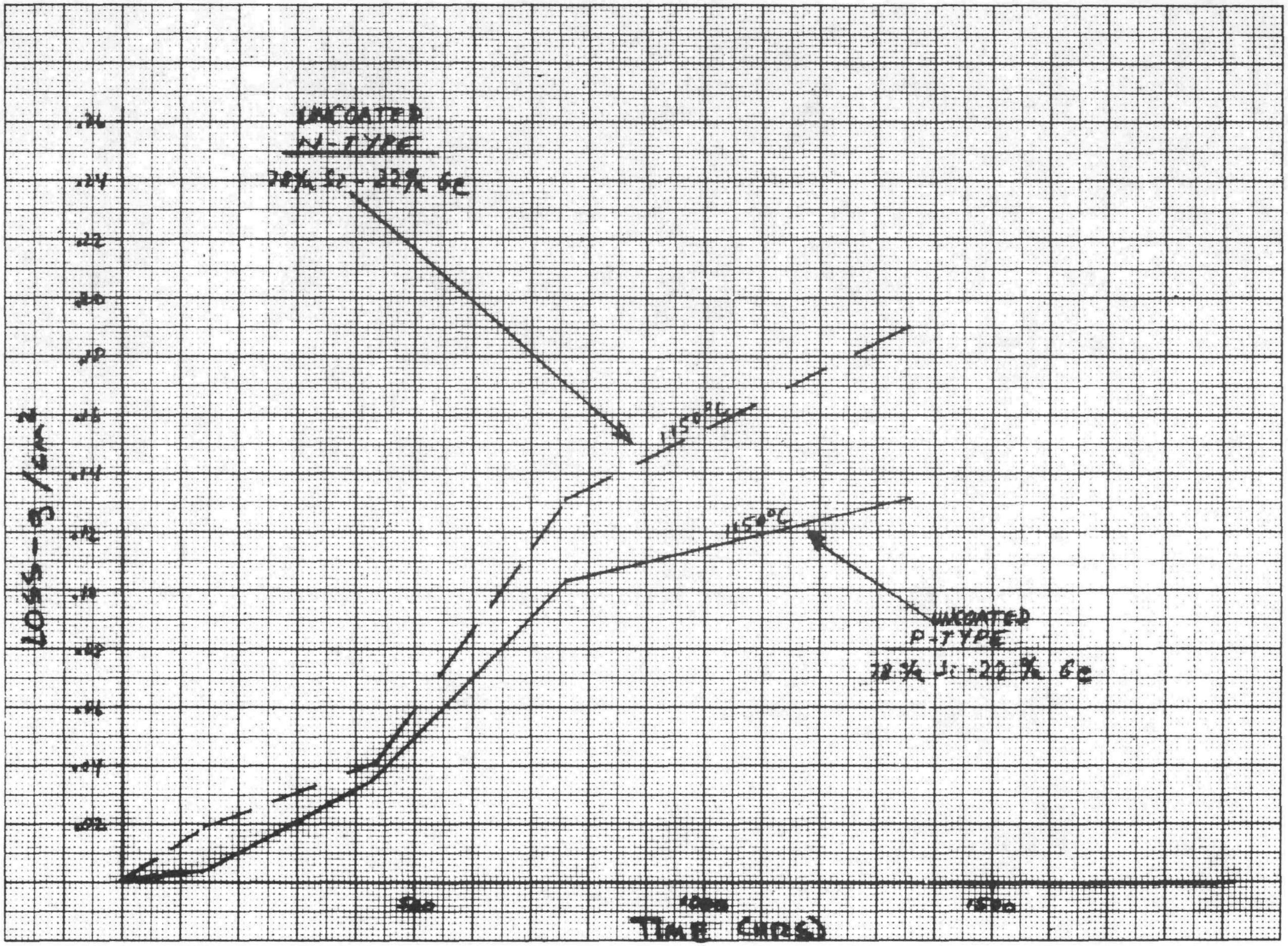


Figure 3. Free Sublimation N- and P-Type SiGe, 78% Si

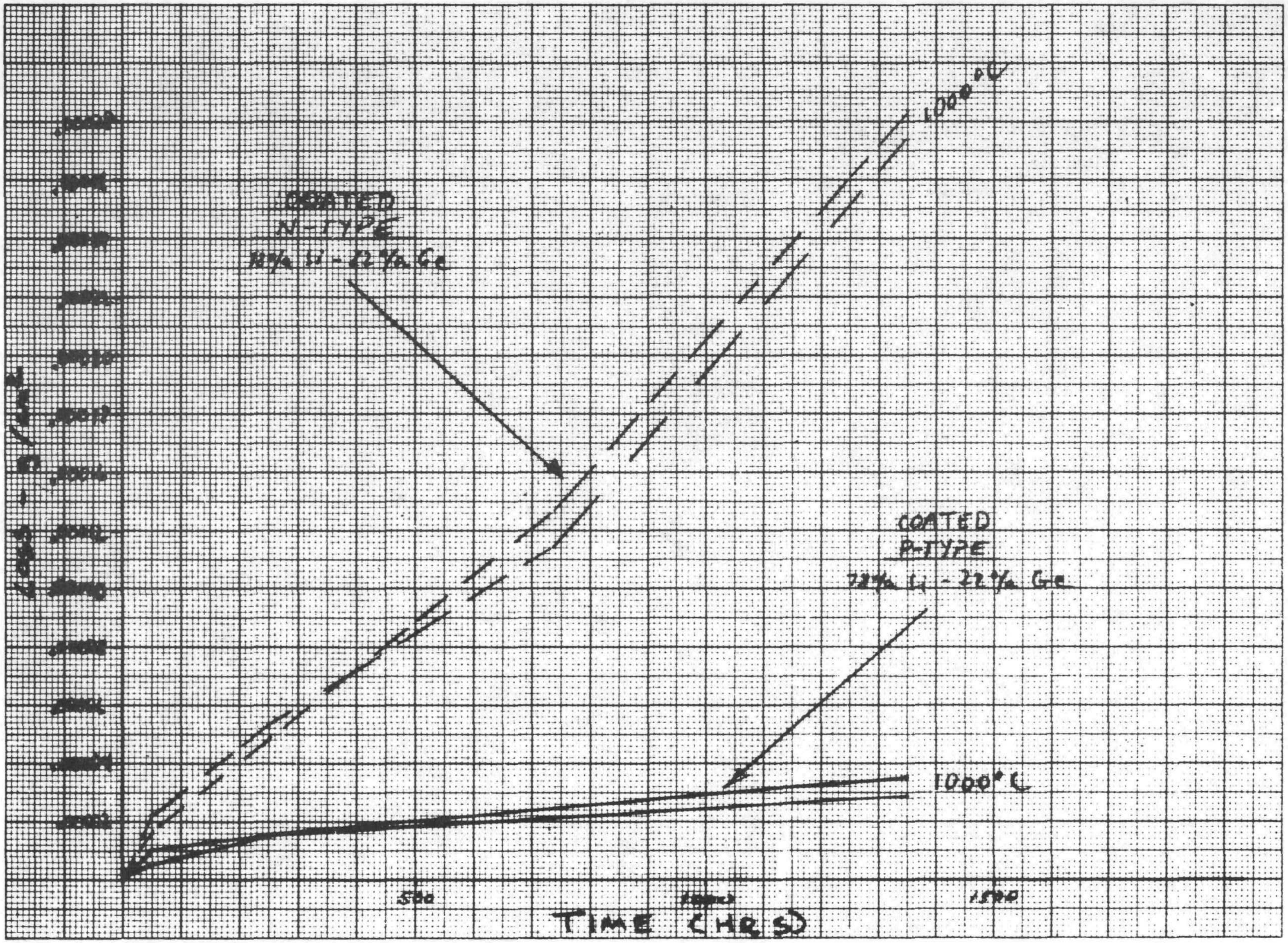


Figure 4. Free Sublimation, Silicon Nitride Coated Legs, N and P



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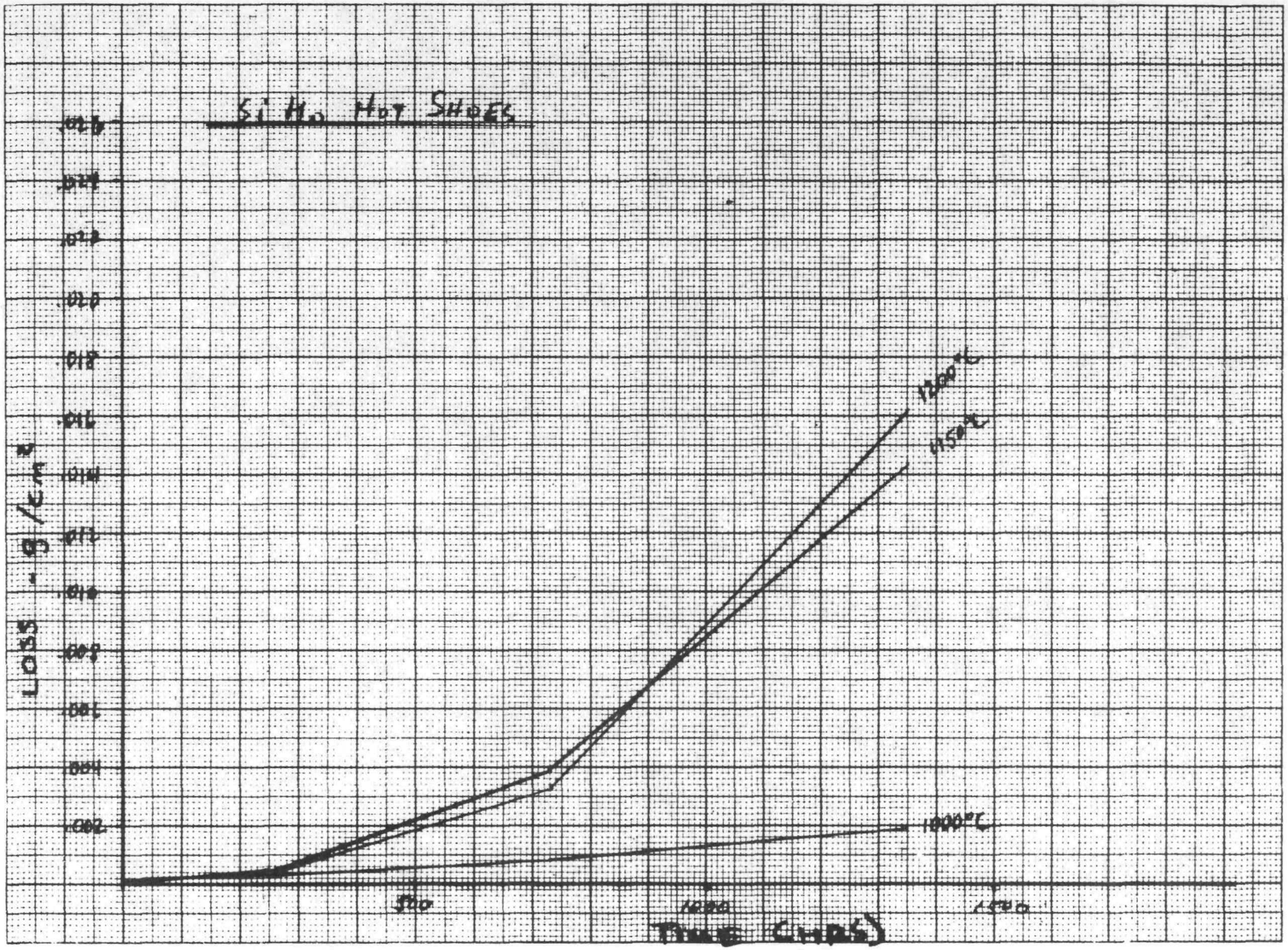


Figure 5. Free Sublimation, Silicon Nitride Coated SiMo Hot Shoes

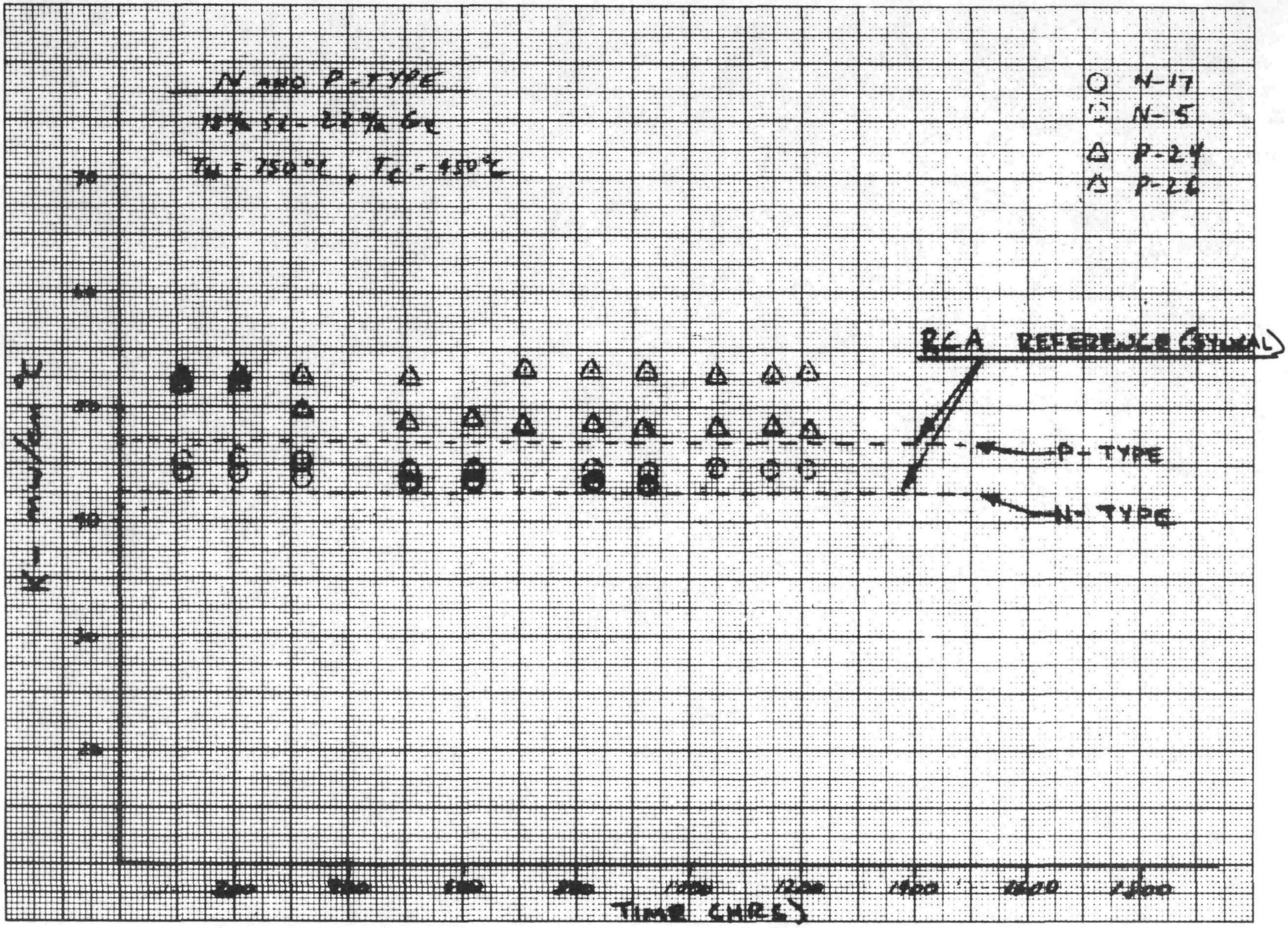


Figure 6. Thermal Conductivity, P-, N-Type SiGe, 78% Si, vs Time

Figure 6 illustrates the stability of the thermal conductivity over time. The hot and cold junction temperatures were respectively, $T_H$ = 750°C and $T_C$ = 450°C. The RCA reference lines are presented in the same figure. There have been no significant changes during the first 1200 hours. Present average values for the n and p type materials are approximately 44 and 50 mw/cm-°C respectively. The corresponding RCA reference value are about 43 and 47 mw/cm-°C. The measurement values and trends are observed to be in good agreement.

# SECTION IV

# THERMOELECTRIC GENERATOR TEST AND EVALUATION

Thermoelectric generators, representing recent and advanced technology, assembled with lead telluride, TAGS-85, and silicon-germanium materials have been tested at JPL. At present one generator, the Q1-A(SiGe), representative of the MHW type generators, is on test. Three 18 couple modules (S/N-1, S/N-2, S/N-3) that were extensively tested at RCA were received for JPL evaluation in support of the Galileo Program. Both the S/N-1 and the S/N-3 generators were on test during this reporting period. The results of a post-mortem examination of S/N-2 generator are presented in a separate report (JPL 715-57). An interim summary of the operational performance of the 18 couple modules is presented in this report.

## A. MHW GENERATOR Q1-A

This generator has operated for a total time of 26,797 hours. During the last 1203 hours of operation the generator power out has decreased by 1.2 watts. Presently the generator power out is 129.4 watts. The open circuit voltage shows a slight decrease from $E_{oc}$ = 57.16 volts to $E_{oc}$ = 57.00 volts. The internal resistance has increased slightly from $R_{int}$ = 6.23 ohms to $R_{int}$ = 6.26 ohms. The generator heat source temperature has decreased from AVG $\overline{T}_H$ = 1030°C to AVG $\overline{T}_H$ = 1024°C while the case temperature remains unchanged at AVG $\overline{T}_G$ = 263°C.

The shunt resistance history is presented in Figure 7. The present trend in the value of the shunt resistance has remained consistent.

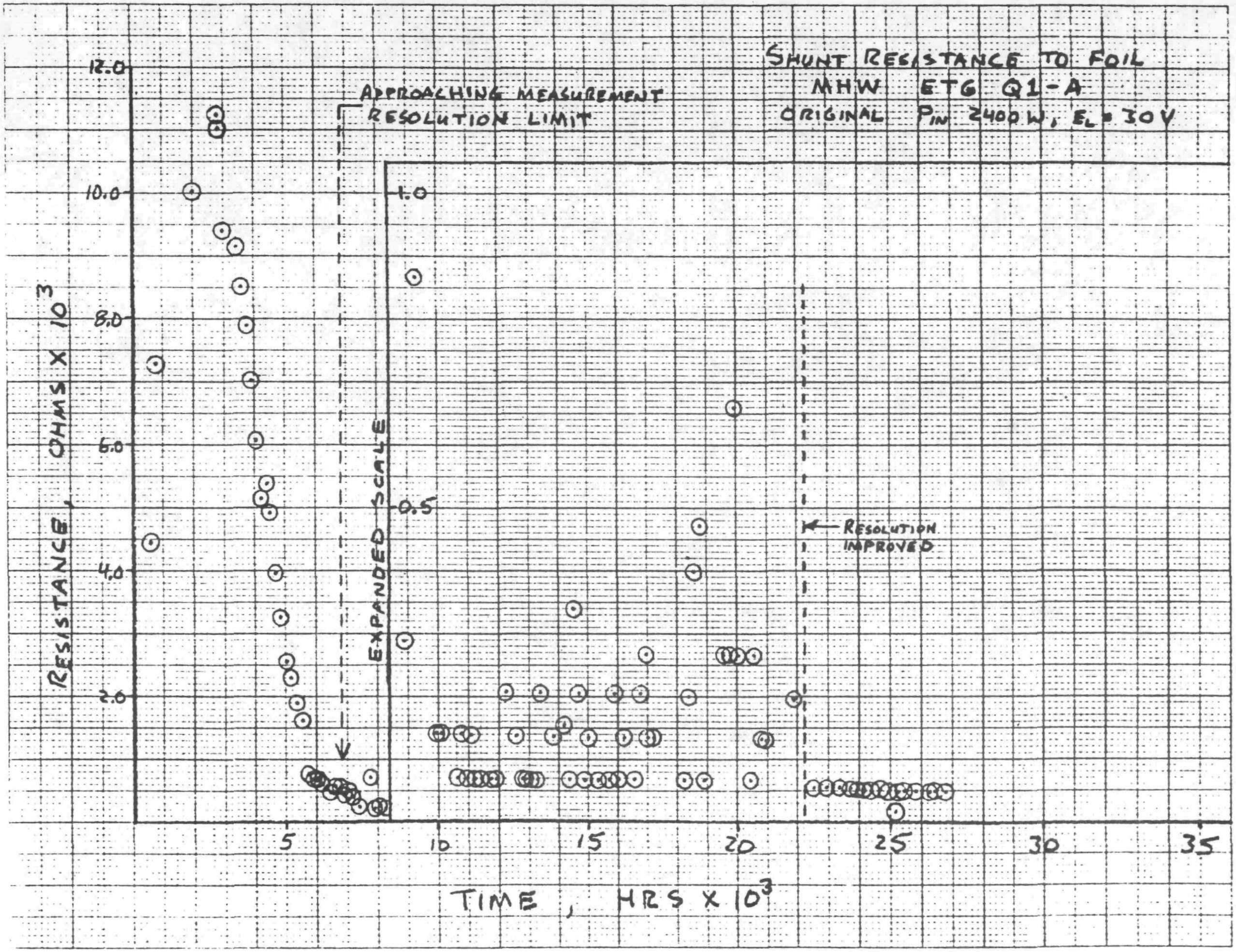


Figure 7. Shunt Resistance History, Generator Q1-A

The maximum power output which would occur without the loss due to the shunt conductance between the module and the insulating foil is shown in Figure 8. The maximum power output is that which would occur with zero electrical leakage to the insulating foil. The power ratio is also present in the same figure. The present calculated $P_{max}$ is 131.0 watts compared to an actual power out of 129.4 watts. This represents a one percent loss in power.

The generator life history is illustrated in Figures 9 and 10. The generator degradation rate for the last 5,000 hours of operation was 0.30 percent/1,000 hours. The corresponding generator degradation rate obtained using the DEGRA2 RTG degradation model for uncoated unicouples is 0.28 percent/1,000 hours for the same period of operation. The Q1-A generator and the DEGRA2 code are in excellent agreement. The model used is the same as that presently used to predict the Voyager 1 and 2 performance. Figure 11 shows power output versus $\sqrt{\text{time}}$. Parametric test results are shown in Figure 12. The power output versus load voltage shows that the optimum load voltage is slightly different from the actual load used. Since this difference is of the order of 1% after an operational lifetime of nearly 27,000 hours it is not considered significant.

B. PERFORMANCE SUMMARY OF THE RCA 18 COUPLE MODULES S/N-1, S/N-2, S/N-3

The performance of the 18 couple modules presently under test has been summarized to provide a better picture of our present understanding. This summary is as follows.

Of the three 18 couple modules received from RCA, tests have been continued on two: the S/N-1 and S/N-3 modules. The S/N-2 module was disassembled for structural examination.

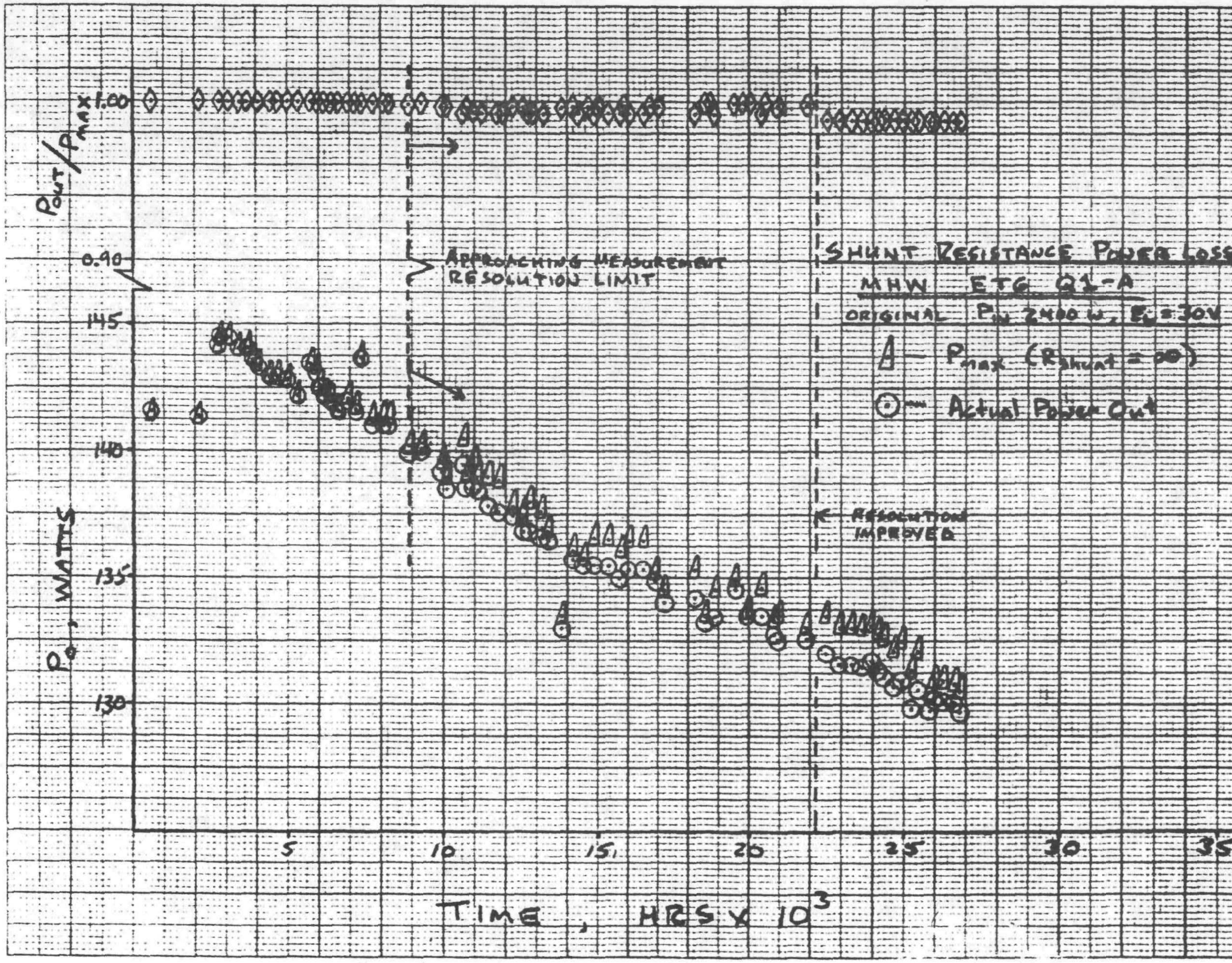


Figure 8. Shunt Resistance Power Loss, Q1-A

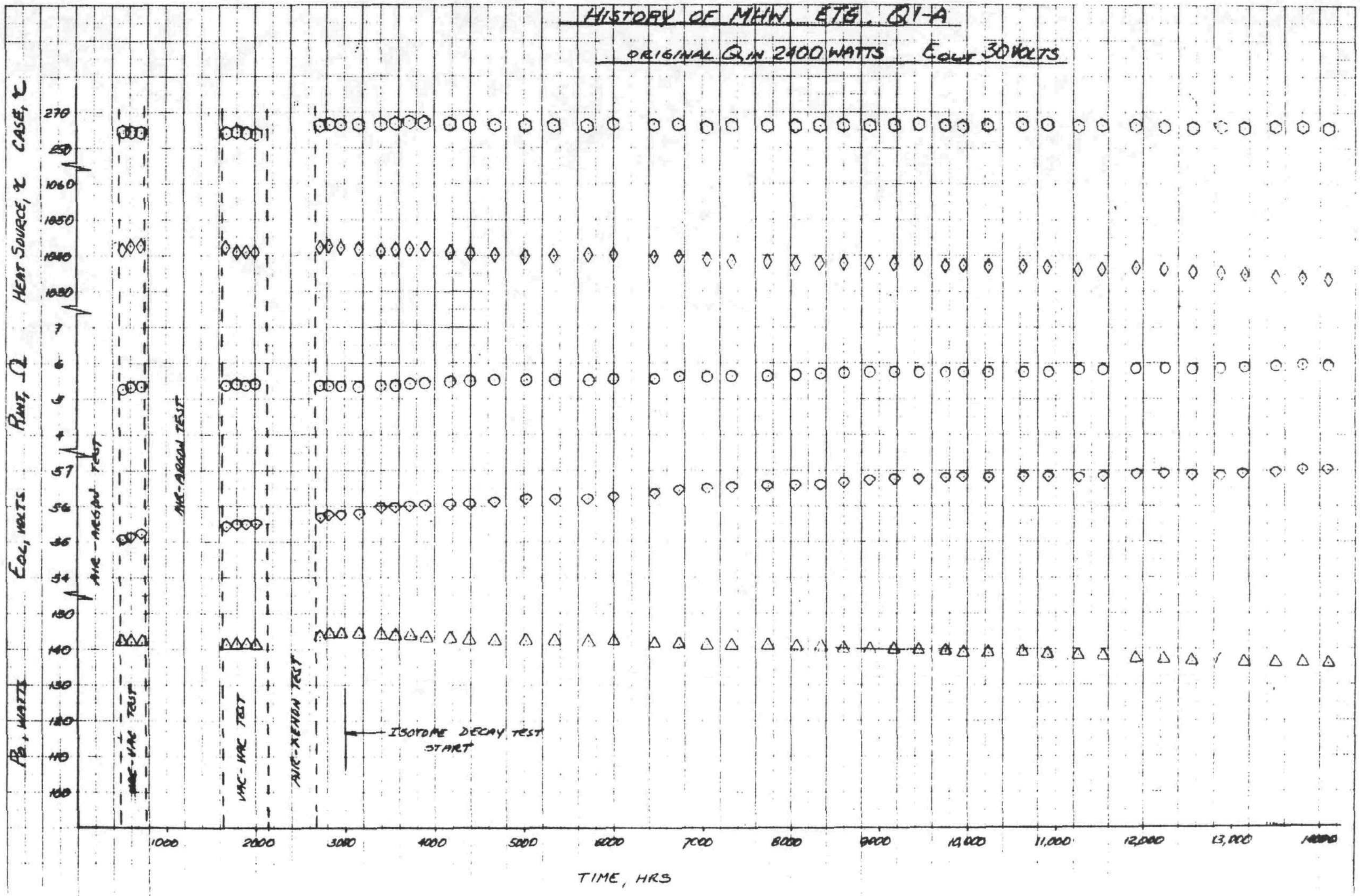


Figure 9. Q1-A History

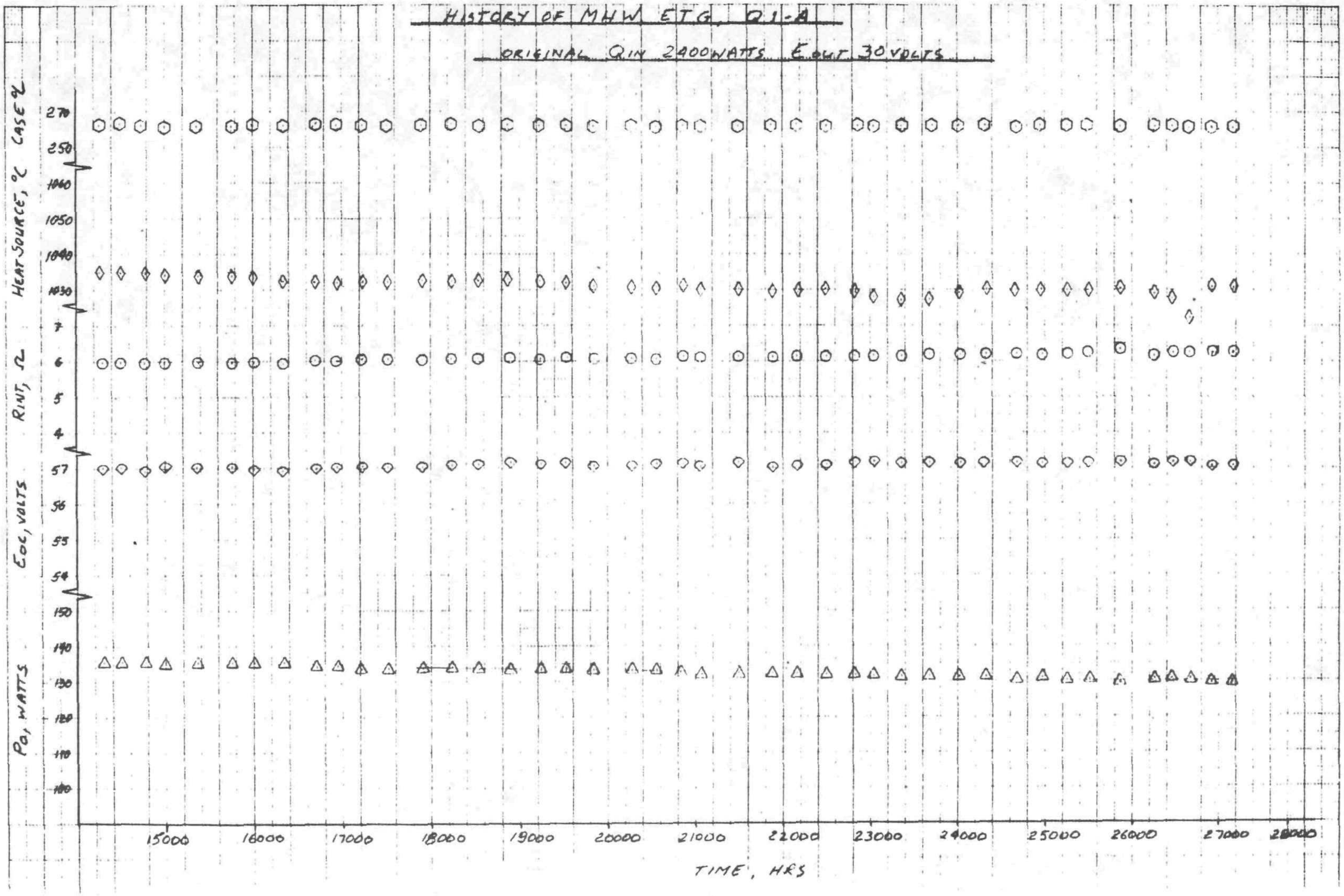


Figure 10. Q1-A History

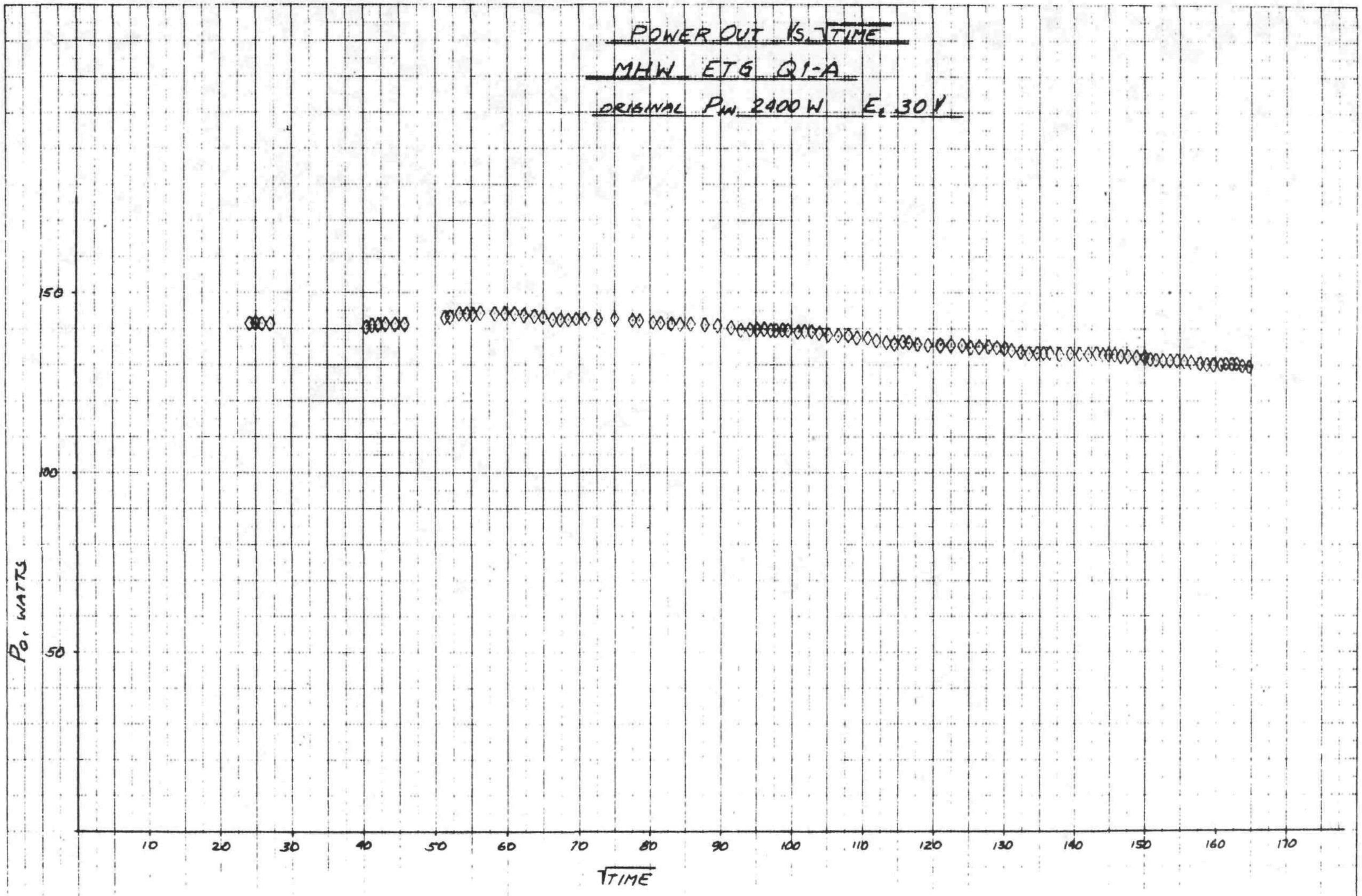


Figure 11. Q1-A Power Out Versus √Time



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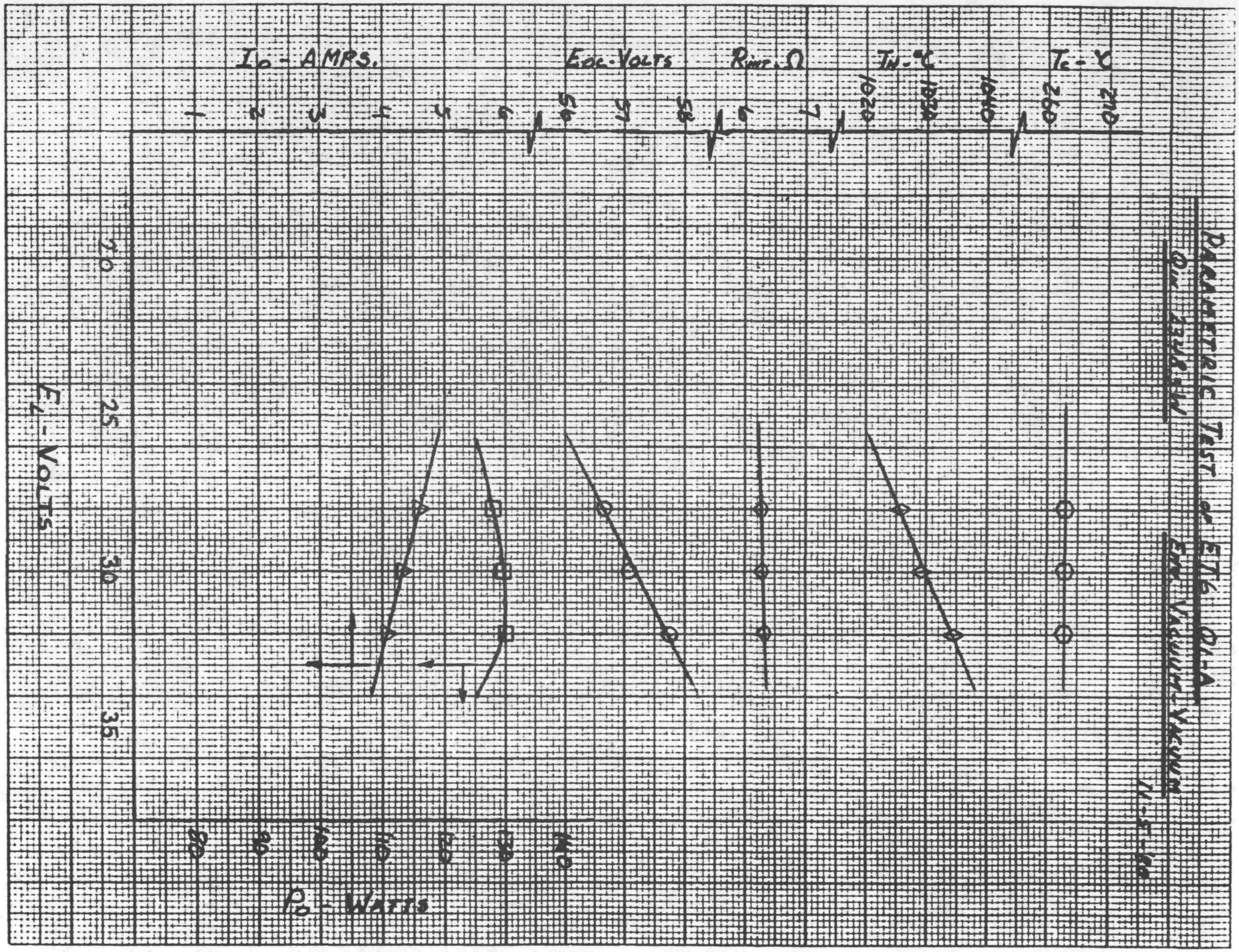

Figure 12. Parametric Test of Q1-A

The tests performed are of two categories, life testing and parametric testing. Life testing consists of continuous operation in a vacuum environment at a predetermined hot shoe temperature and load voltage. The measured parameters consist of the load resistance, the open circuit voltage, the open circuit voltage between the module terminal and the insulating foil, and the closed circuit voltage across a known current resistor located between the module terminal and the insulating foil. These values were then used to calculate the internal resistance, the output power, and the shunt resistance between the module and the insulating foil. These measurements are performed at one week intervals.

Parametric testing consists of measuring the module parameters while varying the load voltage above and below the operating point. The measured parameters were the same as above although no shunt conductance measurements were made. These tests are conducted at two month intervals during operation at JPL.

The S/N-1 module has presently operated for 28,509 hours. This includes 9093 hours of operation at JPL. Figure 13 illustrates the life history of this module. The hot shoe temperature was about 1120$^{o}$C during operation at RCA. The actual hot junction temperature is about 35$^{o}$C less at 1085$^{o}$C due to the temperature drop across the hot shoe.

This temperature is presently approximated by setting the heater input power to the value used at RCA since the hot shoe thermocouple leads were damaged during shipping. Because the S/N-1 module hot junction temperature is about 85$^{o}$C more than 1000$^{o}$C, which is presently used for RTG's, this constitutes an accelerated life test due to the higher temperature. The S/N-1 module is therefore equivalent to a module having operated for over 400,000 hours.

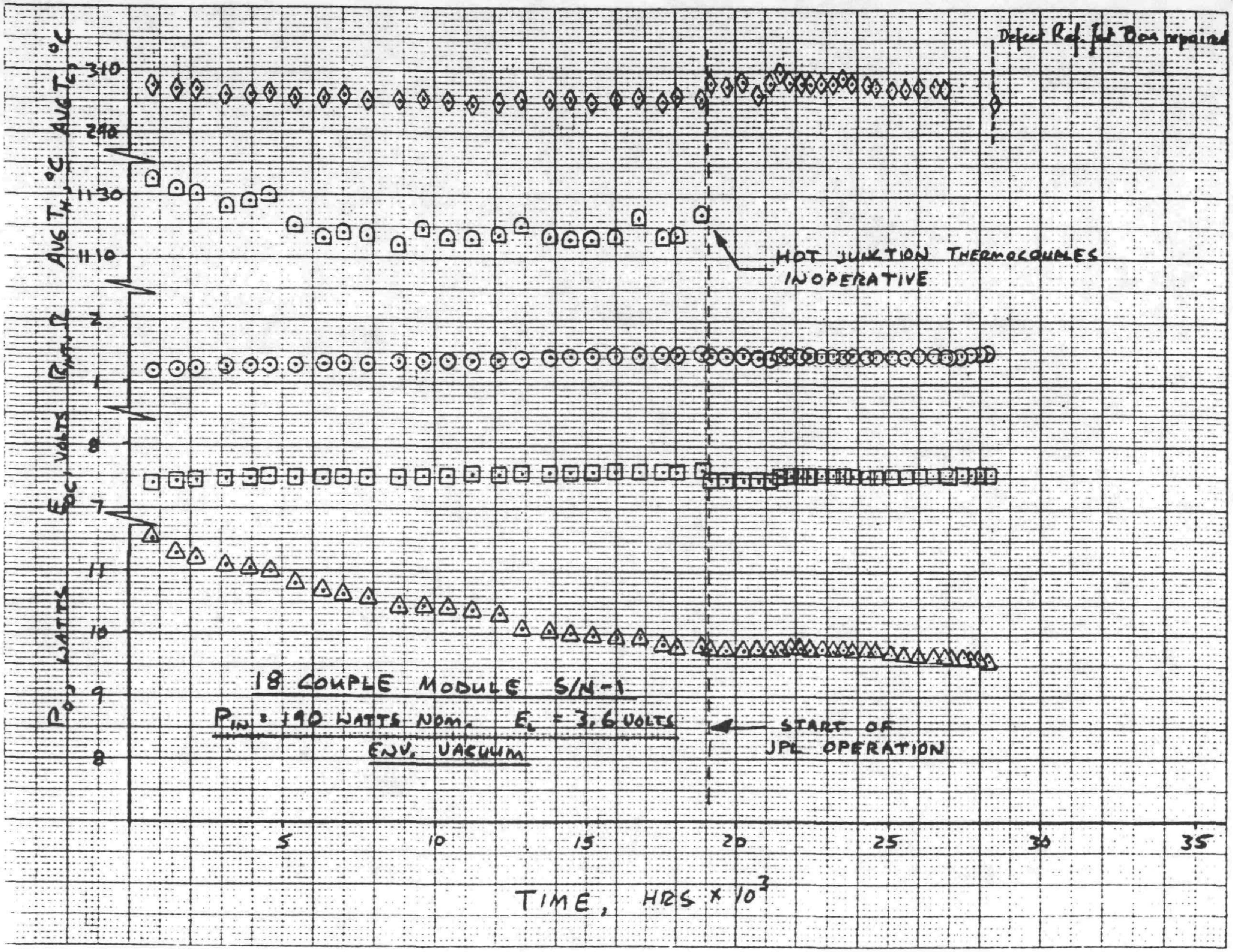


Figure 13. 18 Couple Module S/N-1 Test History

This accelerated time is an extrapolation since no module has actually operated for such an extended period at a hot junction temperature of 1000°C. The model used to determine this value assumes that the $Si_3N_4$ coating remains effective. A better determination of accelerated time values can be made when we know if and/or when the coating becomes ineffective. This time is obtained from our present model as follows. The silicon loss per unicouple which contributes to shunt resistance between to module terminal and the insulating foil and overall insulation degradation is of the form; (e.g., Reference 2, Section V);

$$L \, \Delta\tau = \left(10^{\alpha x \frac{10^4}{T} + \beta}\right) \Delta\tau; \; \alpha, \beta = -2.3752, 10.8338$$

Where

L = silicon loss rate in g/unicouple-hr

$\Delta\tau$ = elapsed time of operation

$\alpha,\beta$ = geometric constants derived from least squares fit of data; values given above are for $Si_3N_4$ coated unicouples

T = hot junction temperature in °K

By assuming an equal weight loss for unicouples operating at different temperatures and equating them, we derive the following relation;

$$\Delta\tau_2 = \Delta\tau_1 \, 10^{\left[\alpha x 10^4 \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]}$$

Where $\Delta\tau_i$, $T_i$ refers to the relative times and temperatures for modules being compared. This gives the acceleration factor as

$$\frac{\Delta\tau_2}{\Delta\tau_1} = 10^{\left[\alpha x 10^4 \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]}$$

This relation is presently only valid over the range, 950°C to 1150°C; this being the extent of the 18 couple module data.

Figure 13 shows that the power degradation over the period of JPL operation has been less than 0.5%. All other parameters have reached a very stable level. Since this includes the shunt resistance between the module terminal and the insulating foil, as presented in Figure 14, this substantiates the assumption that the deposits caused by the reaction being sublimed silicon and the silicon dioxide insulation gives rise to a maximum level of shunt conductance. There is at present not enough information to determine whether or not the deposits are uniform throughout the insulation. Any power loss due to this mechanism would therefore also reach a level of stabilization. Figure 15 shows the maximum power output without any loss due to shunt conductance compared with the actual power output. As the power loss due to the shunt conductance is presently much less than 1% this process has a minimal effect.

The S/N-3 module has presently operated for 25,611 hours. This includes 7094 hours of operation at JPL. Figure 16 illustrates the life history of this module. The hot shoe temperature was about 1040$^{o}$C during operation at JPL. This corresponds to a hot junction temperature of about 1005$^{o}$C for the same reason as for the S/N-1 module. The hot junction temperature of this module is therefore essentially that which is used presently for RTG's. Two of the three hot shoe thermocouples have become detached from the hot shoe surface. The single remaining hot shoe thermocouple presently measures a lower temperature than is actually obtained due to a partial separation of its contact. The hot shoe temperature is set by matching our heater input power to that obtained at RCA during their tests. The 1020$^{o}$C temperature presently recorded by this thermocouple is used as a monitor and aid in obtaining a stable hot shoe temperature.

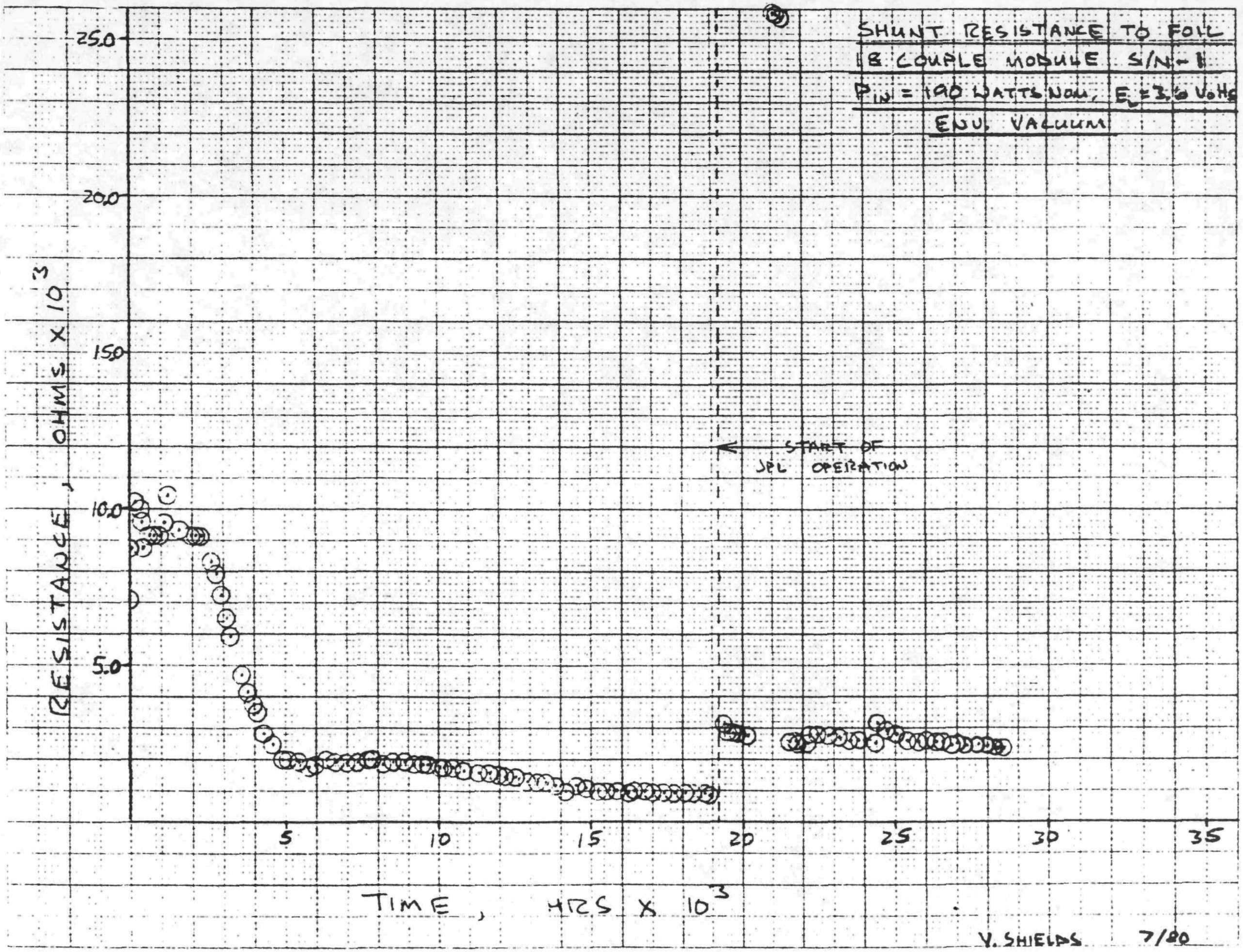


Figure 14. S/N-1 Shunt Resistance, Module to Foil

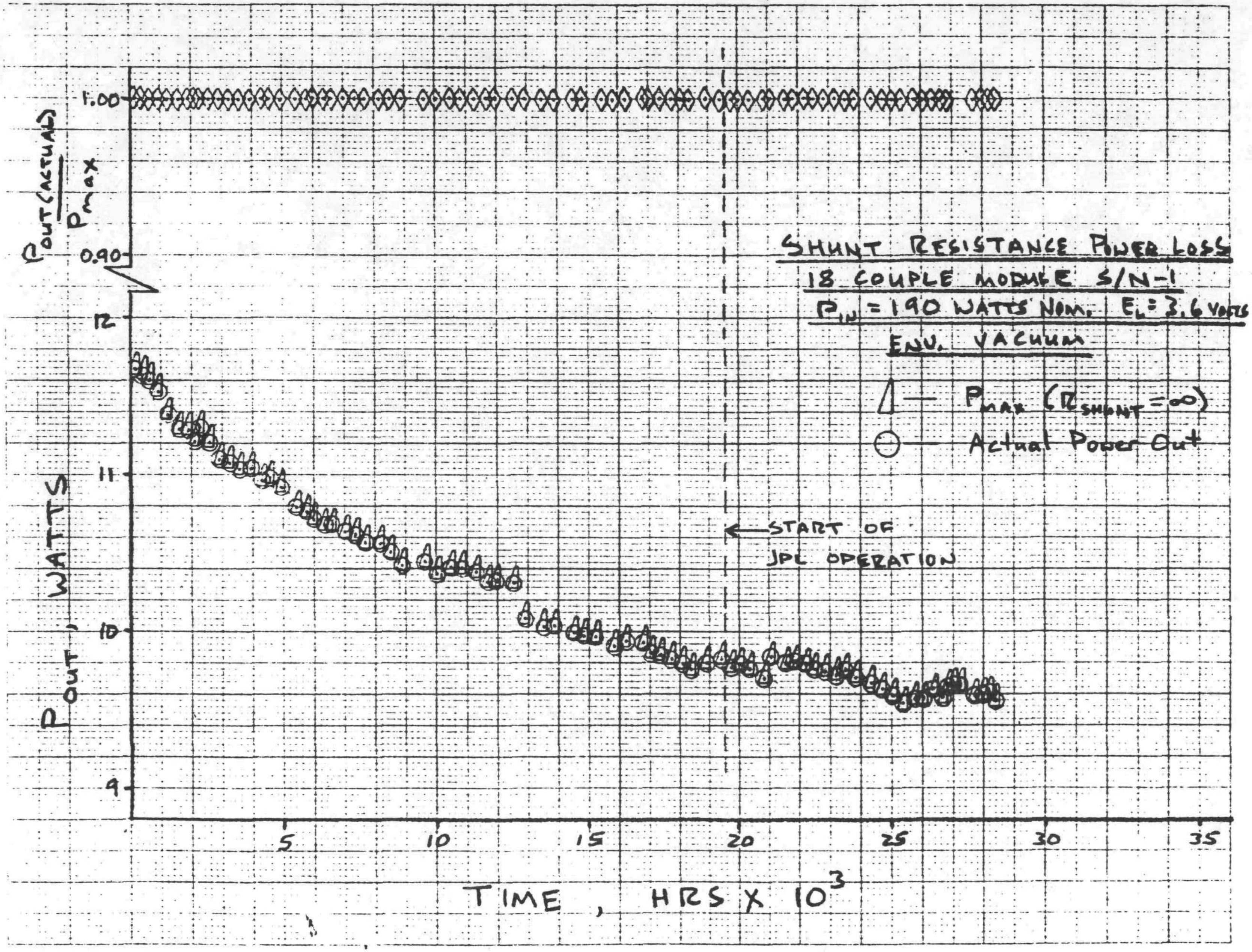


Figure 15. S/N-1 Shunt Resistance Power Loss

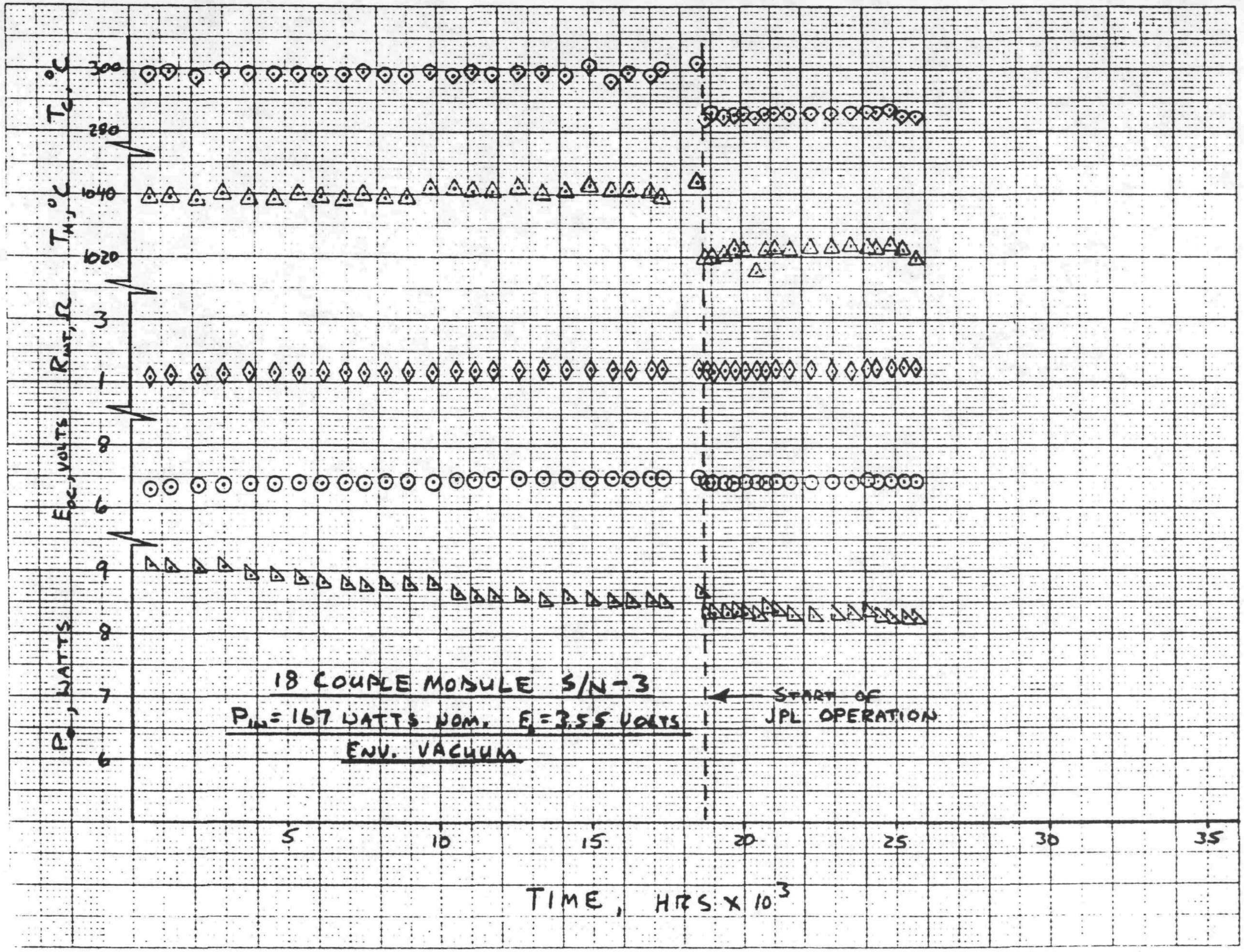


Figure 16. 18 Couple Module S/N-3 Test History

Figure 16 shows that the power degradation over the period of JPL operation has not been significant. As with the S/N-1 module, all other parameters have reached a very stable level. The shunt resistance between the module terminal and the insulating foil, as shown in Figure 17, has reached a level which also supports the assumption made concerning material deposition in the insulation. Figure 18 shows the maximum power output without any loss due to shunt conductance compared with the actual power output. Again, the shunt power loss is much less than 1%.

Both the S/N-1 and the S/N-3 modules are displaying degradation rates for the parameters measured that are nearly equivalent. This is interesting since the S/N-1 module has operated for a period that is effectively 16 times longer than that of the S/N-3 generator. This would seem to say that operation for periods of at least 50 years still produces stable operation. Even though the material which has sublimed from the unicouple is much greater for the S/N-1 module than for the S/N-3 module, as pictured in Figure 19, the stability has not degenerated. It must be noted though that this figure does not include the material sublimed from the hot shoe surface facing the heat source. The amount of material being lost would imply that these modules can operate at a stable performance level at least until they reach a stage where the structural integrity is considerably reduced. In addition to this it is observed that although operation has been suspended for a period of approximately two years, each of these modules has resumed operation at their prior level of stable performance.

The current parametric tests for the S/N-1 and S/N-3 modules are shown in Figures 20 and 21 respectively. There is no significant difference between the operational load voltage and the optimum load voltage for maximum power for

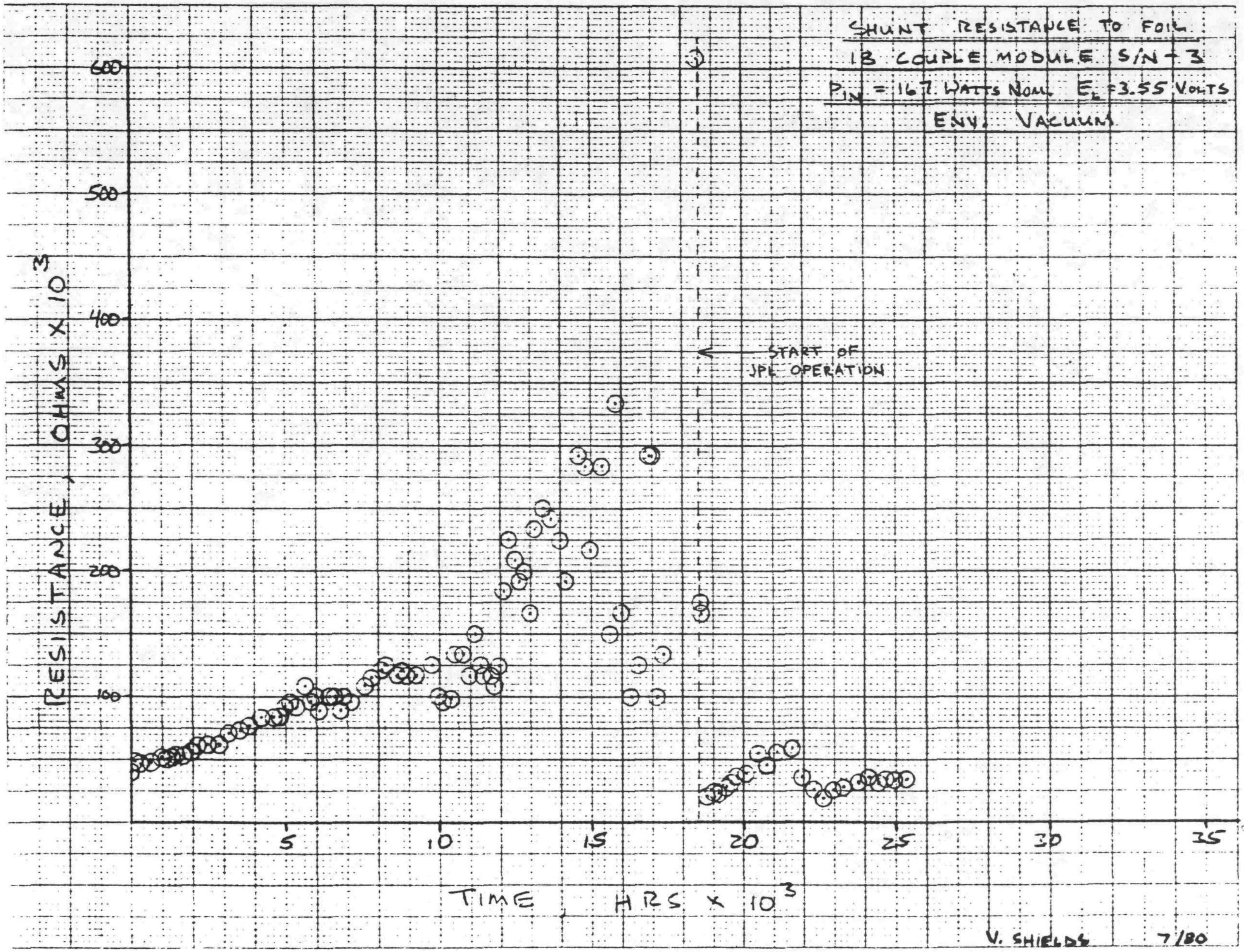


Figure 17. S/N-3 Shunt Resistance, Module to Foil



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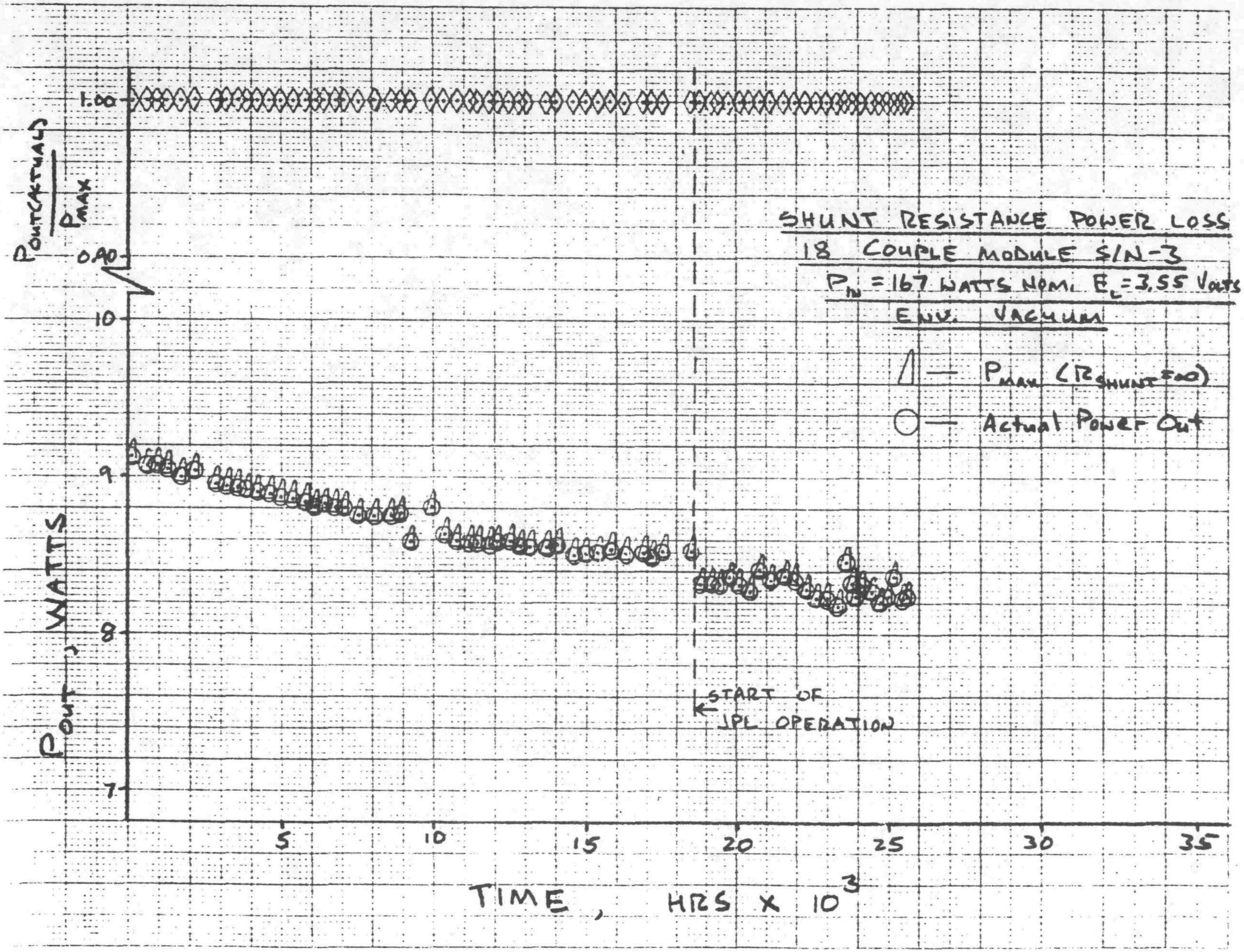


Figure 18. S/N-3 Shunt Resistance Power Loss

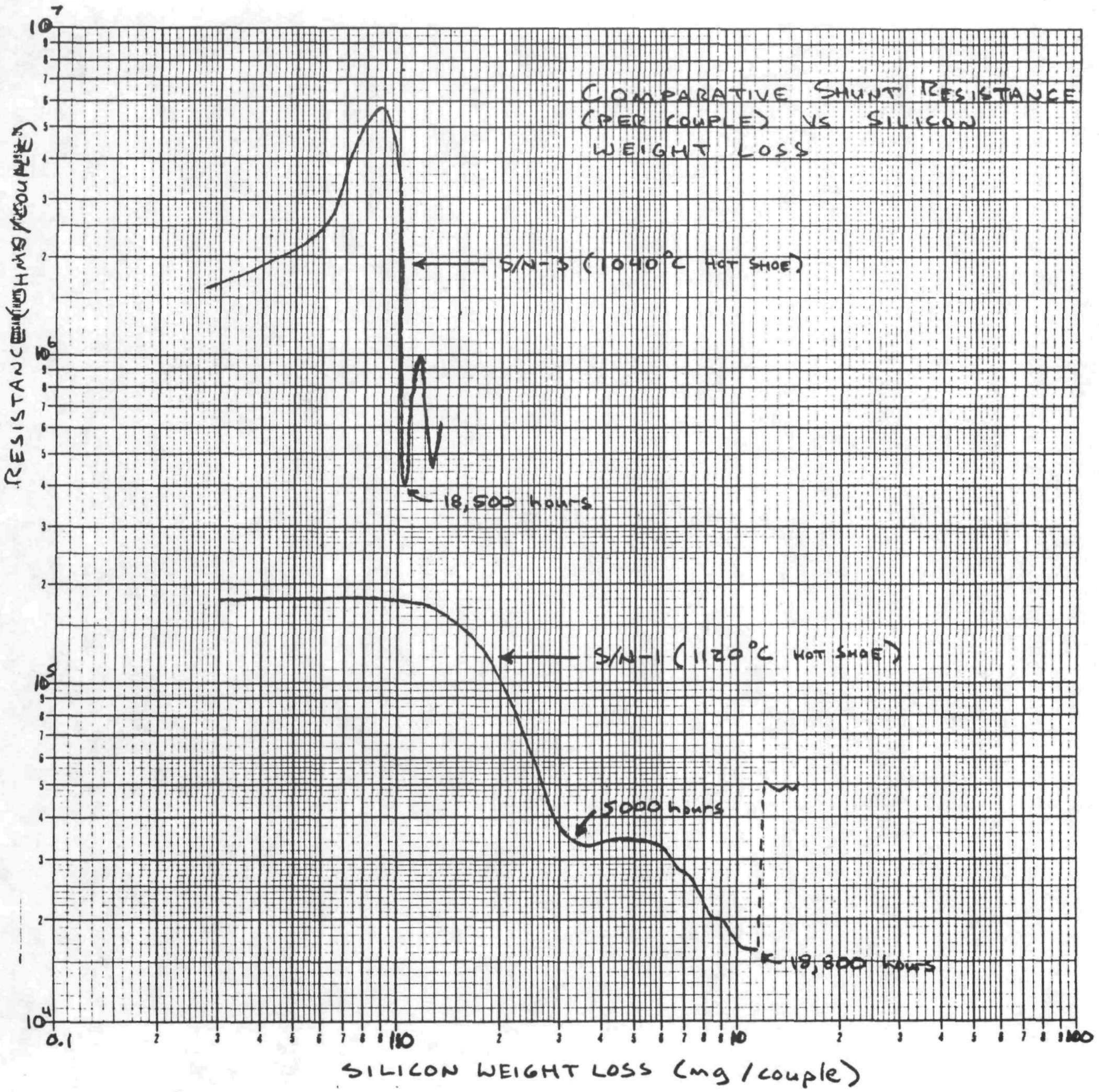


Figure 19. Comparative Shunt Resistance vs Calculated Weight Loss

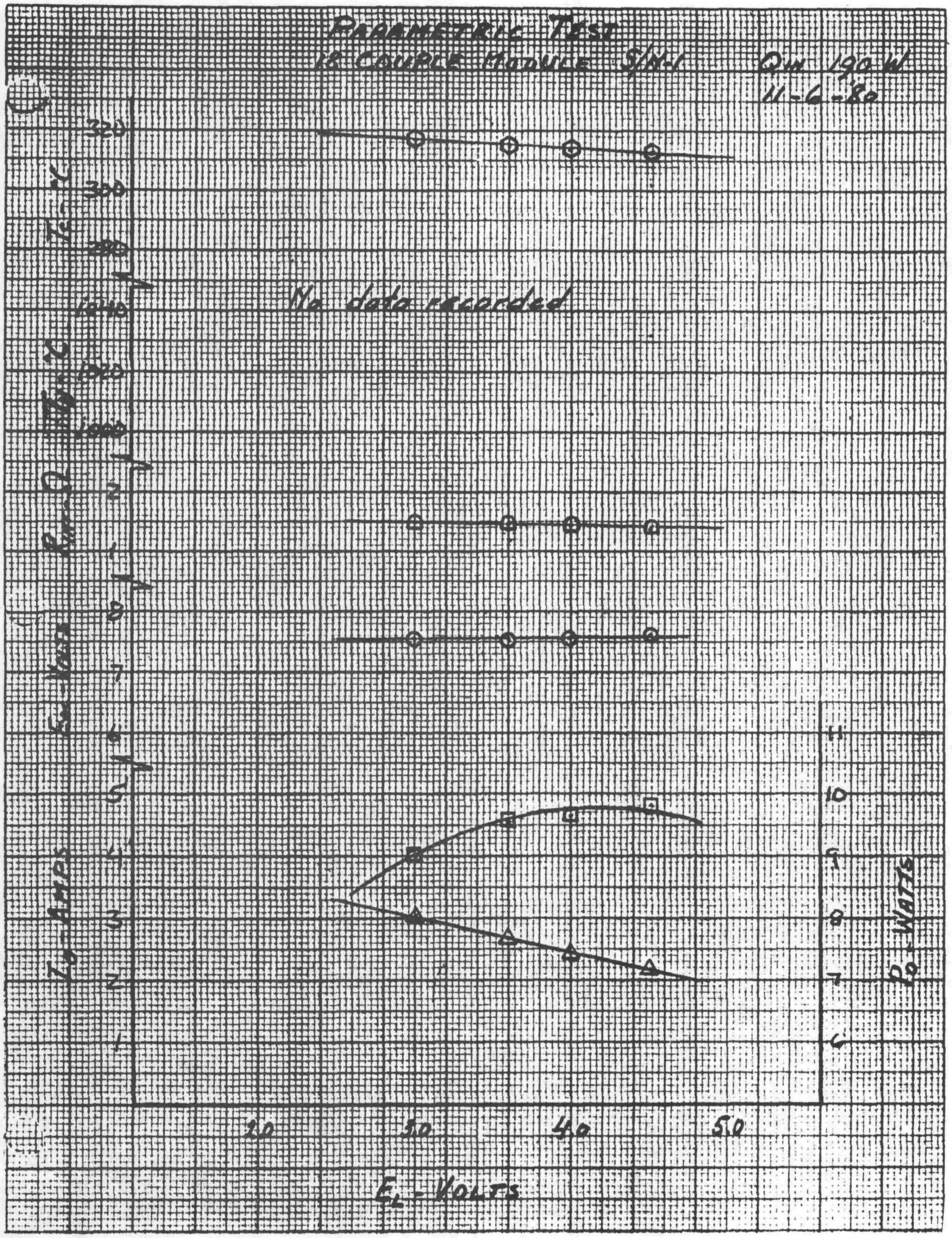


Figure 20. 18 Couple Module S/N-1 Parametric Test

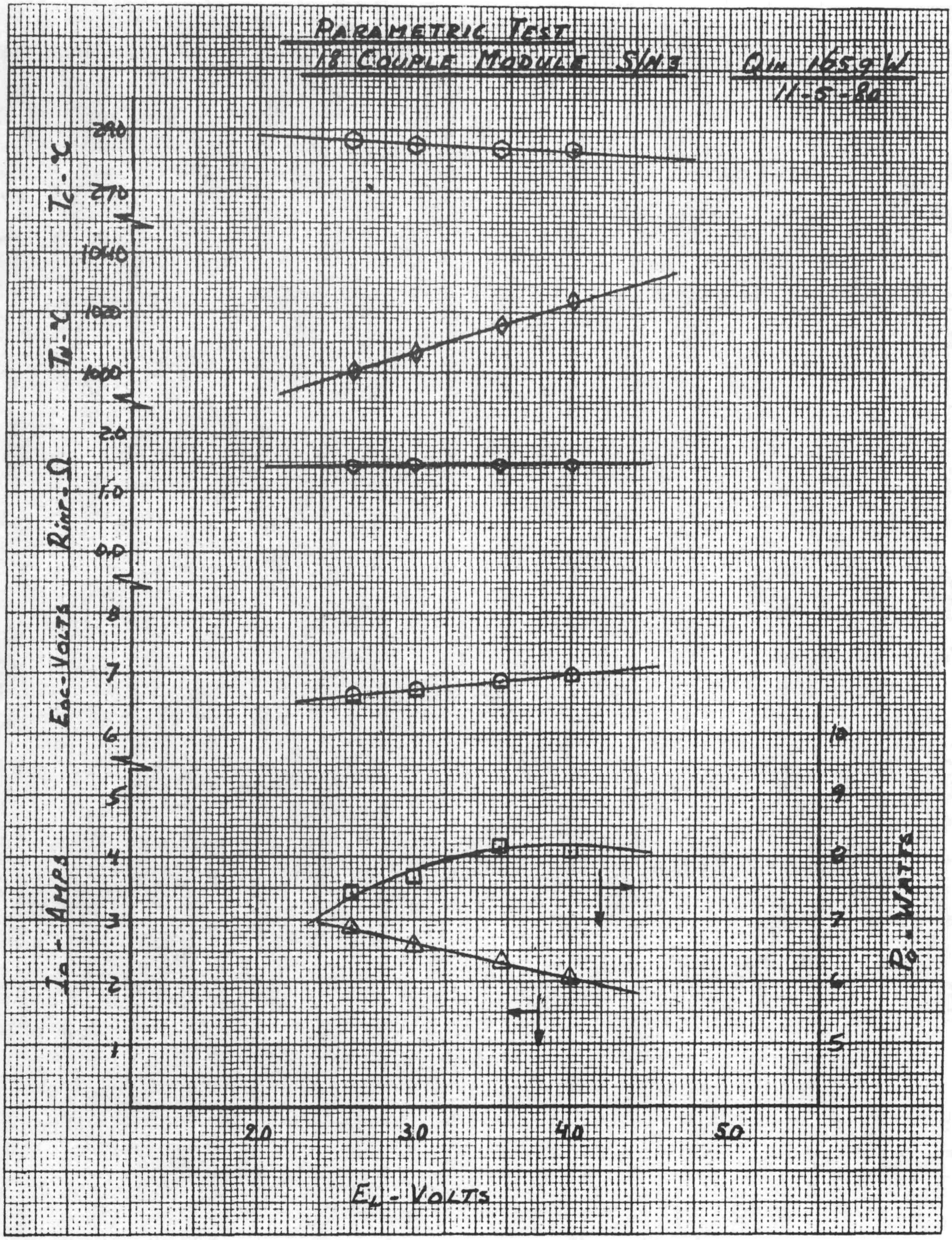


Figure 21. 18 Couple Module S/N-3 Parametric Test

the S/N-3 generator although the S/N-1 module shows a difference of about 0.6 volts which results in 2% less than maximum power.

To determine if there exists any structural damage the remaining S/N-2 module was disassembled for examination (e.g., Reference 2). The life history of the S/N-2 module is shown in Figure 22 along with its shunt resistance history in Figure 23. There are no deviations from the trends observed in the S/N-1 and S/N-3 performance. Figure 24 shows that the maximum power output without losses due to shunt conductance is not significantly different from the actual power output. The use of this module was appropriate since although it has operated for about 16,750 hours at a hot shoe and hot junction temperature of 1090$^{o}$C and 1055$^{o}$C respectively, the lifetime acceleration factor increases this to approximately 99,300 hours, or 11 years. This covers the lifetime of present space missions.

Several observations resulted from this metallurgical examination. First, it was observed that besides Si and $SiO_2$, molybdenum in the form of an oxide was also deposited within the thermal insulation. Because this material is an oxide and therefore an insulator it does not affect the shunt conductance of the module. Aside from this, the lack of published thermal conductivity data on oxides of molybdenum prevents our evaluation of effects due to this parameter. The source of the oxide is not presently known although it is probably due to residual oxygen or oxides in the system at the start of operation or due to exposure to air at some point during its operation.

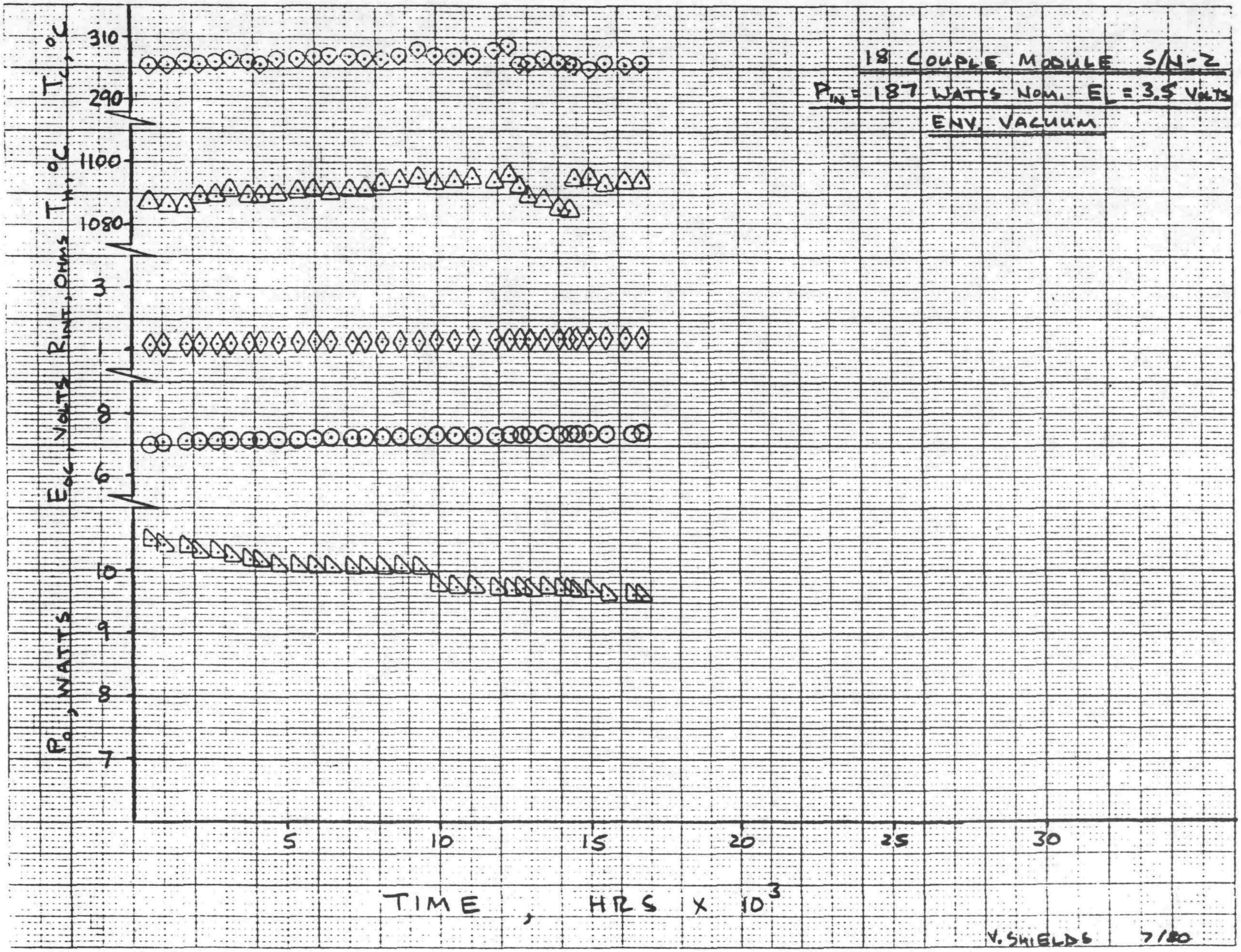


Figure 22. 18 Couple Module S/N-2 Test History

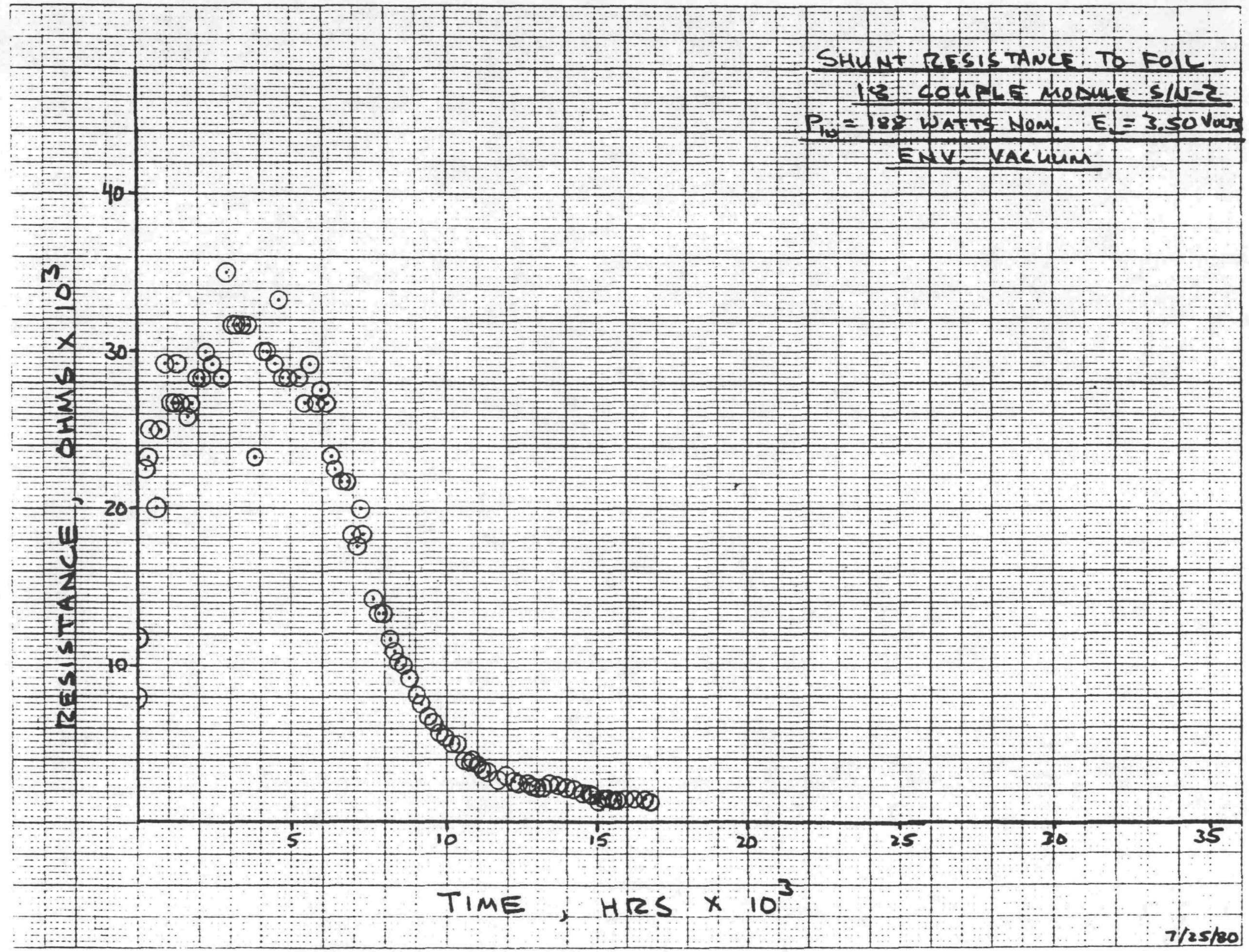


Figure 23. S/N-2 Shunt Resistance, Module to Foil

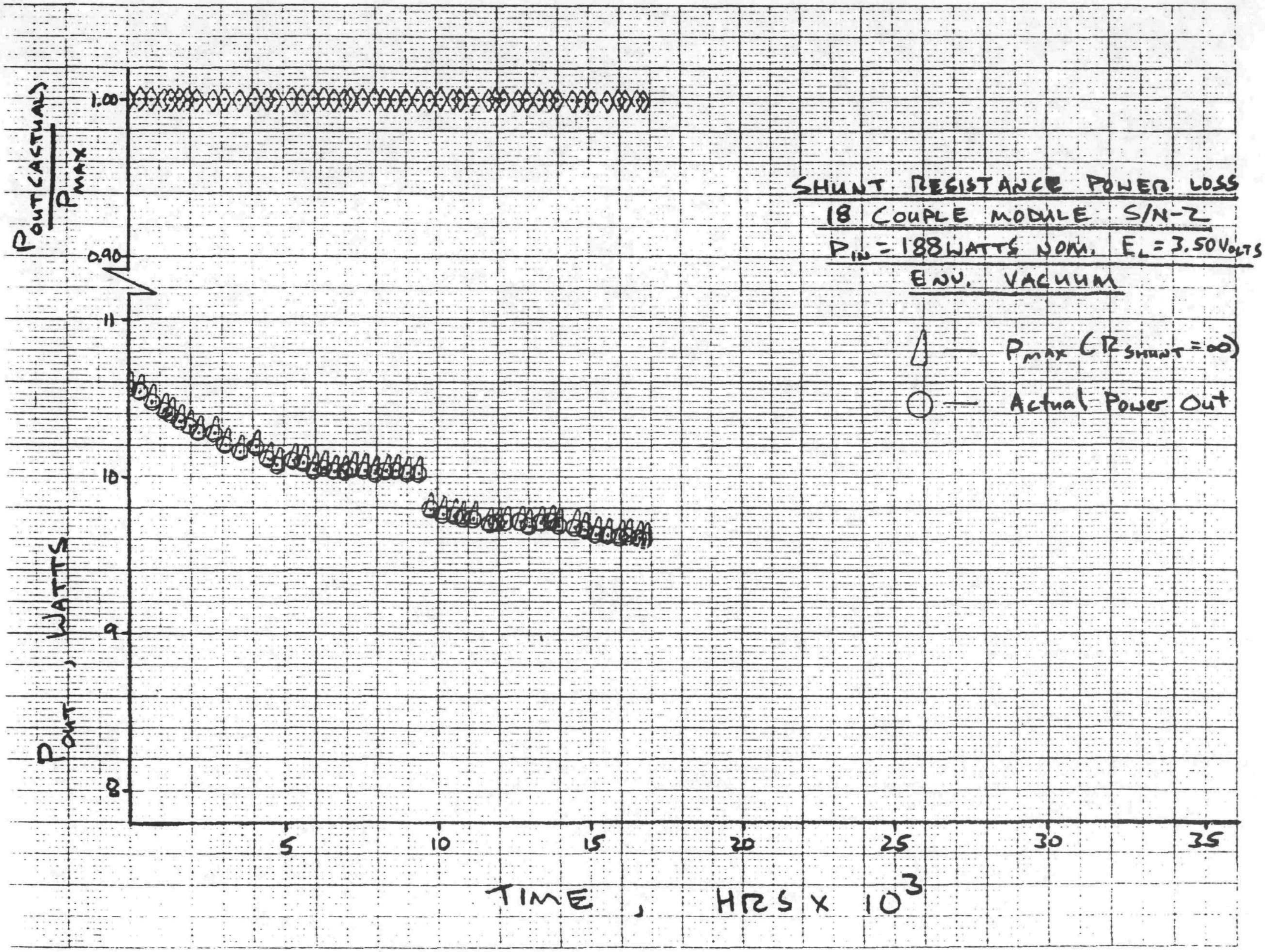


Figure 24. S/N-2 Shunt Resistance Power Loss

Second, it was observed that the $Si_3N_4$ coating had deteriorated significantly on the N-doped side of the hot shoe facing the heat source. This was expected due to the volatile nature of the phosphorus dopant. There were no significant difference between the coatings on the N- and P-doped sides of the hot shoe facing the insulation. The deterioration was less on this side because it is not directly irradiated by the heat source. Also the presence of the $Al_2O_3$ insulator aids in preventing coating loss.

Examination of a cross section of a unicouple showed that the titanium originally at the bond site between the N and P sides of the hot shoe had diffused towards the cooler regions of the junction (i.e., towards the surface of the hot shoe facing the insulation). Figure 25 illustrates the direction of diffusion and the present distribution of the titanium. Later upon handling, a hot shoe fell apart at this junction. This says that the integrity of the junction had degraded. Although the possibility exists that further diffusion of titanium will cause an abrupt failure of the module, the continued stable performance of the S/N-1 module, which represents an operational lifetime four times that of the S/N-2 module, implies that this would not occur within the lifetime of a mission.

Upon examining the leg hot-shoe junctions, it was observed that molybdenum was diffusing along each leg away from the hot shoe. Figure 26 illustrates the location of that diffusion. Since the hot shoe contains approximately six atomic percent molybdenum, this is probably the source, although an EDAX analysis of a cross section of the junction region was inconclusive due to the small quantity of material involved. The molybdenum was originally placed within the hot shoe to enhance its thermal properties. And although its usefulness is questionable, it has not adversely affected the performance of any of the modules.

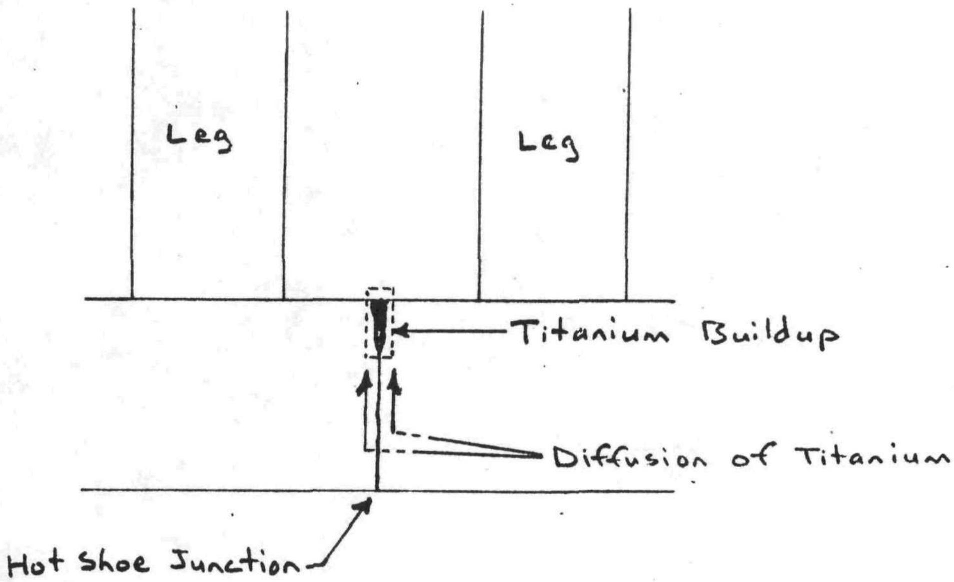


Figure 25. Titanium Diffusion along Hot Shoe Junction

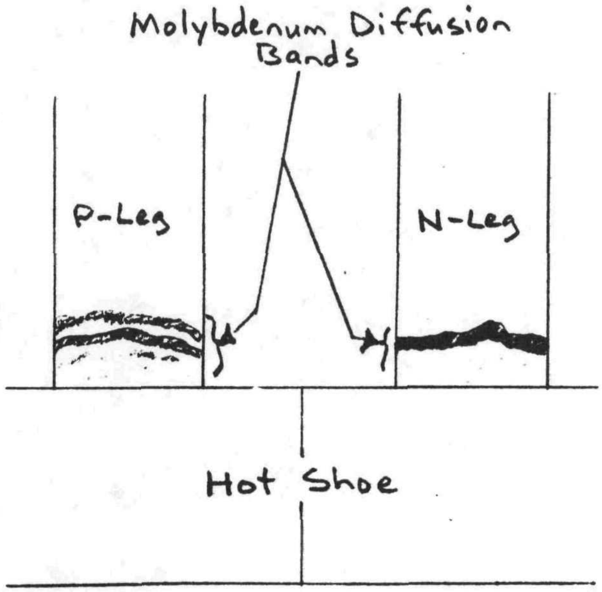


Figure 26. Molybdenum Diffusion along Unicouple Legs

Aside from the fore-mentioned diffusion, there was no observable deterioration of either leg hot-shoe junction. This says that the material sublimed from the unicouple has not been enough to cause significant erosion of the junction regions of the unicouple. This would similarly apply to the S/N-3 module which operates at a lower hot junction temperature, but not necessarily to the S/N-1 module which has a higher hot junction temperature. The approximately 30°C temperature difference give rise to a factor of 2.5 increase in the silicon loss rate for the S/N-1 module over that for the S/N-2 module. This factor will increase to 40 times if the coating on the S/N-1 module has effectively come off due to the higher operating temperature. But again, the continued stable performance of the S/N-1 module which represents a lifetime well in excess of any presently conceived mission should alleviate any concern regarding structural deterioration.

The purpose of the present tests conducted on these modules is to determine how the two year storage period at RCA since their last operation has affected their performance. It is concluded from the data presently available that there is no structural damage to any of these modules which could be attributed to the period of handling and storage. Since the present operational performance shows pronounced stability, it appears that there have been no degradation effects which can be associated with the storage of these modules.

# SECTION V

## MHW FLIGHT PERFORMANCE

The power output of both the LES 8 and 9 spacecraft MHW generators continue to follow the performance trend predicted by the DEGRA2 code as presented in the July 1980 report. Both Voyager spacecraft MHW generators show no significant change in performance.

## REFERENCES


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