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BALTIMORE, MARYLAND

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THERMOELECTRIC BONDING STUDY

PHASE II
SUMMARY REPORT

April 1966

Prepared by:
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Prepared under Contract NAS5-3973 for
National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

HITTMAN ASSOCIATES, INC
BALTIMORE, MARYLAND

LEGAL NOTICE

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FOREWORD

This report covers the work accomplished during Phase II of the Thermoelectric Bonding Study performed for the National Aeronautics and Space Administration, under Contract NAS5-3973. Mr. Joseph Epstein is Technical Officer for GSFC.

I. INTRODUCTION

The development of long-lived power supplies capable of reliable operation in space has been a major concern of the National Aeronautics and Space Administration for some time. Thermoelectric systems utilizing radioisotope heat sources and lead telluride thermoelectric elements hold considerable promise for meeting this requirement in the range of a few watts to one kilowatt or more. Systems of this type that have been built, however, often do not perform as expected. Rapid decline in power output is often observed.

It is believed that the limited success of lead telluride thermoelectric generators is associated with increased internal resistance and that this in turn is caused by gradual failure of the bond between the lead telluride and the electrical contacts to which it must be attached. Hittman Associates, Inc. under NASA Contract NAS5-3973, has been studying the nature of the bond between lead telluride and commonly used electrical contact materials. The program objective was to determine the mechanism causing the observed degradation. A secondary aim was to ultimately develop a bonded lead telluride thermoelement with reliable long term performance.

During the first phase of this program, it was found that the two major mechanisms causing failure in the bond zone were diffusion of material from the braze into the thermoelectric material and cracking caused by stresses resulting from the difference in thermal expansion between the thermoelectric and shoe material. It was demonstrated that p-PbTe is far more susceptible to both these phenomena then is n-PbTe.

During this phase, a reproducible technique for bonding lead telluride to iron shoes with a modified tin telluride braze was developed. The strengthening of p-PbTe was studied and life tests were undertaken to study the effect of time under operating conditions on the properties of bonded lead telluride thermoelements.

The accomplishments of this program are reported in the following chapters.

II. SUMMARY AND CONCLUSIONS

The studies of lead telluride carried out under this program have contributed to a firmer understanding of the nature of degradation and failure of lead telluride thermoelectric elements. During the first phase of this program, it was shown that initially sound bonds could be produced between lead telluride and electrical contact materials. Several braze alloys could be used in the operation. However, it was demonstrated that, should appreciable diffusion between the lead telluride and braze material occur, the thermoelectric material would be poisoned and the properties could be expected to degrade.

It was further observed that p-type lead telluride was more susceptible to this failure mechanism than n-type lead telluride. Indeed the n-type material was substantially unaffected by many of the additives. Tin telluride and tin telluride modified by the addition of one percent by weight of titanium caused the smallest deleterious effect on p-PbTe and were selected for further evaluation during the current phase of the work.

A stress analysis performed as part of the initial effort indicated that large stresses could be set up at the thermoelement - shoe interface. These stresses are partly relieved by flow of the braze. Torsion tests of bonded samples showed that this residual bond stress is greater than the strength of p-PbTe, but does not exceed the strength of n-PbTe.

In order to determine which of the two effects described above was primarily responsible for the failure of bonded lead telluride thermoelectric elements, a program in which life tests were a principal tool was undertaken. Procedures for fabrication and bonding of n-PbTe and p-PbTe to iron shoes were developed. Life test equipment capable of handling twenty-four individual thermoelectric elements was designed, built, checked out and placed into operation.

Tests of n-PbTe, up to 4000 hours in duration, have been completed. Results show that, under near isothermal operation, as would occur in isotope heated space power supplies, appreciable degradation does not occur. Although metallographic studies of elements removed from test showed no apparent evidence of diffusion, measurements made by the electron microprobe technique demonstrated that extensive interdiffusion between the thermoelectric element and braze material occurs within the first 500 hours.

Life testing of p-PbTe has not proceeded as far, but it is clear that gradual degradation of the power output consistently occurs, resulting from increased electrical resistance in the vicinity of the bond. Electron microprobe results for p-type samples are not yet available but they are expected to show diffusion analogous to that found in n-PbTe. Such diffusion could well be the cause of the increased bond resistance. The rate of degradation with time is declining and further testing will be needed to determine if the p-PbTe will eventually operate at a relatively constant reduced output. If this occurs, or if a consistent pattern of degradation can be established, consideration of the performance of p-PbTe with time could result in improved equipment designs that can reliably provide the required output for a scheduled lifetime.

A limited study of the effects of additives on p-PbTe showed that additions of one to two percent of molybdenum will increase the strength of p-PbTe to values similar to those measured for n-PbTe. Tungsten also appears to effectively strengthen p-PbTe and alumina in the form of sapphire fibers may have a similar effect. Performance of elements containing one weight percent of molybdenum during life tests was not significantly different from elements containing no additive.

The work to date on this program has demonstrated that degradation in lead telluride thermoelectric materials is localized in the p-element. Further testing to determine the ultimate magnitude of this degradation is underway.

It has been shown that p-PbTe can be strengthened to the level of n-PbTe by the addition of molybdenum or other materials in small quantities without apparent effect on the thermoelectric properties.

III. FABRICATION OF THERMOELECTRIC ELEMENTS

Almost all of the thermoelectric elements used in this program were fabricated at Hittman Associates by a hot pressing technique. This was done because several tasks called for the intentional addition of foreign material into the PbTe, a procedure that required "in-house" fabrication. Non-additive samples were manufactured by the same process to provide a standard for comparison. In addition, several cold-pressed and sintered elements were purchased from Minnesota Mining and Manufacturing Company (3M) and compared with Hittman Associates produced thermoelectric elements.

The raw materials used in element fabrication were purchased as doped powders from 3M Company. Analyses of these powders were not provided. However, the vendor stated that the properties of elements cold pressed and sintered by them from powder taken from each lot would be within ± 10 percent of their published values. The quality control release data provided by 3M on each lot of powder is shown in Table I along with the published values (Reference 2 and 3) and actual deviations from these published values. From the data in this table, it is apparent, that none of the four lots of powder was within specification, two deviating by more than 10 percent in resistivity, one in Seebeck coefficient and one in both these parameters.

Because of program delays that would have resulted and because the deviations from acceptable limits were generally small, the powders were accepted and used in the program.

A. n-PbTe Element Production

More than one hundred n-PbTe elements were produced by hot pressing the TEG-2N powder described above. The standard hot pressing procedure was as follows. The powder was weighed out and placed in a graphite die. The ends of the die pins were coated with high purity alumina to prevent sticking to the compact. The die assembly was placed inside an induction coil within an argon atmosphere chamber, purged, heated, pressed and cooled under load. Pressing conditions were:

Temperature:	1450 - 1500°F (788 - 816°C)
Load:	2500 - 3000 psi
Time:	5 minutes

Variations of this procedure were used on a few samples, but with none of these was a superior product achieved.

Hot pressed samples were sound in appearance and had measured densities in excess of 97 percent of theoretical. Room temperature electrical resistivity and Seebeck coefficients at 100 to 200°C (212 - 392°F) were measured on all elements. The n-PbTe thermoelectric elements generally had Seebeck coefficients about 5 - 15 percent below the published 3M values. This was remarkably close to the -11.3 percent reported by 3M in their quality control data which were obtained by a different measurement technique. Resistivity values were

Table I

Quality Control Data on PbTe Powders Purchased From 3M Company

	n-PbTe	p-PbSnTe	p-PbTe	p-PbTe
3M Type	TEG-2N	TEG-3P	TEG-2P	TEG-2P
Lot Number	942-B-1	943-B-1	1002-B-1	1047-B-1
Lot Resistivity, $\mu\Omega$-in	195	353	198	194
3M Published Resistivity, $\mu\Omega$-in	205	405	170	170
% Deviation	-4.9	-12.8	+16.4	+14.1
Lot Emf, mv	63	68	64	54 - 55
at ΔT, °F	600	800	600	600
3M Published Emf at same ΔT	71	69	56	56
% Deviation	-11.3	-1.4	+14.3	-2.7

consistently below both the published and lot values supplied by 3M, probably because of the higher density of our hot pressed elements. Figure 1 shows the deviations from 3M published value of the Seebeck coefficient and the distribution of the resistivity around the mean value.

Our results of lower Seebeck and resistivity are consistent with data obtained at other laboratories. Values of these parameters about 10 percent below those published by 3M are frequently encountered (Reference 4).

B. p-PbSnTe Element Production

A hot pressing procedure for p-PbSnTe elements was developed which was similar to that used for n-PbTe, but the hot pressing parameters were changed to:

Temperature:	1500°F (816°C)
Load:	3000 psi
Time:	5 minutes

Approximately one hundred elements were manufactured by this process. As with the n-PbTe, measurements of room temperature resistivity and low temperature Seebeck coefficient were made on all samples. Resistivity results were somewhat erratic but generally fell within ten percent of the value reported by 3M for the lot of powder supplied. Seebeck coefficients were also erratic, but for the early production elements, most were within ten percent of the published 3M values. Tests of later production yielded results consistently below the 3M values, the latest samples being about 40 percent below predicted. Figure 2 shows the properties of the individual elements. During this period, there was no discernable change in the processing procedures. Two p-PbSnTe elements were examined by the electron microprobe technique at GSFC. One was produced early in the program and had satisfactory thermoelectric properties. The second was manufactured later and demonstrated the degraded properties typical of later production. Each element was mounted, polished, and placed in the probe apparatus. Counts were taken at ten randomly selected points on the polished surface for the principal x-ray spectra of tin, lead, and tellurium. It was found that the compositions of both samples were approximately 21% Sn, 27% Pb and 52% Te. Less than one percent manganese, employed as a dopant, was found. The significant difference between the two thermoelectric elements was that considerably greater scatter in point to point composition was measured in the more recently produced sample. The tentative conclusion drawn from this test is that the poor properties observed in later production are the result of microscale inhomogeneity in the elements. Whether this is caused by inhomogeneity in the starting material or oxide contamination of the powder that prevents homogenization from taking place during hot pressing is not known.

In addition to the poor thermoelectric properties, p-PbSnTe thermoelements produced at our laboratory were very fragile and fractured readily during bonding operations. For all these reasons, work on PbSnTe was suspended at the end of the second quarter and p-PbTe, Type TEG-2P was substituted.

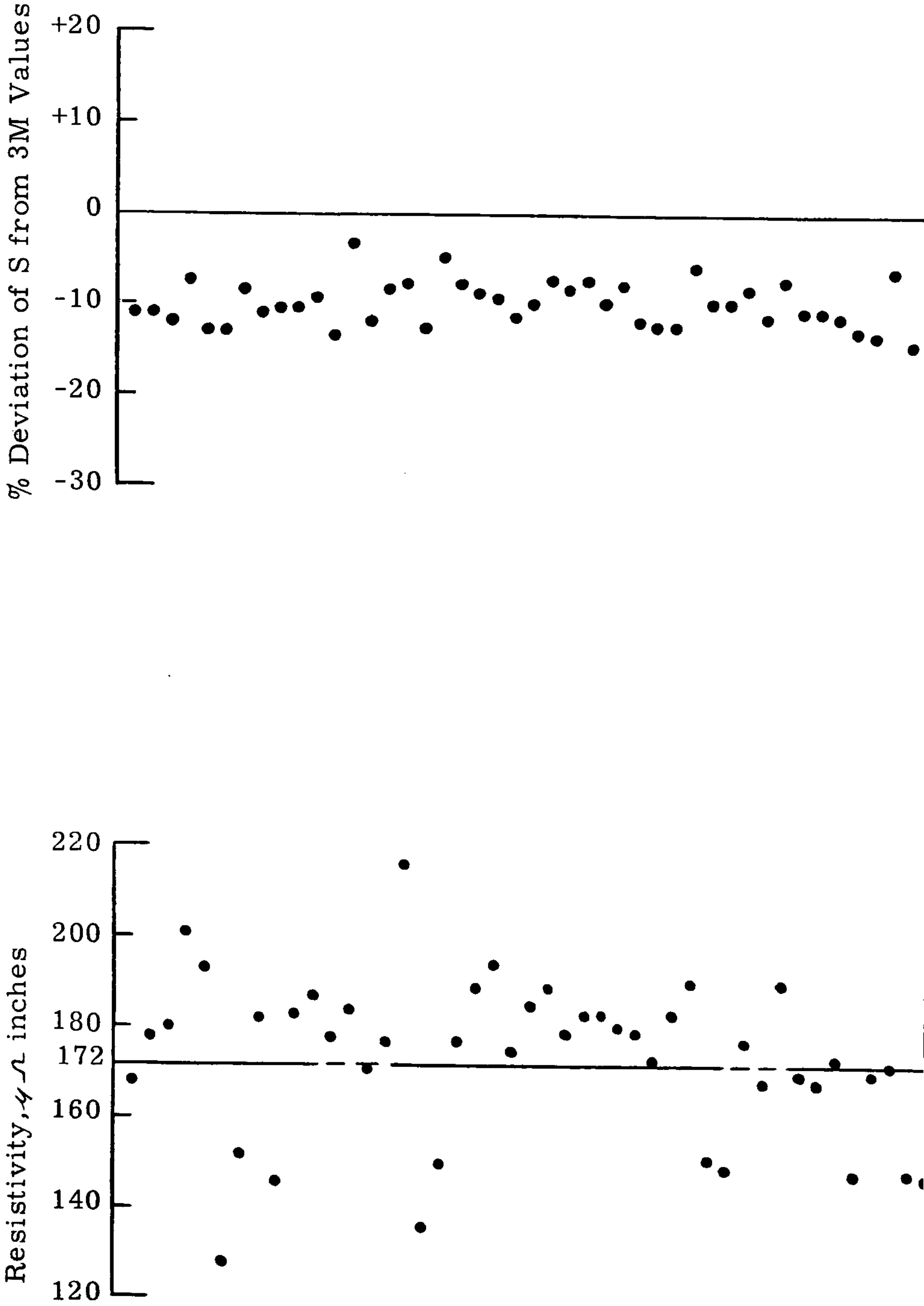
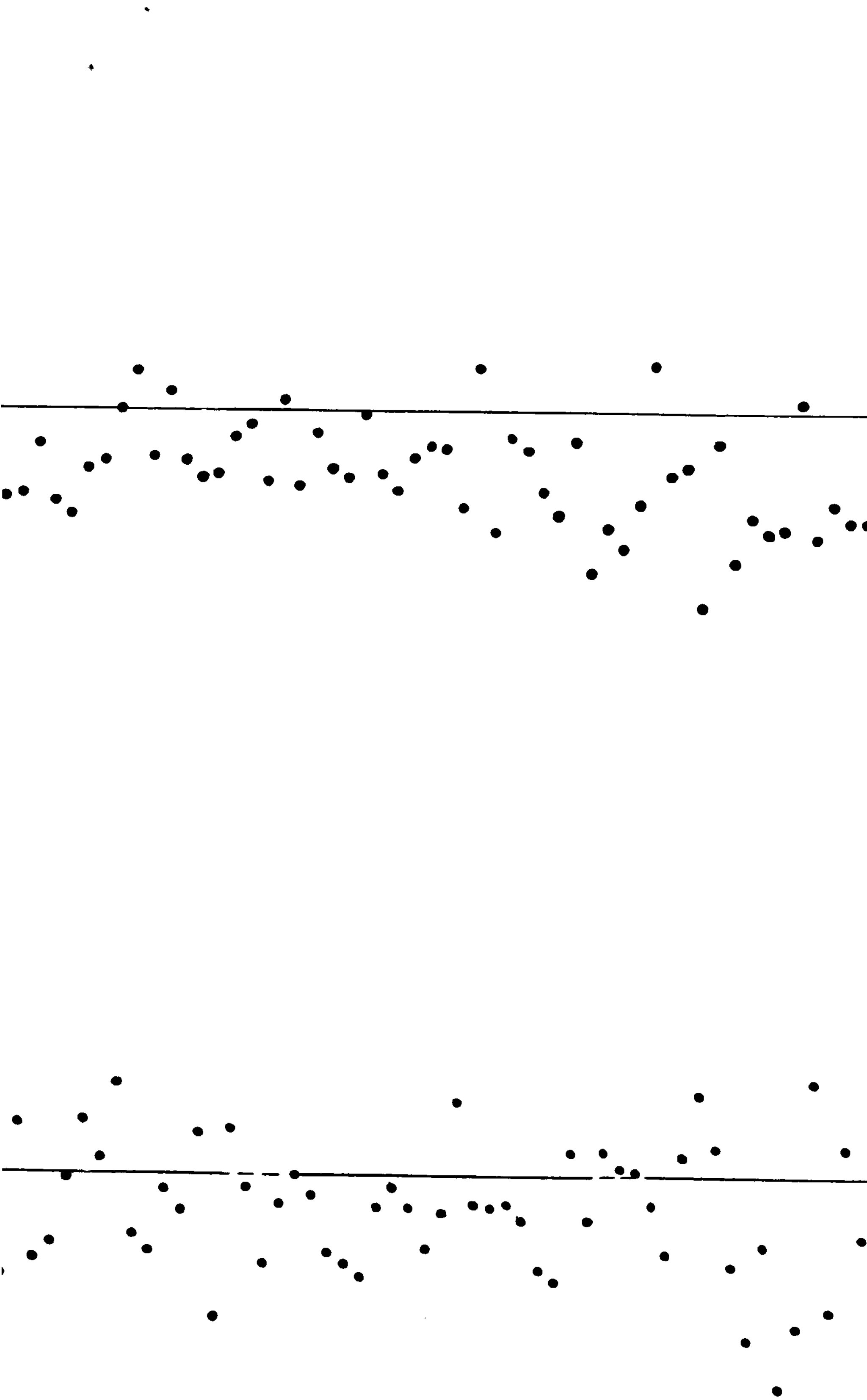
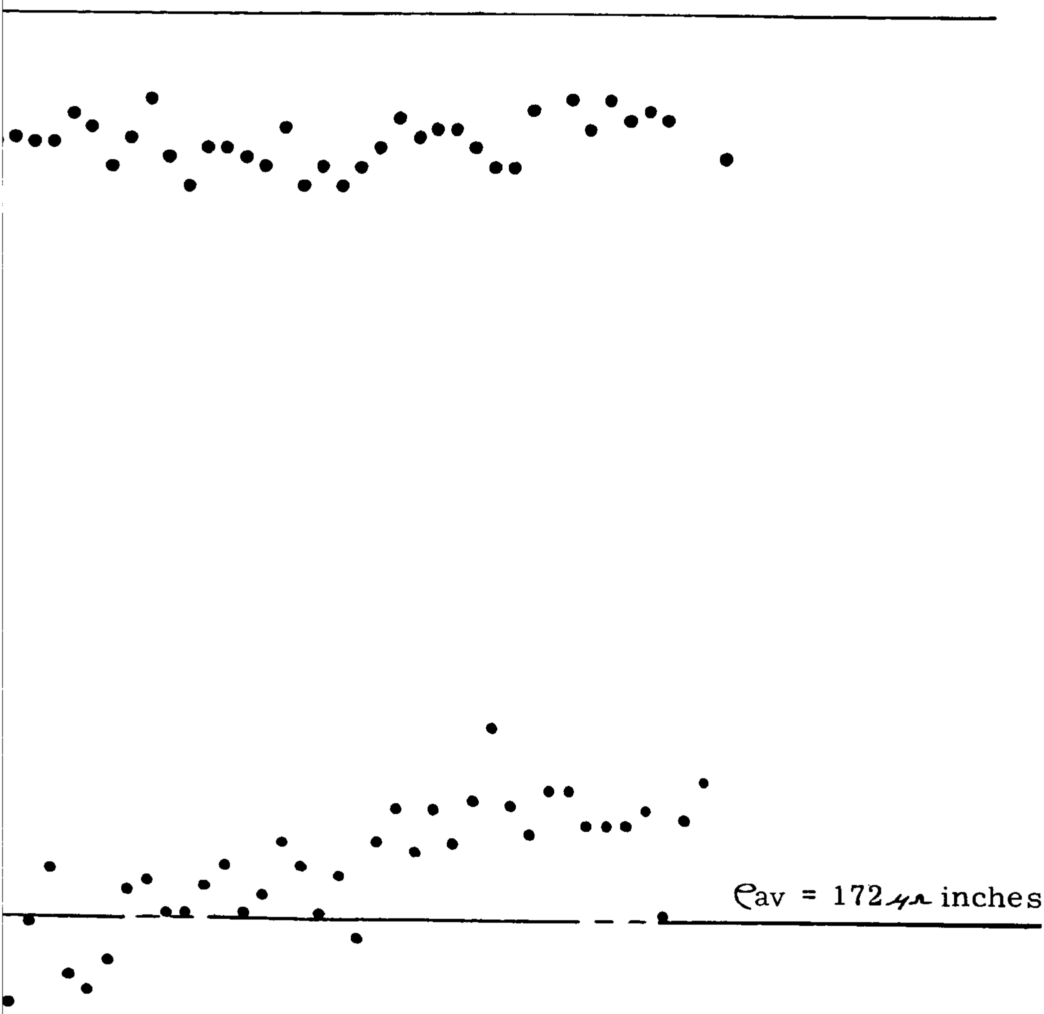


Figure 1. Seebeck Coefficient and Resi



stivity Data for Hot Pressed n-PbTe Thermoelectric Elements


ℓ_{av} = 172 μ inches

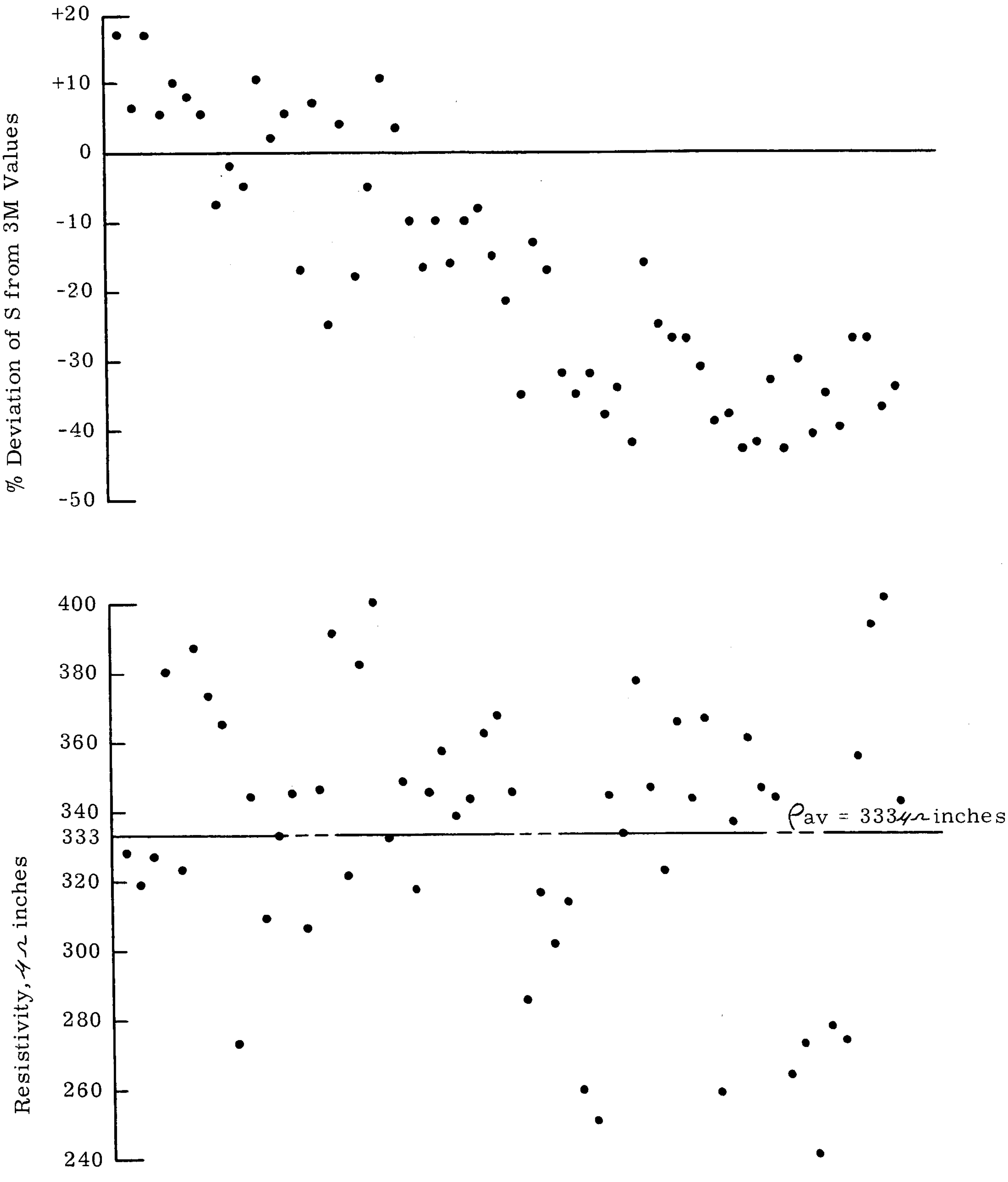


Figure 2. Seebeck Coefficient and Resistivity Data for Hot Pressed TEG-3P, p-PbSnTe Elements Produced at Hittman Associates

C. p-PbTe Element Production

The hot pressing process for p-PbTe was similar to those described above. Pressing parameters were:

Temperature: 1500°F (816°C)

Load: 3000 psi

Time: 5 minutes

As with the other lead telluride materials the Seebeck coefficients and resistivities of our hot pressed elements were below the published 3M values. Figure 3 shows the measured properties of p-PbTe elements produced at Hittman Associates. Seebeck coefficients were consistently within ten percent of the published values but deviations were generally in the negative direction. Resistivities were, with only one exception, below the published value of 170$\mu\Omega$in, and substantially below the reported lot resistivities of 198 and 194$\mu\Omega$in measured by 3M. The difference is undoubtedly due to the much higher density of our hot pressed elements compared to those made by 3M by cold pressing and sintering. Figure 4 shows the porosity observed in a typical 3M TEGS-2P element and the almost fully dense structure achieved at Hittman Associates by hot pressing powder purchased from 3M Company.

D. Thermoelectric Elements Containing Additives

A number of p-PbTe thermoelectric elements containing one-half to two percent of metallic or oxide additives were prepared to study the effects of such dispersants on the strength of p-PbTe. These samples, which are discussed elsewhere in this report, were fabricated by the same process employed for p-PbTe containing no additives.

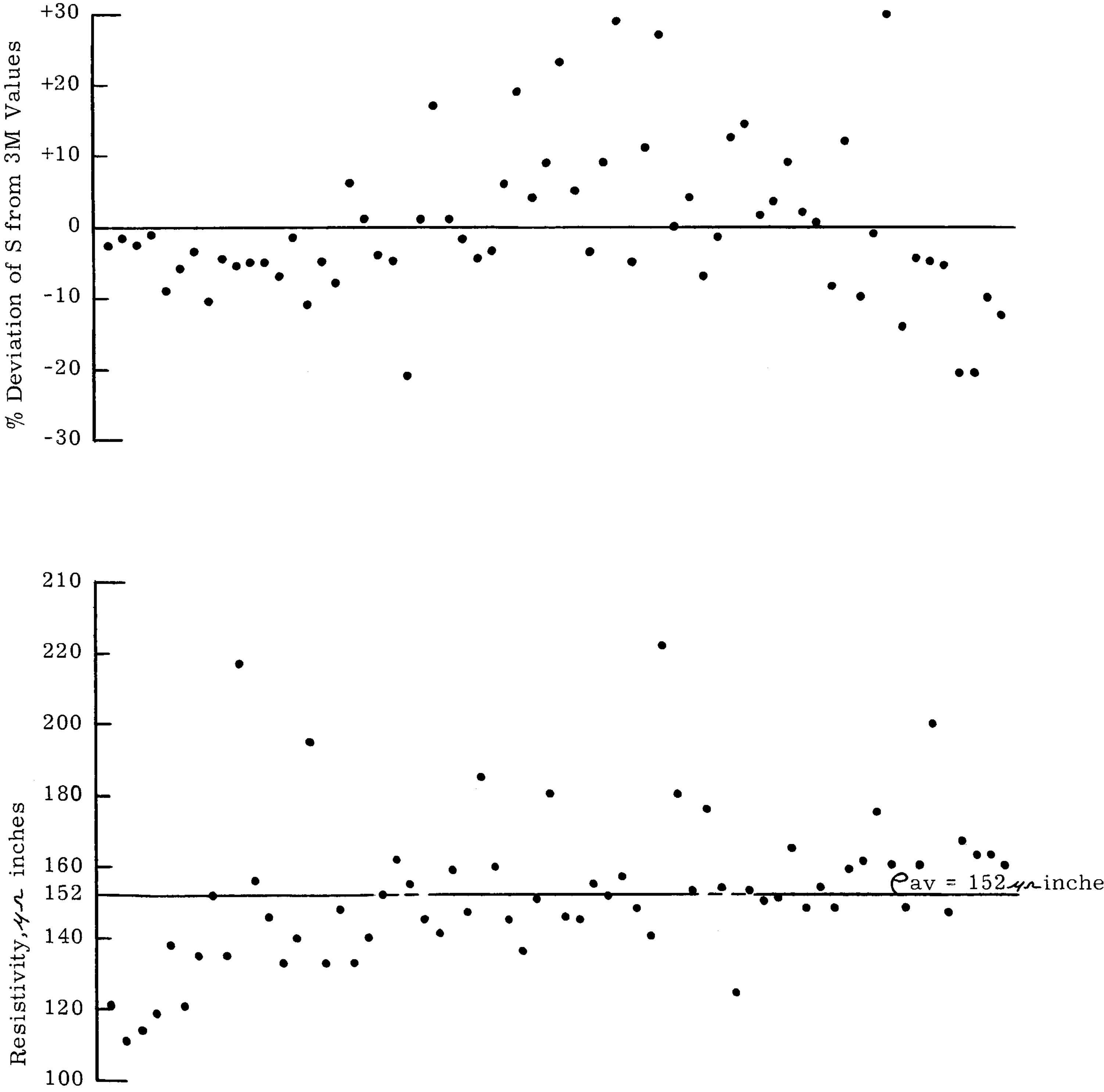
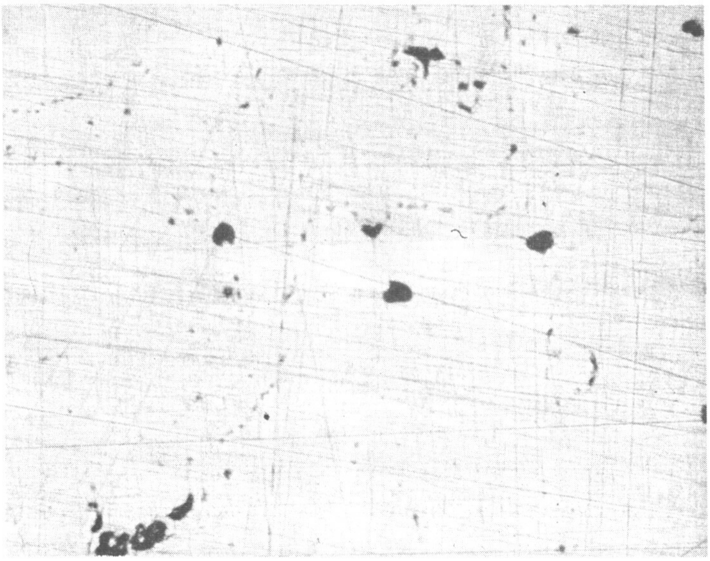
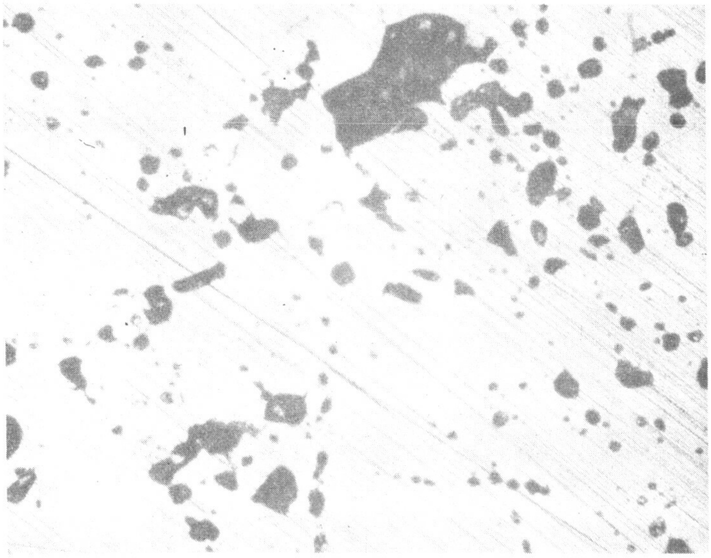


Figure 3. Seebeck Coefficient and Resistivity Data for Hot Pressed TEG-2P, p-PbTe Elements Produced at Hittman Associates



a) TEG-2P Element Hot Pressed at Hittman Associates 130X



b) TEGS-2P Element Cold Pressed and Sintered at 3M 130X

Figure 4. p-PbTe Thermoelectric Elements

IV. BONDING LEAD TELLURIDE THERMOELECTRIC ELEMENTS

As a result of the work performed in Phase I of this program, tin telluride, modified by the addition of one percent by weight of titanium, was selected as the reference braze material for bonding lead telluride to iron electrical contacts or shoes. Satisfactory processes for individually bonding n-PbTe and p-PbTe have been developed.

Initial effort was concentrated on n-PbTe because of the difficulties (discussed in the previous chapter) encountered in preparing satisfactory elements from the p-PbSnTe powder first selected for use in this program. After the change was made to p-PbTe (TEG-2P) from p-PbSnTe a suitable bonding process was achieved.

A. n-PbTe Bonding

Several variations of the bond process developed during Phase I were studied. It was found that slight variations in process parameters did not affect the results. For example, varying the diameter of the braze wafer between 1/4 inch and 3/8 inch had no effect on the appearance or performance of the bond. A similar result was obtained when the peak bonding temperature was varied by plus or minus 30°F from the nominal temperature.

During early runs, the ends of the n-PbTe thermoelements were scored by drawing them across 180 grit paper. It was later found that this step could be omitted without affecting the ultimate bond.

The process currently in use yields satisfactory bonds with high reliability. The tentative specification includes three steps: (1) preparation of the braze, (2) preparation of the element and shoe for bonding, and (3) the bonding operation itself. Each step is described below:

1. Preparation of the Braze Material

The braze alloy consists of SnTe modified by the addition of one percent by weight of titanium metal. The alloy composition is approximately 46.2 w/o Sn - 52.8 w/o Te - 1 w/o Ti. Purity of the starting tin and tellurium is 99.999 while that of the titanium is 99 percent. The braze is prepared in twenty-five gram batches by weighing out the constituents to the nearest 0.01 gram and placing them in a clean vycor tube. The tube is then evacuated and backfilled with dried argon. This evacuation-filling operation is repeated at least ten times and the tube is finally filled with argon at one half atmosphere and sealed. The capsule is placed in a furnace at 1600°F and held for approximately one hour, being agitated periodically to assure alloying. The resultant melt is crushed and sifted through a -200 mesh screen and the powder is reblended to assure homogeneity. Braze wafers, approximately 3/8 inch diameter by 0.01 inch high, are pressed in a steel die at 45,000 psi. The wafers, separated by alundum sand, are sealed in a vycor capsule by a process identical with that described above for the alloy constituents. Sintering is carried out at 1000°F for one hour. The wafers are stored in an argon atmosphere until used.

2. Preparation of the Element and Shoes

The present procedure is identical for preparing elements and shoes. The ends of the element or shoe are ground square in a vee block using 240 grit metallographic paper. The sample is then polished successively through 320, 400, and 600 grit papers and is finished on a billiard cloth polishing wheel with #3 universal diamond paste. The element or shoe is then cleaned with soap and water, rinsed with hot water, dried, wiped thoroughly with acetone twice, rinsed with methanol twice, and dried.

3. Bonding Operation

The cleaned iron shoe, a braze wafer, and the thermoelectric element are placed in a graphite bonding die and this is, in turn, inserted into a stainless steel retaining fixture. Light pressure is applied by means of a spring. This apparatus is shown in Figure 5. The assembled bonding fixture is placed in a vycor tube located in a furnace. The tube is evacuated and then backfilled with argon. A slight argon flow is maintained during bonding. The temperature is raised to 1500°F, held for five minutes, and allowed to cool to 1000 - 1100°F in the furnace. The assembly, still in the vycor tube, is then removed from the furnace and placed in a brick holding chamber in which it cools to about 400°F in thirty minutes. The bonded element may be removed from the fixture at or below this temperature.

B. p-PbTe and p-PbSnTe Bonding

Only a few attempts were made to bond p-PbSnTe elements (TEG-3P). Successful joints could be made by the process employed for n-PbTe but, because of the weakness of the material, fracture usually occurred in the PbSnTe near the interface. This result was not unexpected since the thermal stress analysis in Reference 1 indicated that cracking during bonding was likely in the case of p-PbTe and 3M reports that p-PbSnTe is weaker than p-PbTe.

When the reference p-material was changed to p-PbTe (TEG-2P) the n-PbTe bonding process was again evaluated. Most elements failed by cracking similar to that observed with p-PbSnTe, but some usable samples were obtained. Yield was substantially increased by permitting the bonded elements to slowly cool to room temperature in the bonding furnace. This resulted in a three to four hour cooling cycle and limited production to a maximum of three elements per day.

To further increase yield and to overcome the production limitations of the previous method, the multiple element bonding fixture depicted in Figure 6 was designed and built. The major differences between the this device and that employed for n-PbTe are that up to eight elements are bonded simultaneously and the small compressive load is applied by steel weights rather than by spring loading. Bonding is carried out in an argon atmosphere stainless steel pot furnace.

Sample preparation is identical to that described in the preceeding section. Several time-temperature cycles have been studied and the one which yields the most satisfactory results is as follows. The assembled elements are heated to

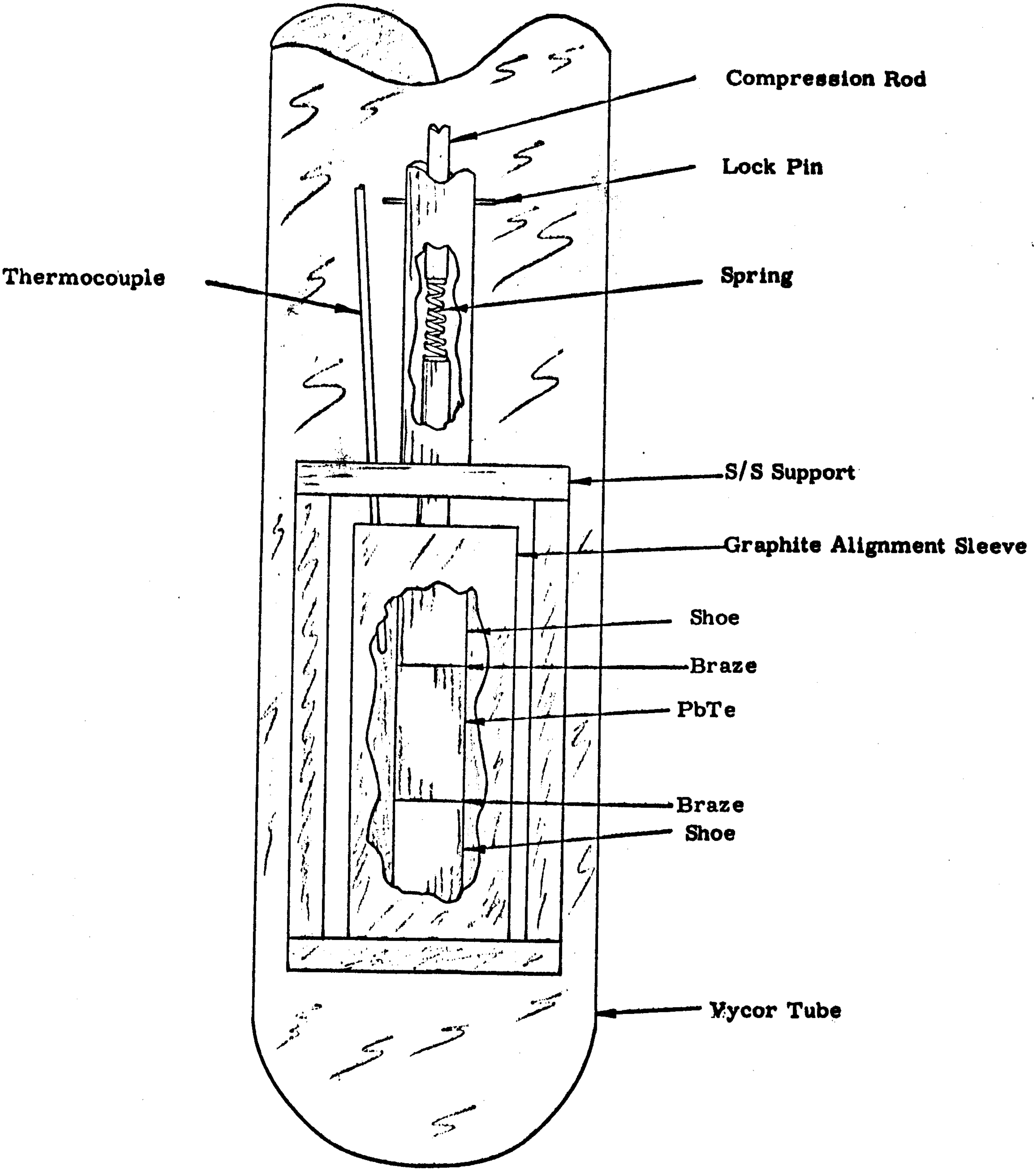


Figure 5. Bonding Fixture for n-PbTe Thermoelectric Elements

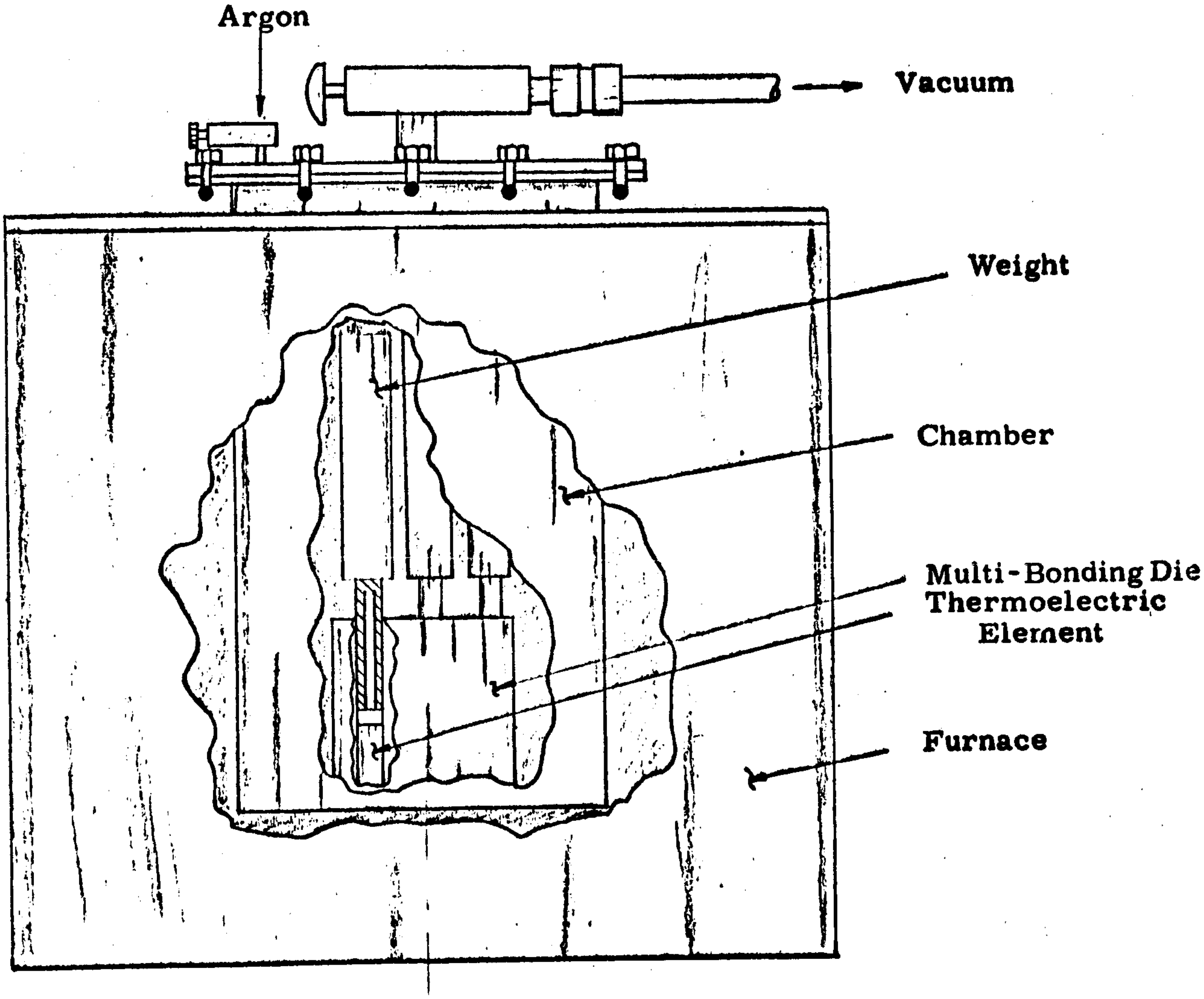


Figure 6. Multiple Element Bonding Fixture

1500°F in about thirty minutes and are held at temperature for three minutes. Furnace power is then cut off and the samples are allowed to cool to 1400°F. The furnace is then restarted and is operated in conjunction with a program controller which cools it at the rate of 50°F per hour. The steel pot is removed from the furnace at 500°F or below and can be opened and the elements removed after the temperature has dropped another 100°F.

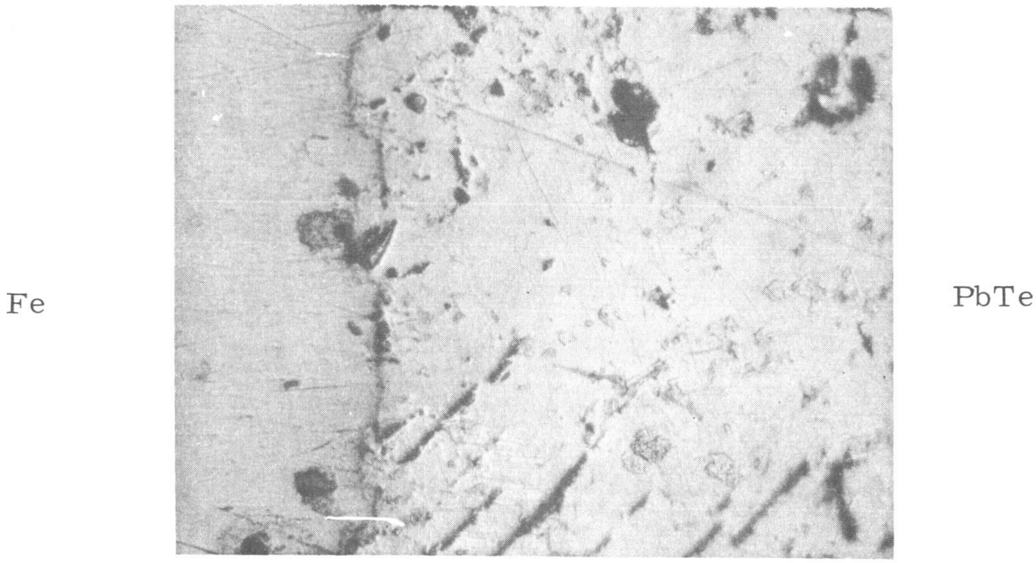
The same process has been used to bond p-PbTe elements containing additives which have been studied as part of this program and are described elsewhere in this report.

Since a program goal is to develop a process by which couples or modules may eventually be produced it will be necessary to bond both p- and n-PbTe to hot shoes simultaneously. Therefore, several n-PbTe elements were bonded in the multi-element fixture and a bonding run in which both p-PbTe and n-PbTe were included was successfully accomplished. Thus, the feasibility of bonding lead telluride to iron shoes with SnTe-Ti braze has been demonstrated for a practical application.

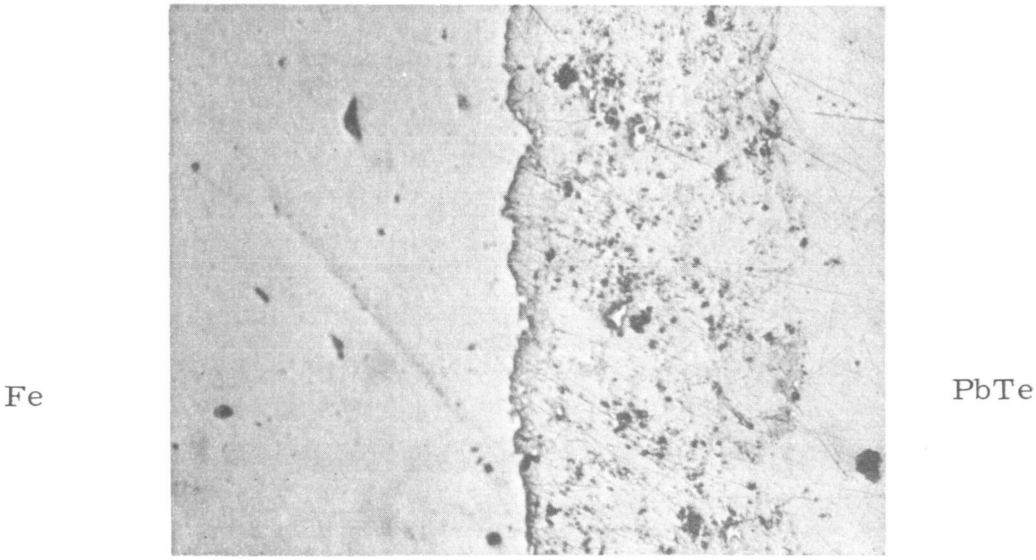
C. Properties of Bonds in Lead Telluride

Approximately 170 bonded lead telluride thermoelectric elements were evaluated during this phase of the work. Typically bonds were sound in appearance. Metallographic examination showed them to be continuous and largely crack free. Typical bond zones are shown in Figure 7.

Table II shows the average bond resistance obtained during this phase of the program. Bond resistance varied from 0 to about 120$\mu\Omega$ in most n-elements with few having resistance of 200$\mu\Omega$ or higher. Most p-PbTe elements had resistances of 240$\mu\Omega$ or less with several at 0 and most of the rest in the 100 to 200$\mu\Omega$ range. Those p-PbTe elements containing molybdenum or tungsten had lower bond resistances averaging 79 and 23$\mu\Omega$ for molybdenum and tungsten additives respectively. The lower values for the elements containing additives are probably not the result of material differences but rather were related to the fact that these elements were bonded late in the program when processing variables were better defined and controlled. p-PbTe elements without additives also showed lower bond resistances during this period. Thus the bond resistances currently being obtained are generally lower than those listed in Table II for elements not containing additives.



a) p-PbTe 260X



b) n-PbTe 260X

Figure 7. Appearance of Bond Zone in Typical p-PbTe and n-PbTe Thermoelectric Elements

Table II

Bond Resistance of PbTe Brazed to Iron Shoes

PbTe Description	Number of Elements	Average Bond Resistance	
		μΩ	μΩcm^2
n-PbTe (TEG-2N)	87	58	41
p-PbTe (TEG-2P)	50	121	86
p-PbTe + 1 w/o Mo	23	79	56
p-PbTe + 1 w/o W	8	23	16

V. EFFECT OF STRESS ON LEAD TELLURIDE

The stress analysis performed during the first phase of this program (see Reference 1) provided information about the significant stresses present in bonded lead telluride thermoelectric elements. It was shown that for a cylindrical shoe the most important stresses arise from the difference in thermal expansion between the two materials.

If the bond is made by brazing, it is apparent that below the brazing temperature the component having the higher coefficient of expansion will be in tension and that the stress level will continually increase as the bond temperature is lowered. Thus, in the normal functioning of a PbTe element bonded to iron contacts the element is in tension and the stresses are most severe at room temperature, relaxing appreciably as the bond is heated back to the operating temperature.

Were the joint between the element and shoe completely rigid the stress would be concentrated at the outer edge of the lead telluride and would inevitably result in fracture. In actuality, deformation and flow in the braze layer results in at least partial relaxation of the stresses. This situation does not lend itself to analytical solutions. However, based on a simplified model that did not consider deformation of the braze, a value of the stress at the bond between lead telluride and iron was calculated and was found to be in excess of 17, 000 psi. This is far greater than the strength of lead telluride and demonstrates that deformation of the braze layer is a requisite to successful bonding.

As part of the first phase a number of torsion tests were performed on p- and n-PbTe elements bonded at each end to iron shoes. Brittle materials, such as lead telluride, characteristically fracture under an applied torque stress in a 45° helical pattern. If the end loads are applied without stress concentration, the location of the initial fracture site should be random along the cylindrical surface. In this case, where the torque load is applied through two bonded shoes, the torsion stress pattern is complicated by being superimposed on the shoe constraint stresses at the bond interfaces caused by the bonding process. Hence, fracture could be expected to initiate in the thermoelement adjacent to the bond.

The n-PbTe elements tested, failed in torsion at 1100 to 1300 psi while p-PbTe failed at 380 ± 200 psi. Further, the expected helical crack was observed in virtually all fractured n-PbTe elements but was not found in the p-PbTe samples. The p-type fractures suggested that prior cracking had occurred during bonding under the action of stresses resulting from thermal expansion mismatch. It was concluded that the stresses caused by bonding were in excess of the strength of p-PbTe but less than the strength of n-PbTe.

Additional tests performed during the current phase of this program confirmed the earlier results. The elements to be tested were bonded to one-half inch diameter iron shoes which had hexagonal nuts machined into one end so that they could be gripped in a torsion tester. The elements were 3/8 inch in diameter. In order to closely duplicate the configuration of the elements we were producing for evaluation by life tests and other techniques, the diameter of each shoe was reduced to the element diameter for a distance of about 1/4 inch along the length. Bonding of n-PbTe elements was performed in the apparatus pictured in Figure 5 by the standard process. p-PbTe elements were bonded in a multiple element fixture similar to that shown in Figure 6, which could accommodate six elements simultaneously. The process was identical to that currently in use for p-PbTe described in the preceeding chapter except that in place of controlled cooling rate the bonded elements were furnace cooled to room temperature. A typical test sample is shown in Figure 8.

The results of these torsion tests are reported in Table III. Fractured n-PbTe elements displayed the expected helical crack while the appearance of the p-PbTe indicated that cracks were present prior to testing. This was confirmed by the fracture stresses which averaged less than one half of those for n-PbTe.

A. Strengthening of p-PbTe

From the foregoing, it is apparent that a technique that would increase the strength of p-PbTe, particularly TEG-2P material, without serious effect on its thermoelectric properties would be highly advantageous. It has been observed earlier (Reference 1) that additions of one weight percent of molybdenum or columbium appears to significantly strengthen p-PbTe. It was not known if this behavior was due to the dispersion strengthening effect often observed when fine particles of a second phase are dispersed in a homogeneous matrix or if the observed strengthening resulted from some interaction between the PbTe and the additive.

Since n-PbTe is sub-stoichiometric with respect to tellurium and p-PbTe is formulated with an excess of tellurium, the additive may strengthen p-PbTe by reacting with the excess tellurium and removing some or all of it from the lattice. If the additive reacts strongly with the tellurium, drastic changes in thermoelectric properties can be expected. It is known that molybdenum (Reference 5) and columbium (Reference 6) form several compounds with tellurium. The bond strength of these compounds relative to that of lead telluride is not known. Since no clear analytical explanation could be found for the observed phenomenon, an exploratory program to study the effect of additives on p-PbTe was undertaken. The additives were chosen to represent two groups, metals that might provide a measure of ductility while reinforcing the brittle PbTe and oxides which would presumably act only as dispersion hardeners and would be less likely to strengthen the thermoelectric material.

The materials chosen for study are listed in Table IV along with the form in which they were incorporated into the p-PbTe powder. Elements were prepared by the usual hot pressing technique with the exception that in each case the additive was blended into the lead telluride powder prior to hot pressing. Additions of 1/2, 1, and 2 weight percent were made with most of the additives. The thermoelectric properties of these samples are shown in Table V except for those of the elements containing molybdenum which are shown in Figure 9. From Table V it is clear that most of the additives had little effect of the as-pressed thermoelectric properties of p-PbTe. Addition of 2 percent columbium resulted in unacceptably high resistivity. The sample containing 1/2 percent Al_2O_3 fibers also had high resistivity but other Al_2O_3 containing thermoelectric elements were satisfactory, so no final conclusion could be drawn. The sample containing 2 percent ThO_2 had unusually high Seebeck coefficient indicating possible poisoning. The properties of the samples containing molybdenum did not differ appreciably from p-PbTe without additives. Resistivity of elements containing 0.001" wire was somewhat higher than those to which the molybdenum was added as powder.

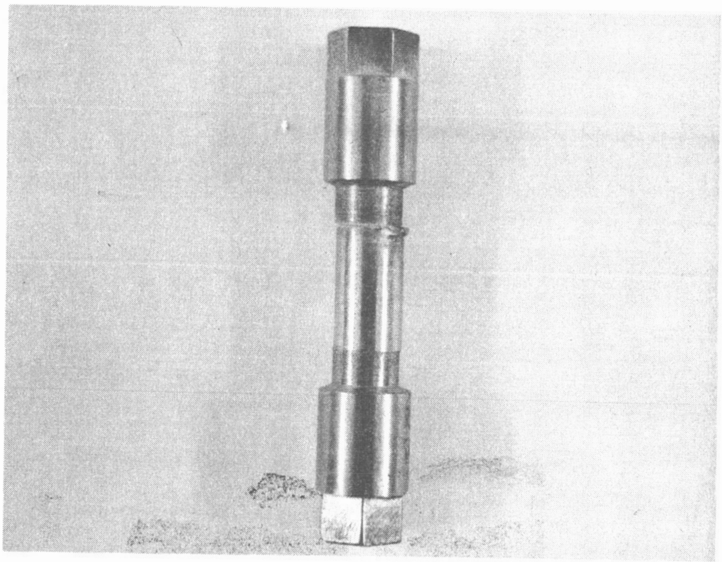


Figure 8. Torsion Test Specimen of PbTe Bonded to Iron Shoes

Table III

Torsion Tests of Lead Telluride Thermoelements - Room Temperature

Material	Torsion Strength, psi	
n-PbTe	1150	
	850	
	1450	
	50	Poor Bond
	1150	
	900	
p-PbTe	400	
	400	
	500	

Table IV

Additives to p-PbTe Studied to Date

Additive	Form	Supplier
Molybdenum	-325 mesh powder - 99.9%	Consolidated Astronautics
Molybdenum	0.001" diameter wire chopped to approx. 1/8" lengths	Sylvania Electric
Tungsten	0.001" diameter wire chopped to approx. 1/8" length	Sylvania Electric
Tungsten	0.0005" diameter wire chopped to approx. 1/8" length	Sylvania Electric
Tungsten	-325 mesh powder - 99.9%	Consolidated Astronautics
Columbium	-325 mesh powder	A. D. Mackay
Al_2O_3	-600 mesh powder	City Chemical Company
Al_2O_3	Levigated alumina	Buehler, Ltd.
Al_2O_3	Sapphire Fibers	Thermokinetic Fibers
ThO_2	Produced by calcining reagent grade $Th(NO_3)_4 \cdot 4H_2O$	J. T. Baker
ZrO_2	Monoclinic Fibers	Owens Corning Fiberglass

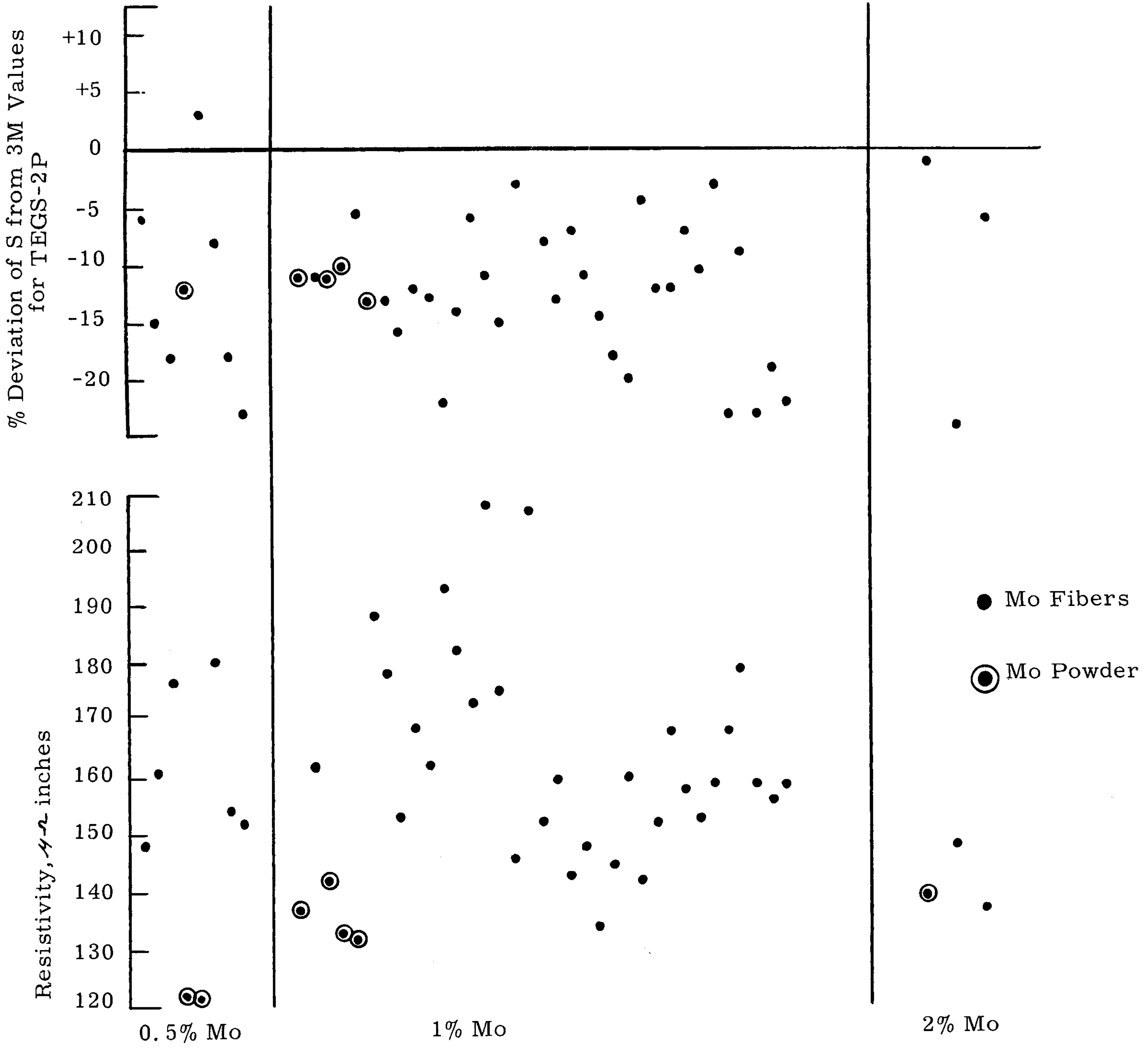


Figure 9. Seebeck and Resistivity of p-PbTe Containing Molybdenum Additives

Table V

Thermoelectric Properties of p-PbTe Containing Additives

Additive	Seebeck Coefficient Data		% Deviation of S From p-PbTe	Room Temperature Electrical Resistivity $\mu\Omega$ in.	Comments
	Temp., °C	S, μv/°C			
1% Cb	90	92	-9.8	140	
	152	135	-6.3		
2% Cb	96	110	+3.6	300	Sample Apparently Cracked or inhomogenious
	157	146	-0.7		
2% Cb	103	95	-10.4	445	
	165	131	-16.0		
2% Cb	88	108	+6.9	488	Sample cracked
	139	151	+11.9		
1/2% W Powder	94	101	-3.8	174	
	140	138	+1.5		
1/2% W Powder	100	104	-4.6	157	
	150	145	+1.4		
1% W Powder	103	106	-4.5	172	
	139	133	+1.5		
2% W Powder	85	108	+8.2	152	
	137	151	+12.7		
2% W Powder	102	109	-0.9	180	
	158	157	+6.1		
1% W Fibers (0.001")	96	92	-13.2	171	
	146	128	-8.6		
1% W Fibers (0.001")	83	84	-14.6	165	
	116	104	-13.4		

Table V (Cont.)

Additive	Seebeck Coefficient Data Temp., ^{o}C	S, $\mu v/^{o}C$	% Deviation of S From p-PbTe	Room Temperature Electrical Resistivity $\mu\Omega$ in.	Comments
1% W Fibers (0.001")	84	83	-15.3	159	
	135	114	-13.7		
1% W Fibers (0.001")	107	95	-16.7	152	
	152	130	-9.7		
1% W Fibers (0.001")	83	82	-16.3	153	
	106	98	-14.0		
1% W Fibers (0.0005")	95	89	-16.1	161	
	154	128	-11.7		
1% W Fibers (0.0005")	108	98	-14.1	159	
	157	142	-3.4		
1% W Fibers (0.0005")	91	94	-8.8	165	
	146	128	-8.6		
1% W Fibers (0.0005")	104	94	-16.1	165	
	154	110	-24.2		
1% W Fibers (0.0005")	105	82	-26.8	151	
	147	125	-10.7		
1/2% Al_2O_3 Powder	93	93	-9.6	140	
	138	125	-7.4		
1% Al_2O_3 Powder	98	99	-8,3	100	
	153	144	0		
2% Al_2O_3 Powder	101	100	-8,2	144	
	157	143	-2,7		
2% Al_2O_3 Powder	96	109	+2,8	204	
	151	149	+4.2		

Table V (Cont.)

Additive	Seebeck Coefficient Data Temp., ^{o}C	S, $\mu v/^{o}C$	% Deviation of S From p-PbTe	Room Temperature Electrical Resistivity $\mu\Omega$ in.	Comments
1/2% Al_2O_3 Fibers	100	102	-7.3	339	Sample apparently cracked
	145	138	-0.7		
1% Al_2O_3 Fibers	97	104	-2.8	134	
	164	156	+2.6		
1/2% ThO_2	73	102	+12.1	141	
	139	135	0		
1/2% ThO_2	89	101	0	154	
	141	135	-0.7		
1% ThO_2	90	91	-10.8	103	Appeared Inhomogeneous
	143	131	-5.1		
2% ThO_2	78	105	+11.7	131	
	135	143	+20.1		
1% ZrO_2 Fibers	106	105	-7.1	135	
	157	152	+3.4		
2% ZrO_2 Fibers	99	107	-0.9	160	
	153	158	+8.9		

Several of the samples containing additives were subjected to a 100 hour isothermal test at approximately 920°F. Each element was sealed in an individual vycor capsule under argon atmosphere. The thermoelectric properties before and after this test are shown in Table VI. There were some changes in the properties of all the elements including the control sample containing no additive. None of the changes were so consistent or severe that any additive could be clearly disqualified from further consideration on the basis of this test.

A number of elements containing additives were bonded to iron shoes and tested in torsion at room temperature. These test results are shown in Table VII. It is clear that molybdenum fibers are particularly effective in strengthening p-PbTe. Al_2O_3, in the form of sapphire fibers, and tungsten may also be effective but further tests will be needed before this can finally be determined.

A number of samples of p-PbTe containing additives were studied metallographically. Sample preparation, particularly in those elements containing oxide inclusions, was extremely difficult. However, it was quite apparent that the lead telluride had reacted extensively with thoria and alumina. Molybdenum and tungsten also react with lead telluride, but apparently to a lesser extent. Figures 10 and 11 are photomicrographs of p-lead telluride with molybdenum and tungsten fibers showing the reaction to be more extensive with the former.

A specimen containing molybdenum fibers dispersed in p-lead telluride was studied by the electron microprobe technique at Goddard Space Flight Center. The reaction zone around the molybdenum fibers was found to be composed of molybdenum and tellurium, the concentration of the latter element being greater than in the lead telluride matrix. No lead was found in this reaction zone. These observations support the hypothesis that the operative strengthening mechanism is removal of excess tellurium in the form of a weakly bound compound from the PbTe lattice so that the lead/tellurium ratio in the matrix approaches that present in n-type material.

Table VI. Effect of 100 Hours at 920°F On The Th

Additive	Seebeck Coefficient Data As Pressed			
	Temperature, °C	S, µV/°C	% Deviation from 3M Data	Tempe
1% Mo fibers	92	89	-14.4	9
	137	123	-8.2	15
1% Mo powder	100	95	-12.8	8
	160	140	-2.8	14
2% Mo powder	96	110	+3.8	10
	154	138	-4.8	16
1% W powder	103	106	-4.5	9
	139	133	-1.5	15
2% W powder	102	109	-0.9	9
	158	157	+6.1	15
1% Al_2O_3 fibers	97	104	-2.8	8
	164	156	+2.6	14
1% Al_2O_3 powder	98	99	-8.3	9
	153	144	0	14
2% Al_2O_3 powder	101	100	-8.2	9
	157	143	-2.7	15
1% ZrO_2 fibers	106	105	-7.1	9
	157	152	+3.4	15
1% ThO_2	90	91	-10.8	9
	143	131	-5.1	15
2% ThO_2	78	105	+11.7	9
	135	143	+20.1	14
p-PbTe	96	101	-4.7	10
	148	139	-1.4	14

ermoelectric Properties p-PbTe Containing Additives

	Seebeck Coefficient Data After 100 Hour Test		Room Temp. Resistivity $\mu \Omega$ in.	
rature, °C	S, μV/°C	% Deviation from 3M Data	As Pressed	After 100 Hr. Test
9	90	-16.7	162	146
7	130	-11.6		
9	96	-4.9	137	161
6	142	+1.4		
0	93	-14.7	139	106
1	134	-10.7		
9	137	+26.8	172	170
2	185	+28.5		
2	106	+1.9	180	157
0	155	+9.2		
7	114	+14.0	134	182
5	159	+14.4		
7	119	+11.2	100	181
9	171	+20.2		
2	104	0	144	188
2	154	+7.6		
7	114	+5.5	135	196
1	157	+9.8		
4	113	+7.6	103	264
0	159	+12.0		
5	117	+10.4	131	171
3	158	+12.1		
1	125	+13.6	134	171
7	152	+8.6		

Table VII

Effects of Additives On The Torsion Strength of p-PbTe

Additive	Torsion Strength, psi	Remarks
1/2% Mo fibers	850	Helical fracture
1/2% Mo fibers	750	Sample corroded during bonding
1% Mo fibers	1100	Helical fracture
1% Mo fibers	850	Helical fracture in center of element
2% Mo fibers	1250	Helical fracture
1/2% Mo powder	300	Sample corroded during bonding, crack present prior to test
1/2% Mo powder	400	Sample broke into several pieces
2% Mo powder	850	Broke in element adjacent to bond
2% Mo powder	625	Oxidation on fracture surface indicating cracks prior to test
1% W fibers	750	Helical fracture in center of element
1% W fibers	750	Helical fracture near bond
1/2% W powder	550	Crack initiated at corrosion Typical p-PbTe fracture
1/2% Al_2O_3 fibers	850	Helical fracture; many chips fell out
1% Al_2O_3 fibers	400	Broke in braze
1% Al_2O_3 powder	300	Broke in element near interface
2% Al_2O_3 powder	300	Broke in braze
1% ZrO_2 fibers	300	Broke in element
1% ThO_2	250	Broke in element near interface
2% ThO_2	400	Separated at interface; element cracked
p-PbTe no additive	400	All samples failed in a manner typical of previous p-PbTe elements tested
p-PbTe no additive	400	
p-PbTe no additive	500	

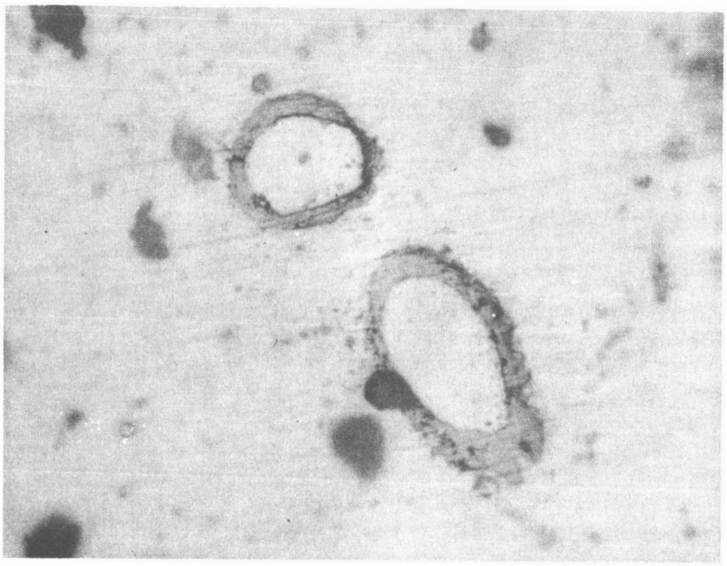


Figure 10. p-PbTe Thermoelement Containing 1 w/o Molybdenum Fibers (520X)

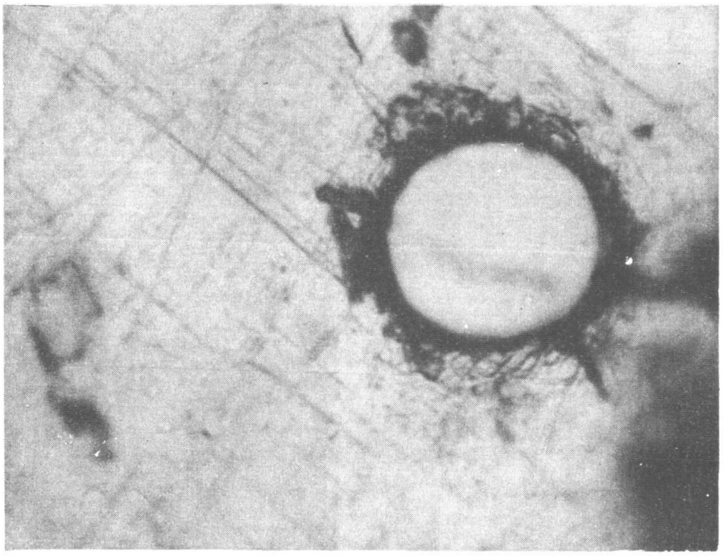


Figure 11. p-PbTe Thermoelement Containing 1 w/o Tungsten Fibers (1040X)

VI. LIFE TESTING OF LEAD TELLURIDE ELEMENTS

In order to pursue our objectives of obtaining a better understanding of lead telluride to shoe joints, it was necessary to conduct life tests of thermoelectric elements under controlled conditions similar to those that might be encountered in operating space systems. Most life tests are performed on couples or modules since power output of a system as a function of time is the parameter of primary interest to most investigators. Since we desired to isolate the effects to the extent possible our test program was based on measurements of individual elements.

A. Life Test Equipment

The major requirements of the test system are as follows:

1. Individual PbTe thermoelectric elements, rather than couples or modules are tested.
2. Parameters measured include:
    a. Hot junction temperature
    b. Cold junction temperature
    c. Open circuit voltage
    d. Element resistance
    e. Power output
3. All measurements are made remotely without disturbing the element on test
4. All tests are carried out under inert atmosphere (argon)
5. Isolation is provided for groups of specimens
6. Provision is made for replacement of failed or degraded elements with minimum disruption of testing
7. Materials of construction were chosen so as to assure no contamination of the thermoelectric elements

The device that resulted from these requirements consists of four individual water cooled chambers, each capable of holding six thermoelectric elements. Each chamber, one of which is pictured in Figure 12, has its own water and argon supply, an individually controlled heater block, and a low resistance junction box immediately adjacent. The hot shoe of each element under test is grounded to the aluminum chamber and the cold shoe is connected to a terminal at the junction box. The open circuit voltage is measured with a portable potentiometer between each junction box terminal and the chamber. Resistance is measured by placing a calibrated resistor in series with each element and precisely measuring the voltage drop across this resistor From this current, internal resistance and matched load power output can be calculated.

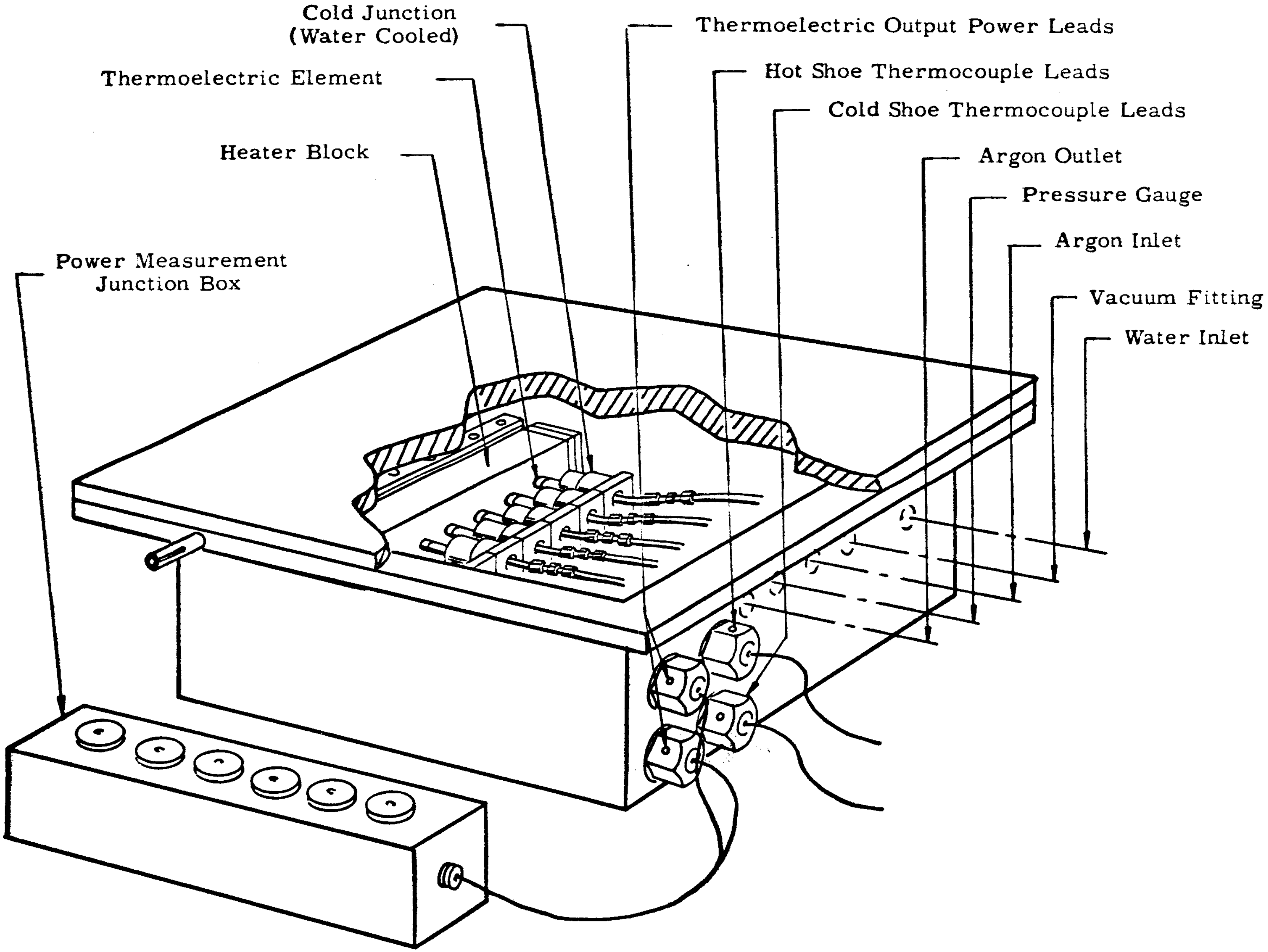


Figure 12

Thermoelectric Test Unit

Thermocouples at the hot and cold junction of each thermoelectric element are connected to one of four patch panels at the control console pictured in Figure 13. At this point each temperature can be read with a millivolt potentiometer or can be recorded on the twelve point Honeywell recorder mounted at the upper left section of the console.

The console also contains the heater block temperature controllers. An extra thermocouple is installed in each heater block. This thermocouple can be connected to the controller by switching leads at a console patch board. Thus, it is not necessary to open the inert atmosphere test chambers in the event of a thermocouple failure. The control system also contains flow switches in series with the heater power supply. These serve to cut off power should cooling water flow be lost and thereby prevent overheating of the system.

Several tests of thermoelectric elements have been completed and three others are now in progress and will be continued through the next phase of this program. Most elements tested were 3/8 inch diameter TEG-2N or TEG-2P made at Hittman Associates from powders purchased from 3M Company. Several of the p-PbTe elements contained molybdenum additives for increased strength. A few elements purchased from 3M Company were included as controls.

The hot shoe bonds were formed by the SnTe-Ti brazing processes described earlier in this report. Most cold shoes were joined at the same time by these same processes. The cold shoes of some early elements were tin soldered into place after the hot end joint was made. Several unbonded control elements were also included in these tests.

A typical element, ready for installation in the life tester, is picutred in Figure 14. The long extension on the hot shoe passes through a hole in the heater block and allows connections to a copper conductor wire to be made at some distance from the thermoelectric material.

B. Tests of n-PbTe Thermoelectric Elements

Four tests of n-PbTe elements have been completed to date and a fifth has passed 4000 hours and is continuing. The first test was a ninety-six hour shakedown run for the tester. Three n-PbTe elements were placed in the unit under an argon atmosphere. Hot shoe temperatures ranged from 957° to 1006°F. A greater variation, 183° to 300°F was found in the cold shoes. Measurements made during operation indicated no changes in thermoelectric properties. Upon removal from the tester, it was found that one hot shoe bond and one cold shoe bond (on different elements) had separated. The hot shoe on the one intact element separated during handling after removal. All the shoes we were badly tarnished. Post-test measurements showed little change in resistivity, but Seebeck coefficient dropped sharply in two of the three elements. Examination of the test chamber indicated that oil from the bubbler at the argon outlet was present. This could have caused to observed degradation. Subsequently, the outlet values were replaced with a new type that permits gas flow only in one direction.

The principal objective of the other tests was to obtain operating data on thermoelectric elements. These tests included a 500 hour run of six elements,

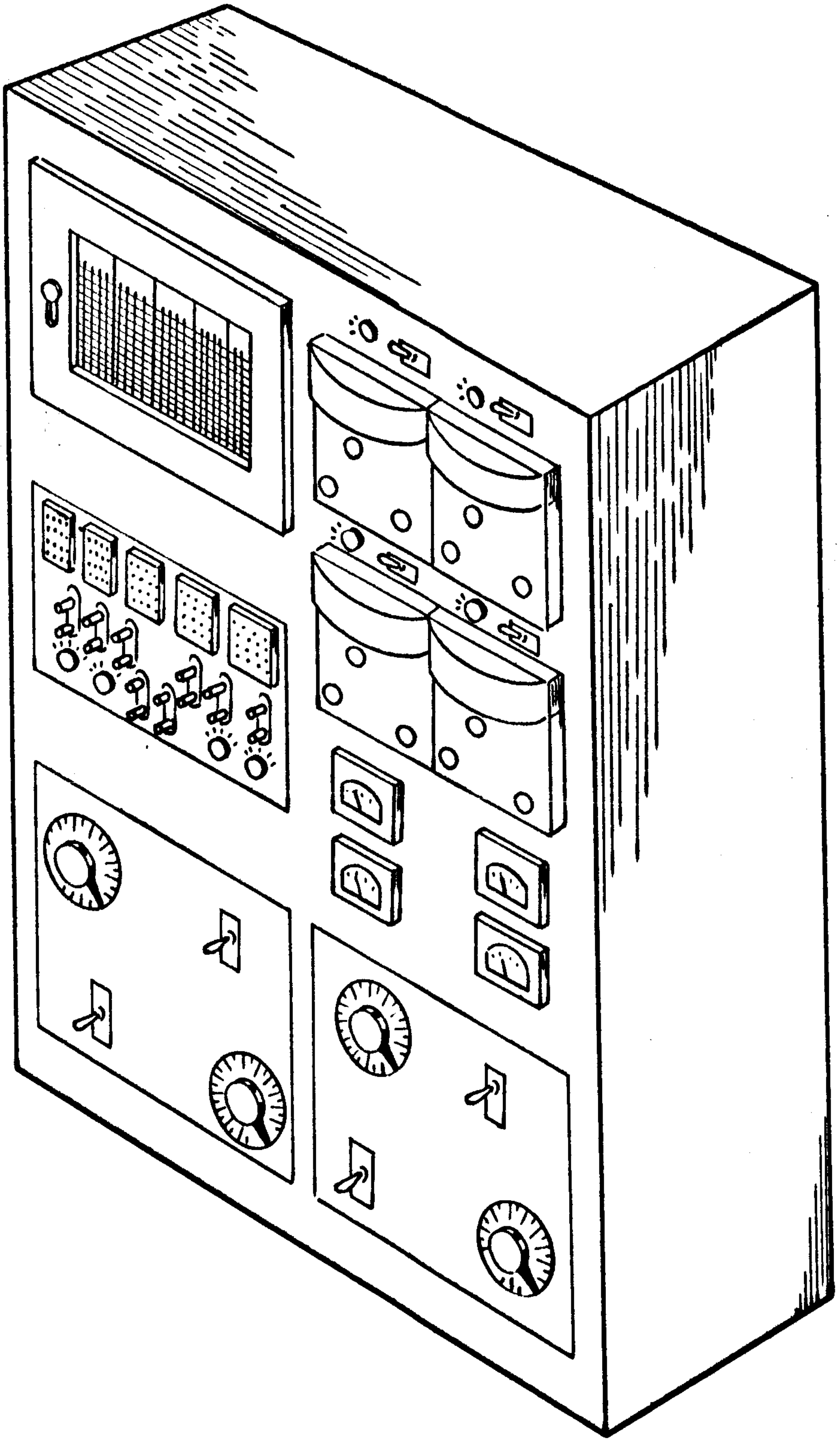


Figure 13

Thermoelectric Element Tester Control Console

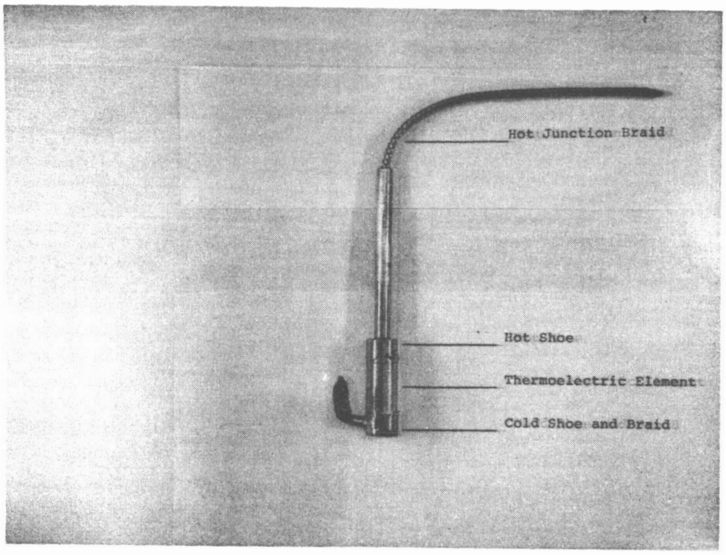


Figure 14

Lead Telluride Thermoelectric Element for Use in Life Test Apparatus a 200 hour run of five elements and a 1000 hour run of three elements. Each will be discussed in turn.

The 500 hour test ran smoothly with no intermediate shutdowns. Hot junction temperatures ranged from 890° to 970°F depending on the position of the element along the heater block. Figures 15 through 20 record the performance of these elements during the test. A gradual increase in ΔT, due both to increases in T_h and decreases in T_c, was observed over the first 200 to 300 hours and resulted in increases of voltage and power. These changes are ascribed to improved thermal contact between the elements and heaters and chill blocks. No degradation was apparent in any of the test elements. The measured power output of these samples was rather low and was due to higher than expected internal resistance in the tester which resulted in operation far off matched load conditions. The internal wiring was changed and the technique for measuring power output was modified to yield matched-load power subsequent to this and the 200 hour test following.

Post test measurements of electrical resistivity and Seebeck coefficient confirmed the absence of significant changes in these parameters. The resistivity data are reported in Table VIII and the Seebeck coefficient data in Figure 21. All the hot shoe bonds were strong and none broke during removal from the tester. Four cold shoe bonds did separate upon removal. However, these were tin brazed joints and may have been exposed to temperatures in excess of their operating limit.

Metallographic examination indicated that cracks were present at or near the bond interface in several elements. No extensive diffusion was observed. Typical good and cracked bond areas are shown in Figures 22a and 22b respectively. These samples were mounted for examination by the conventional heat and pressure technique and it is believed that the mounting operation was responsible for the cracking. Subsequent to this and the 200 hour test discussed next elements were prepared by the cold mount process and no cracking was observed.

One of the metallographic mounts from this test was examined by the electron microprobe technique by L. Kobren of Goddard Space Flight Center. Figures 23 and 24 are pictorial representations of the results of this study. The light and dark areas are an electron backscatter picture of the bond zone in the thermoelectric element. Areas containing high atomic weight atoms, as those in PbTe, appear white in the picture and low atomic weight areas, such as iron, are black. The braze zone is seen to be of intermediate weight. The grid spacing on these photographs is 40 microns (approximately 1.6 mils). The sample was bombarded with electrons along the horizontal path shown as a white line toward the center of each picture. This bombardment results in the generation of x-rays characteristic of the individual elements contained in the area being bombarded, the intensity of each x-ray being proportional to the concentration of the element from which it is generated. Thus, Figure 23 shows the distribution of iron, lead and tin in the bond area after 500 hours of operation and Figure 24 repeats the iron traverse and shows tellurium and titanium distributions under the same conditions. The various traverses are displaced vertically for clarity of presentation. The observations made from these data were:

1. There is no diffusion of any component of the braze or thermoelement into the iron shoe.

2. Iron is present in the braze zone for a distance of at least 20 microns (approximately 0.8 mils) and is distributed inhomogeneously. No iron is found in the PbTe.

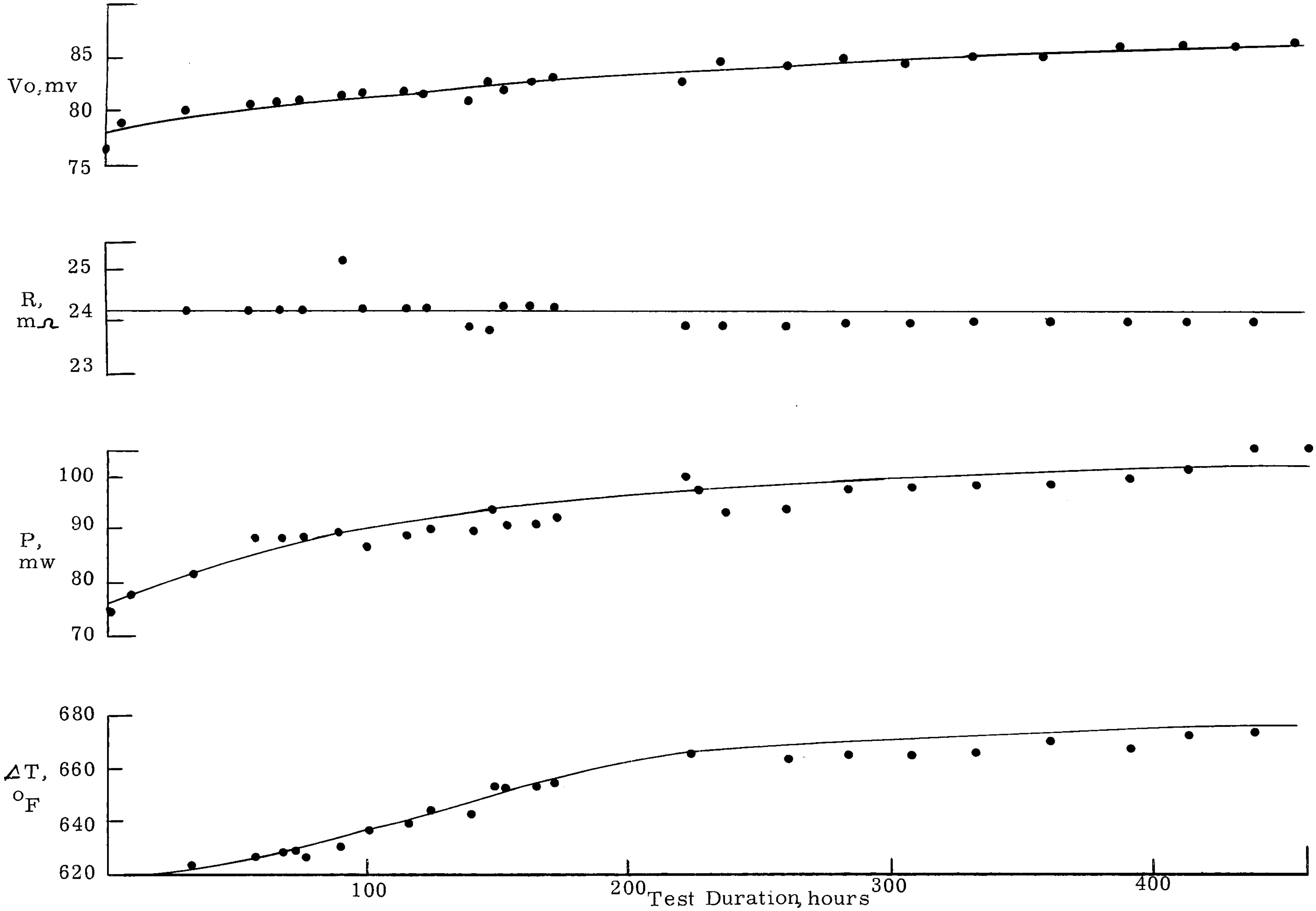


Figure 15. Performance of PbTe Element No. 176 During 500 Hour Test (n- type)

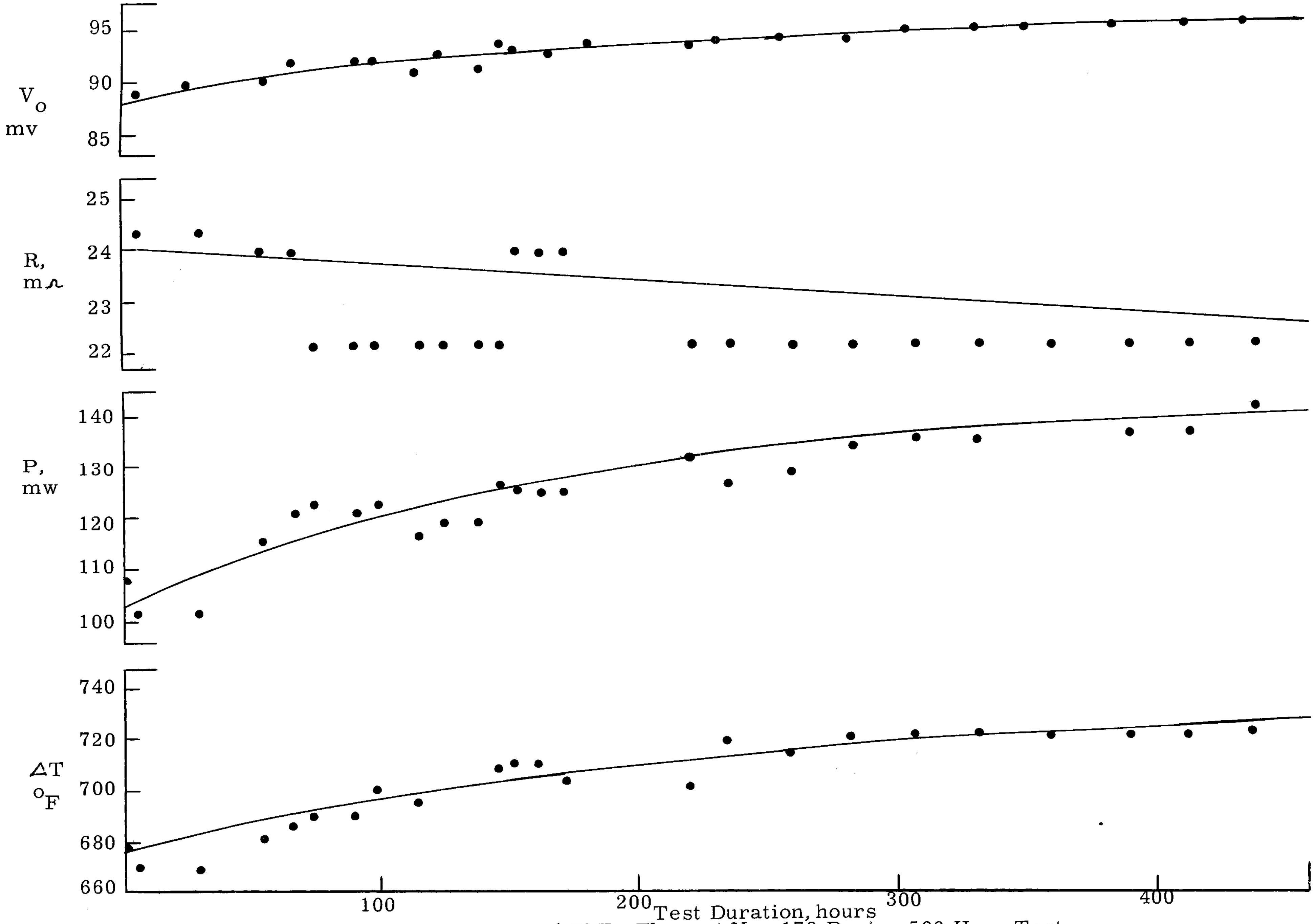


Figure 16. Performance of PbTe Element No. 178 During 500 Hour Test
(n- type)

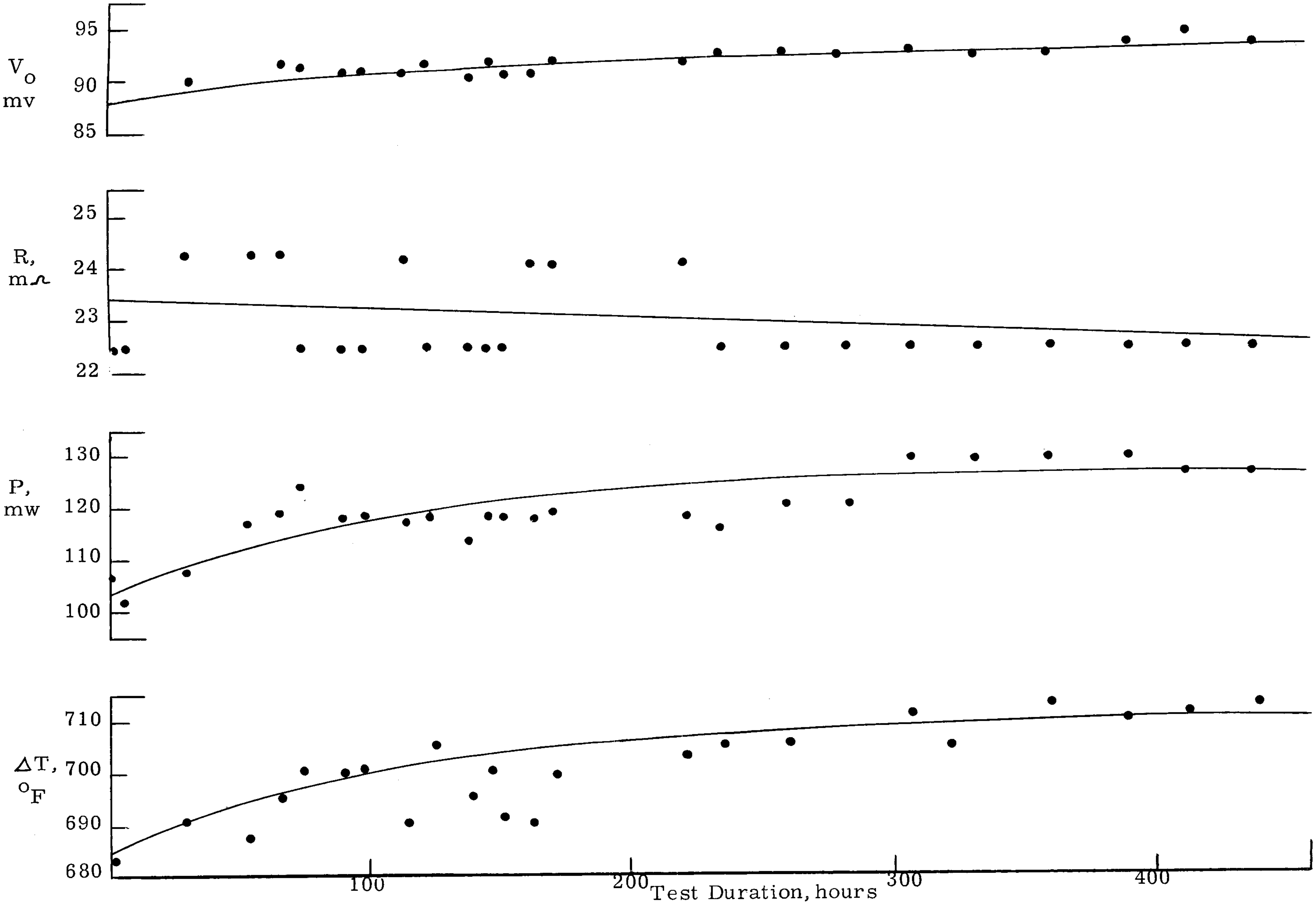


Figure 17. Performance of PbTe Element No. 167 During 500 Hour Test
(n- type)

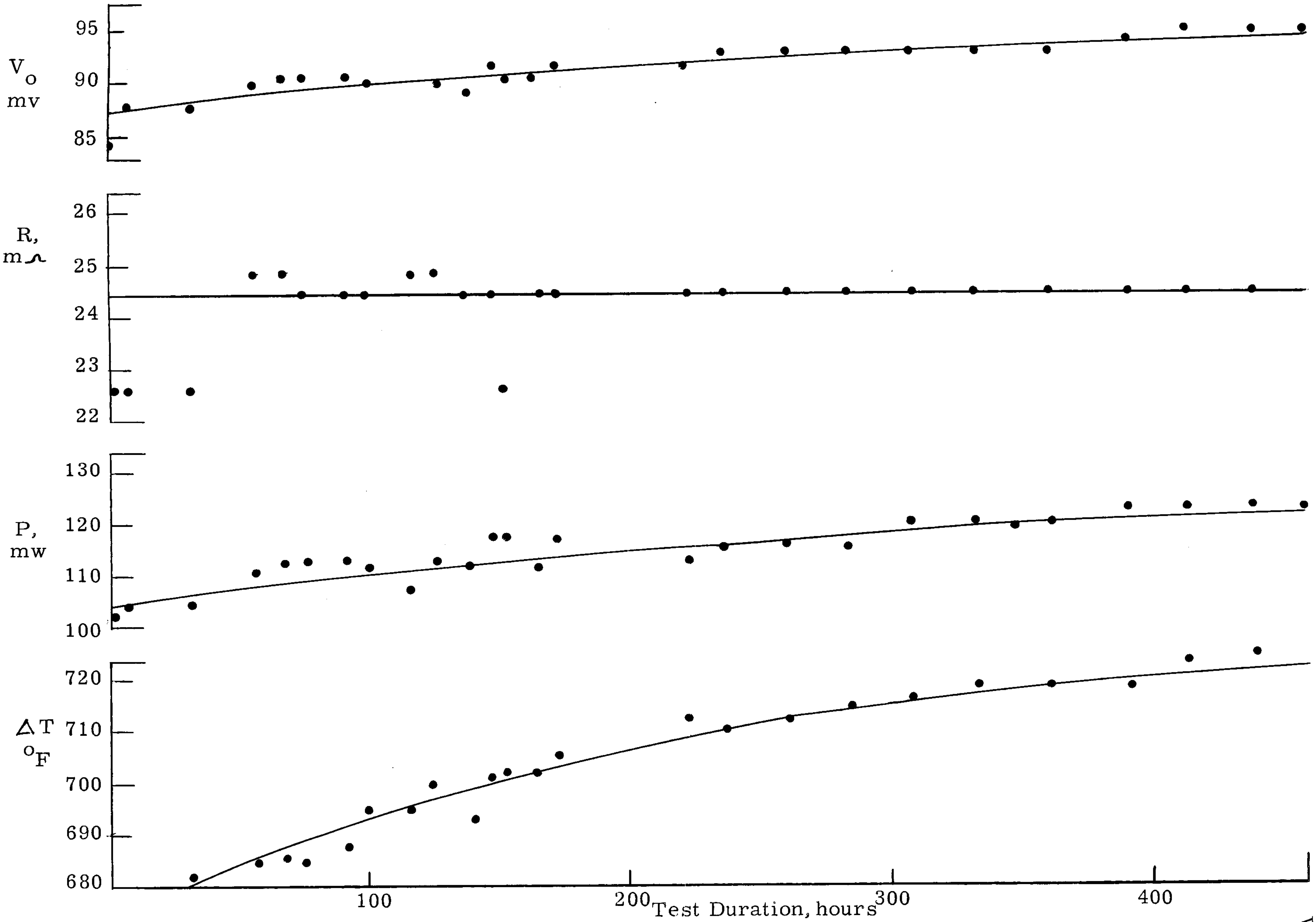


Figure 18. Performance of PbTe Element No. 169 During 500 Hour Test
(n- type)

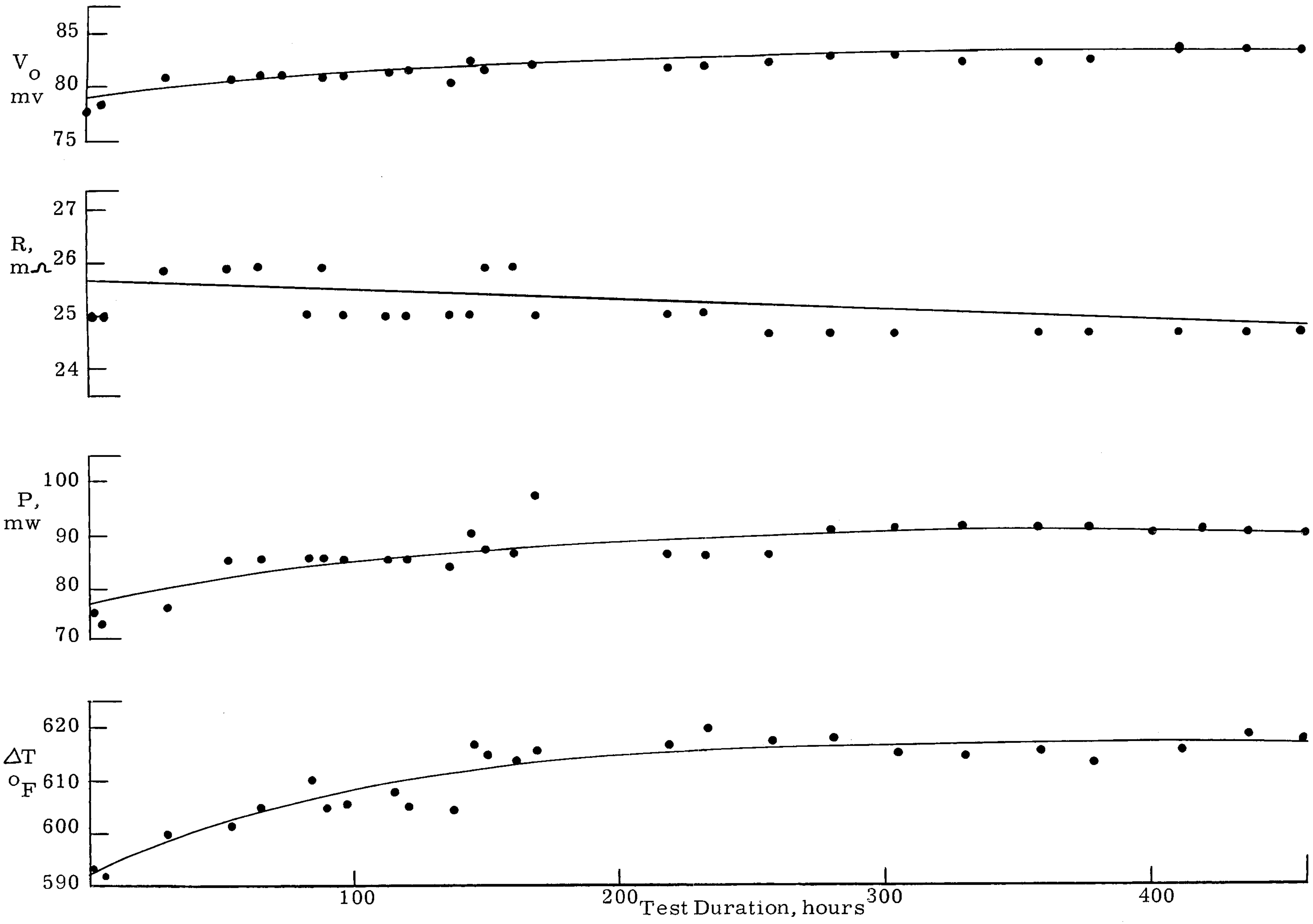


Figure 19. Performance of PbTe Element No. 171 During 500 Hour Test
(n- type)

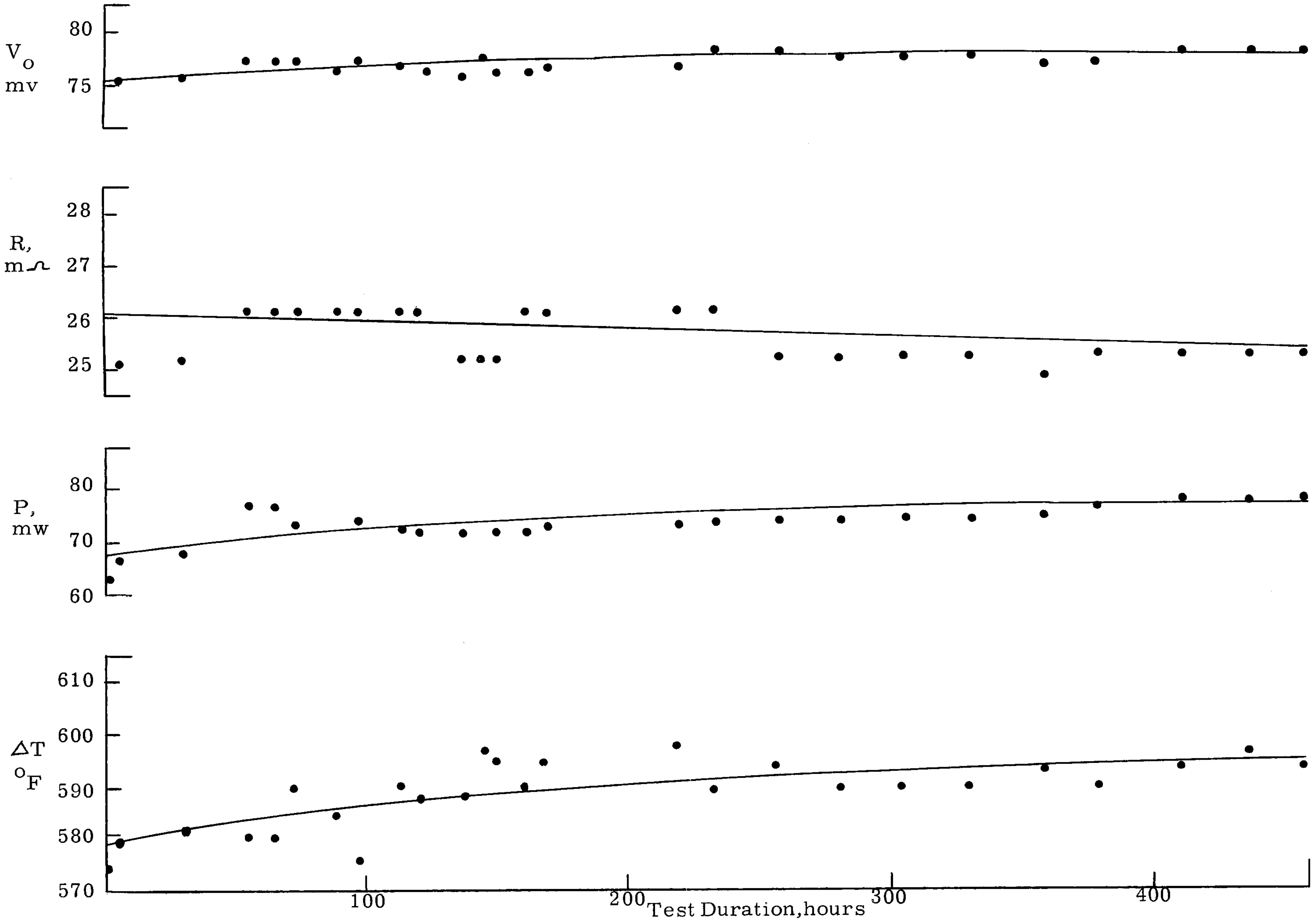
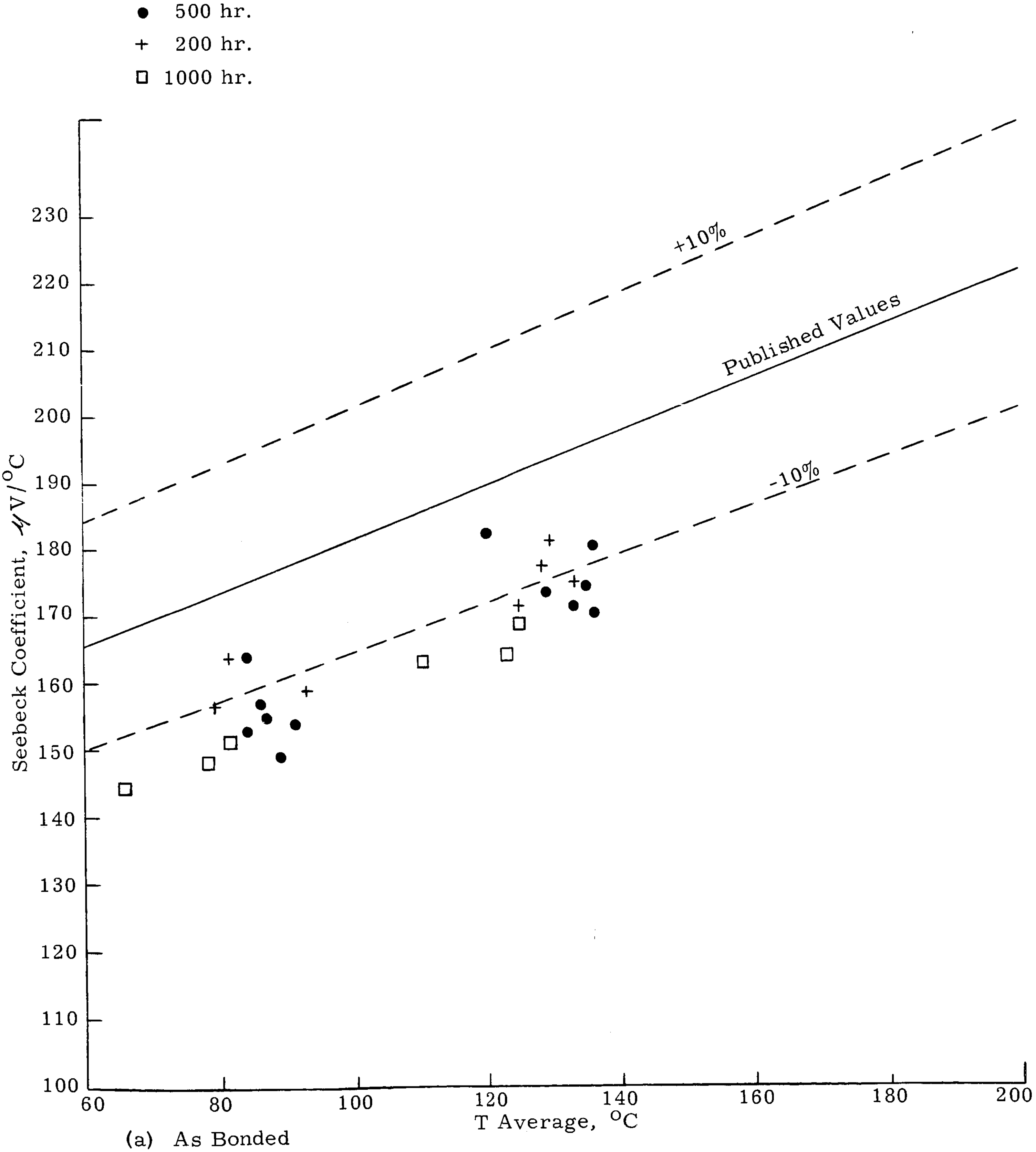


Figure 20. Performance of PbTe Element No. 173 During 500 Hour Test
(n- type)

Table VIII

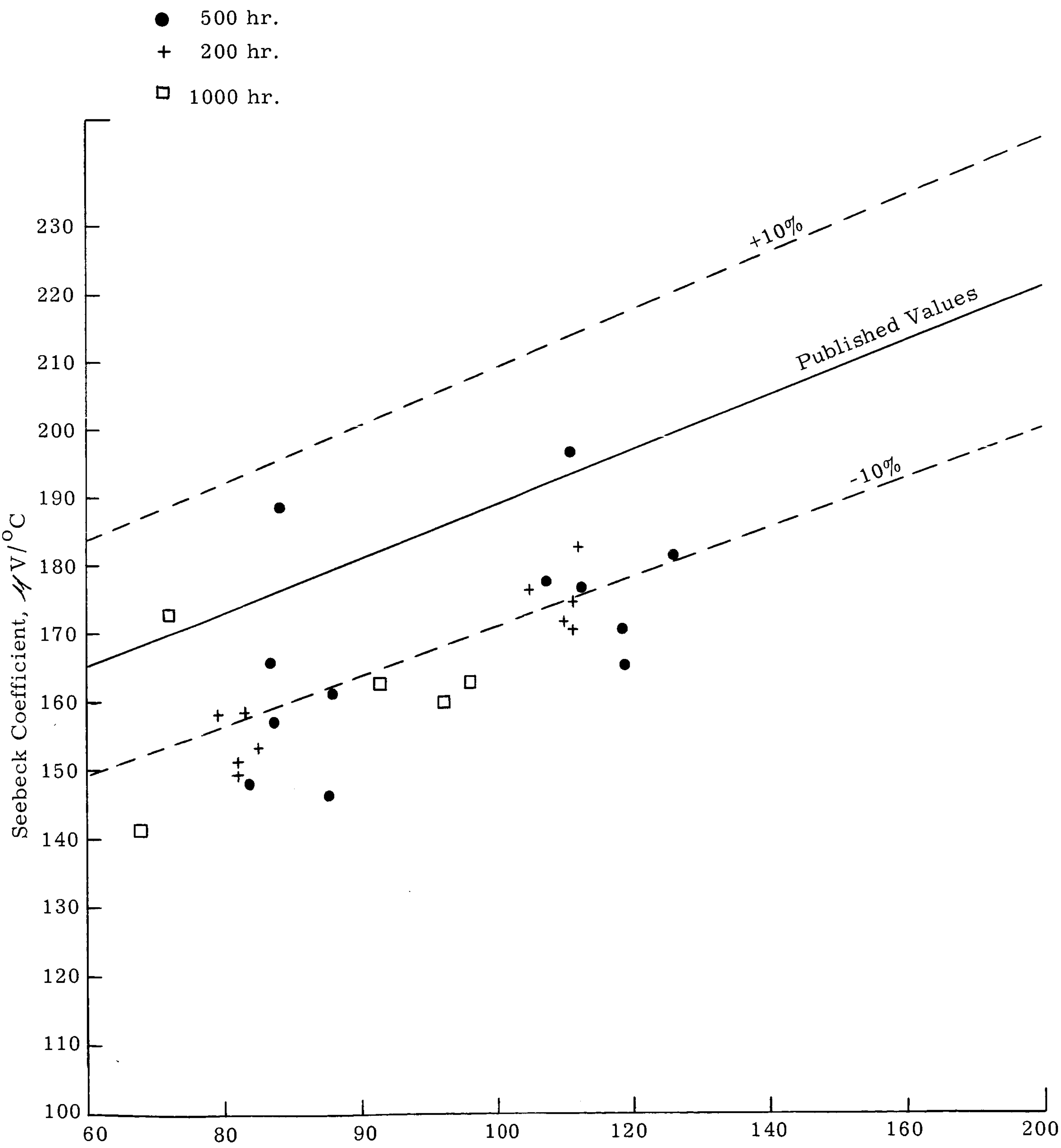
Effect of 200, 500, and 1000 Hour Life Tests on Electrical Resistivity of n-PbTe

Sample No.	Test Time Hr.	Hot Shoe Bond Resistance, $\mu\Omega$		PbTe Electrical Resistivity		% Change
		Before Test	After Test	Before Test $\mu\Omega$ in.	After Test $\mu\Omega$ in.	
167	500	75	0	169	166	-1.8
169	500	0	60	175	182	+4.0
171	500	0	0	179	197	+10.1
173	500	0	195	176	170	-3.4
176	500	38	50	180	190	+5.6
178	500	80	40	171	176	+2.9
Average				175	180	+2.9
179	200	110	190	177	178	+0.6
183	200	120	Broke	167	174	+4.2
180	200	290	260	181	174	-3.9
182	200	50	60	173	171	-1.2
184	200	110	65	170	176	+3.5
Average				174	175	+0.6
213	1000	0	70	180	187	+3.9
222	1000	55	80	172	172	0
3M#1	1000	90	40	183	188	+2.7
Average				178	182	+2.2



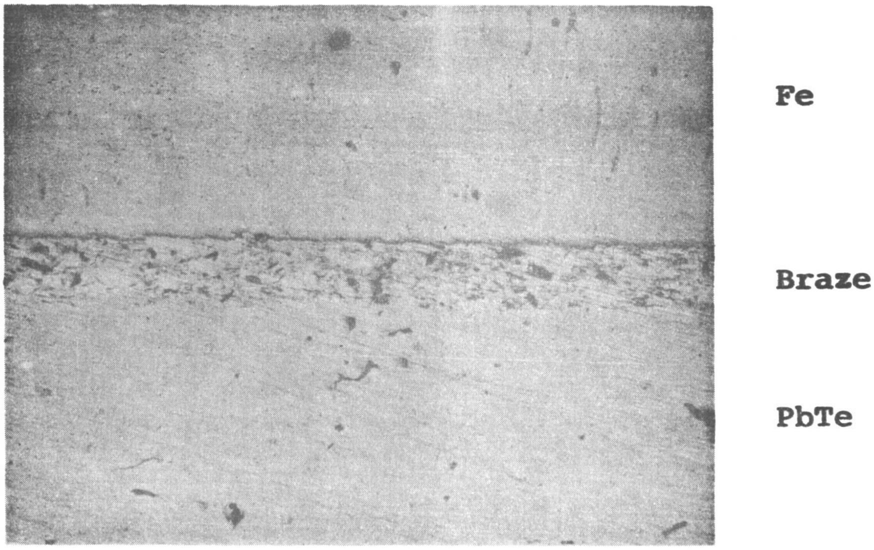
(a) As Bonded

Figure 21. Effect of the 200, 500 and 1000 Hour Life Tests on the Seebeck Coefficient of Bonded n-PbTe

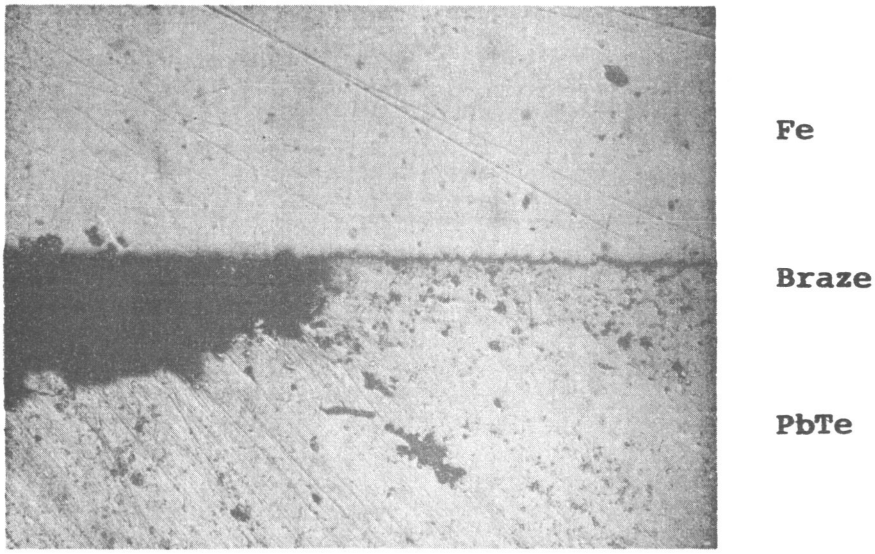


(b) After Life Test

Figure 21. Continued



a) Typical Good Bond 130X



b) Poor Bond Area 130X

Figure 22. Bond Areas After 500 Hour Life Test

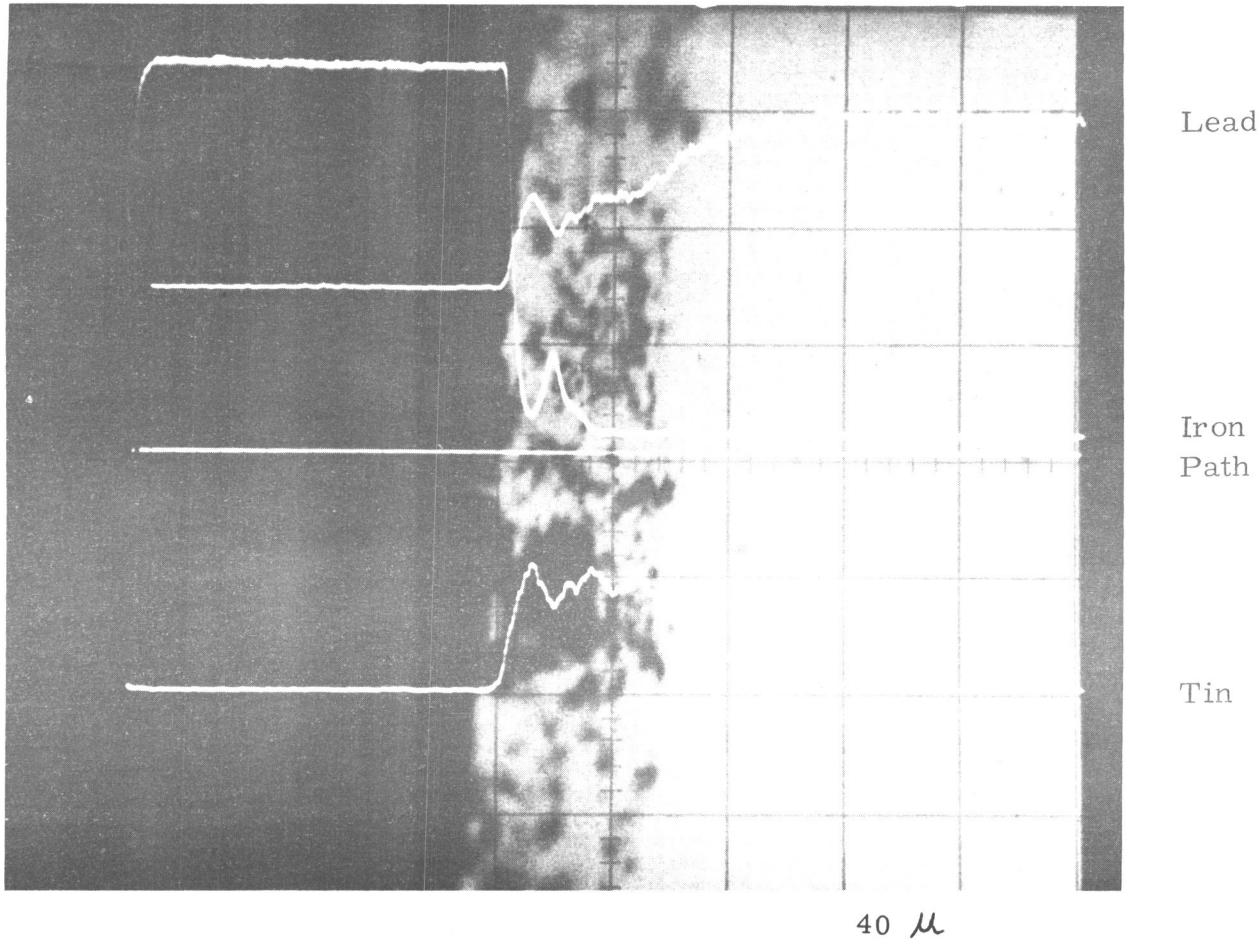


Figure 23. Electron Microprobe Traverse of Hot Junction of n-PbTe Thermoelectric Element After 500 Hour Life Test Showing Concentrations of Iron, Lead and Tin

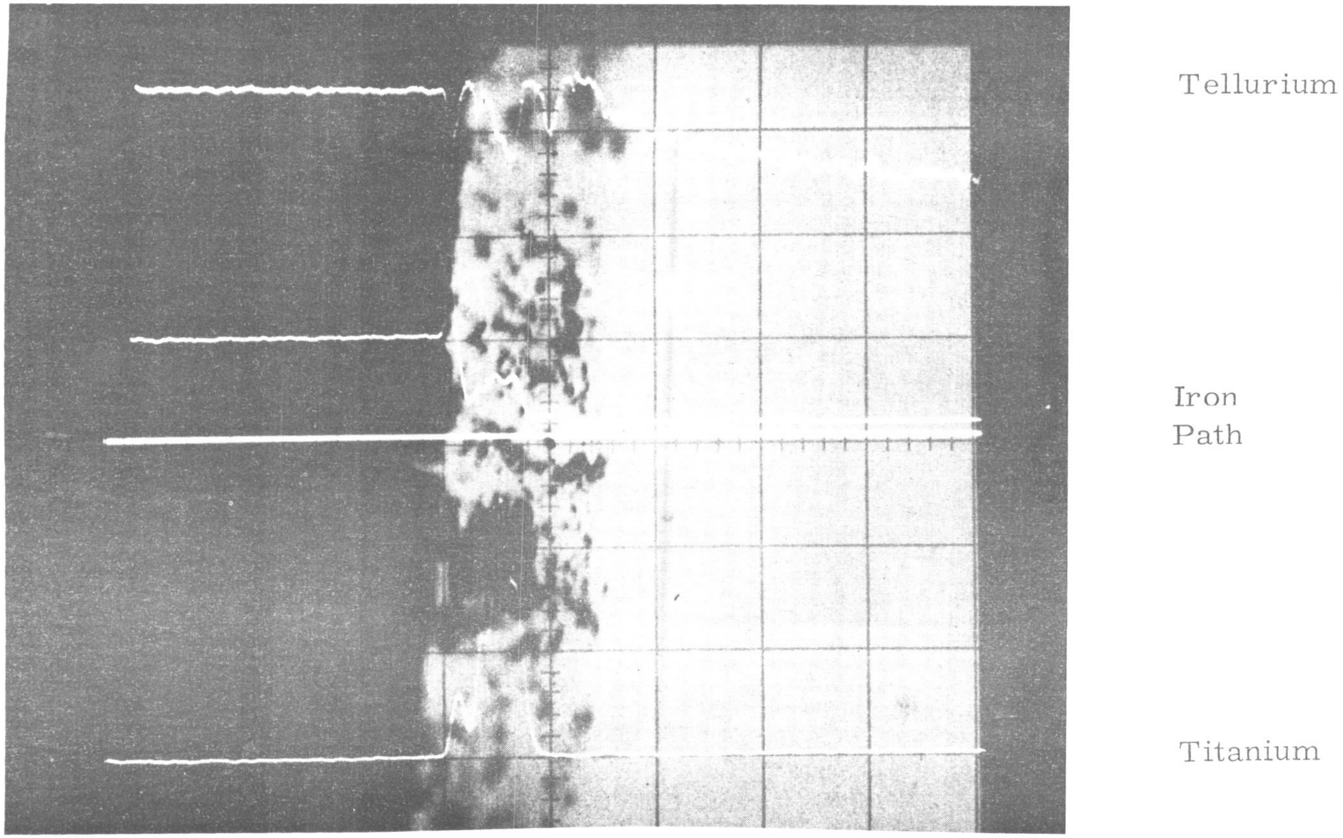


Figure 24. Electron Microprobe Traverse of Hot Junction of n-PbTe Thermoelectric Element After 500 Hour Life Test Showing Concentrations of Iron, Titanium and Tellurium

3. Titanium is found only in the braze zone (to which it is added as one weight percent) and is present as discrete particles. There appears to be some association of iron with titanium based on the coincidence of the peaks for both these elements.

4. Tellurium content is uniform across the braze (the presence of titanium particles results in an indication of tellurium depletion). There is an increased tellurium concentration in the PbTe adjacent to the braze zone. This may result from diffusion of lead from the thermoelement into the braze.

5. Lead was present completely across the braze, the concentration steadily increasing in areas closest to the PbTe.

6. Tin had diffused approximately 100 microns (approximately 4 mils) into the lead telluride.

The 200 hour test duplicated the 500 hour run in performance. Voltage, resistance and power output were relatively constant over the test period. Hot junction temperatures ranged from 890° to 950°F. The performance curves for these elements are shown in Figures 25 through 29. Post-test measurements of resistivity and Seebeck coefficient are compared with pre-test values in Table VIII and Figure 21 respectively. The hot shoe bond on one of these elements broke after removal from the test apparatus, but all the others appeared strong. No cold shoe bonds separated during the test presumably because the cold junction temperature was maintained at a lower level than in the earlier 500 hour run.

Metallographic examination of the four elements with intact hot side bonds showed cracks present in the bond area in two samples. As stated earlier, it is believed that the sample mounting process was primarily responsible for these cracks. Study of an element from this test by the electron microprobe yielded diffusion results similar to those obtained after 500 hours. The extent of the diffusion was less in this shorter time run. For example, tin was found to have penetrated only 32 microns (approximately 1.3 mils) into the lead telluride, compared to 100 microns in the 500 hour sample.

An electron microprobe study was also made of the cold shoe of a 200 hour life test sample. This iron shoe had been brazed to the lead telluride with pure tin. The bond area is represented pictorially in Figure 30 which was made in the same manner as Figure 23 and 24 described above. No iron or lead diffusion can be observed and that of tin is minimal. A substantial tellurium concentration (approximately 23 percent of the tellurium value in PbTe)was found uniformly distributed in the braze. This may be an anomoly caused during sample preparation, but more likely occurred during the bonding process.

The three elements tested for 1000 hours were the first studied following the changes in system wiring to decrease resistance external to the elements and to improve power measurements. These elements, two of which were hot pressed at Hittman Associates and the third purchased from 3M, were operated at slightly higher temperatures than in the earlier tests - 960° to 1000°F. As can be seen from the performance curves, Figures 31 through 33, a gradual increase of power with time was observed for the first 900 hours. This was associated with a reduction in measured resistance. After 900 hours, a utility failure resulted in two brief power interruptions causing thermal cycles. An immediate jump in resistance caused 10 to 20 percent reduction in power output.

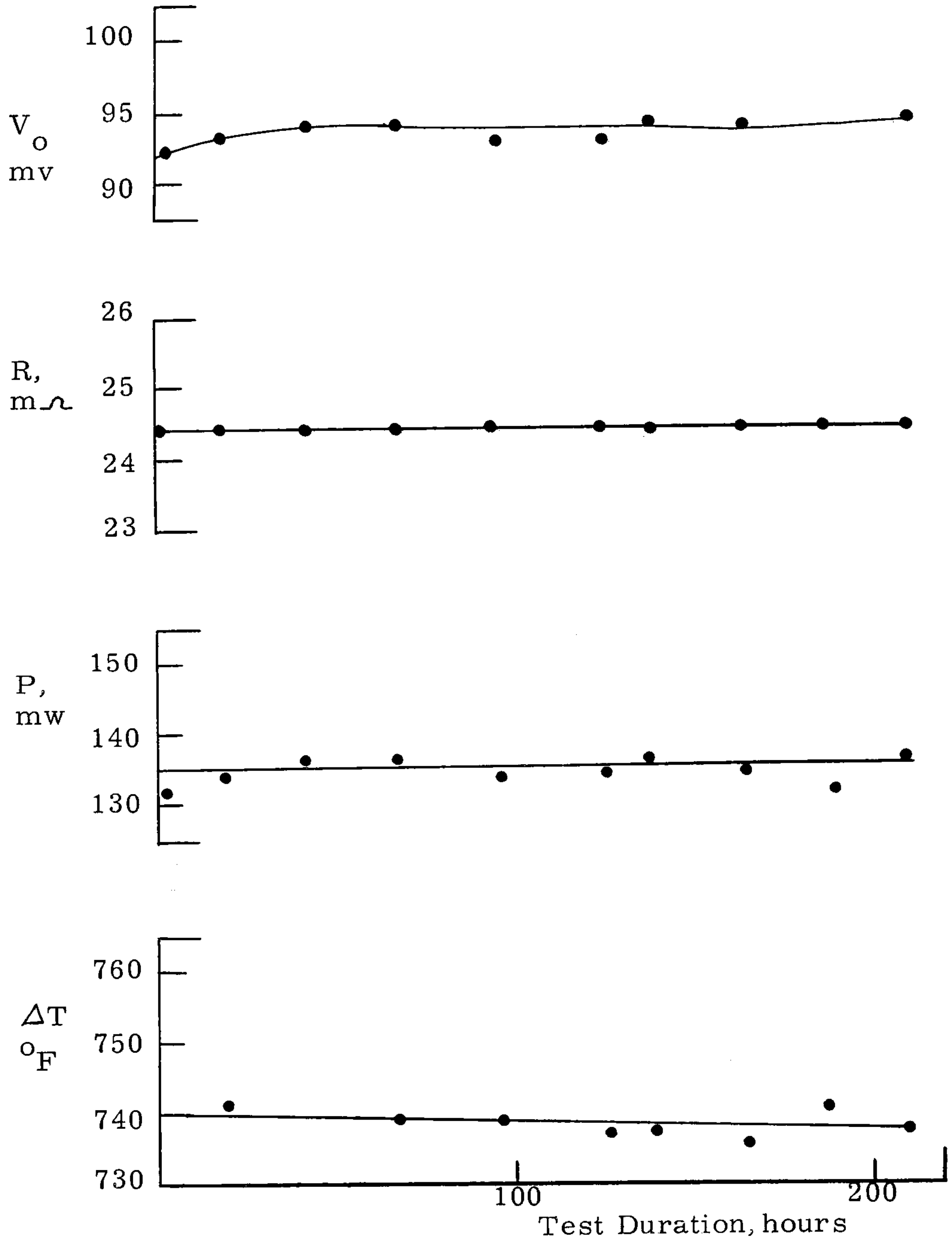


Figure 25. Performance of PbTe Element No. 179A During 200 Hour Test (n- type)

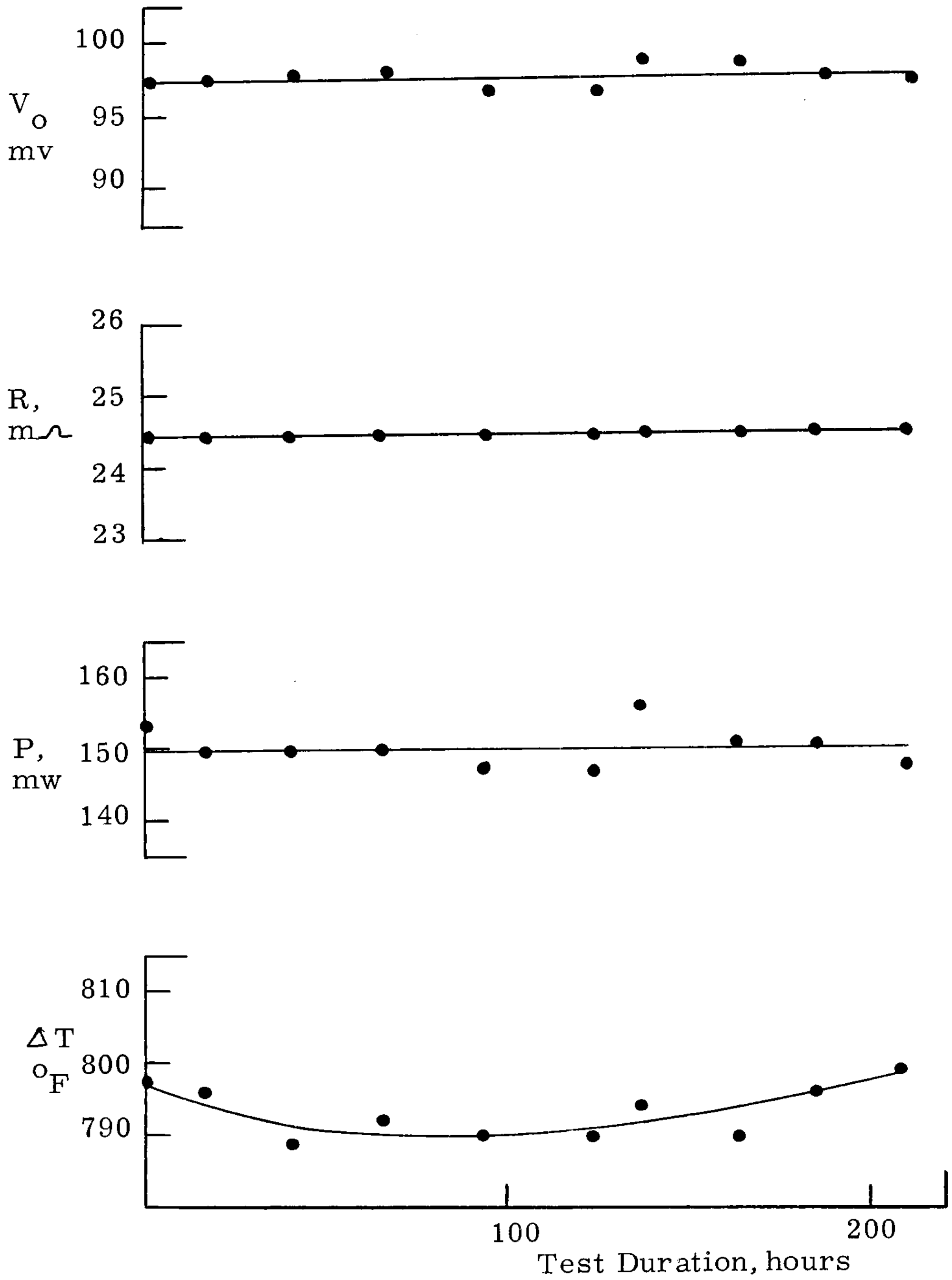


Figure 26. Performance of PbTe Element No. 183A During 200 Hour Test (n- type)

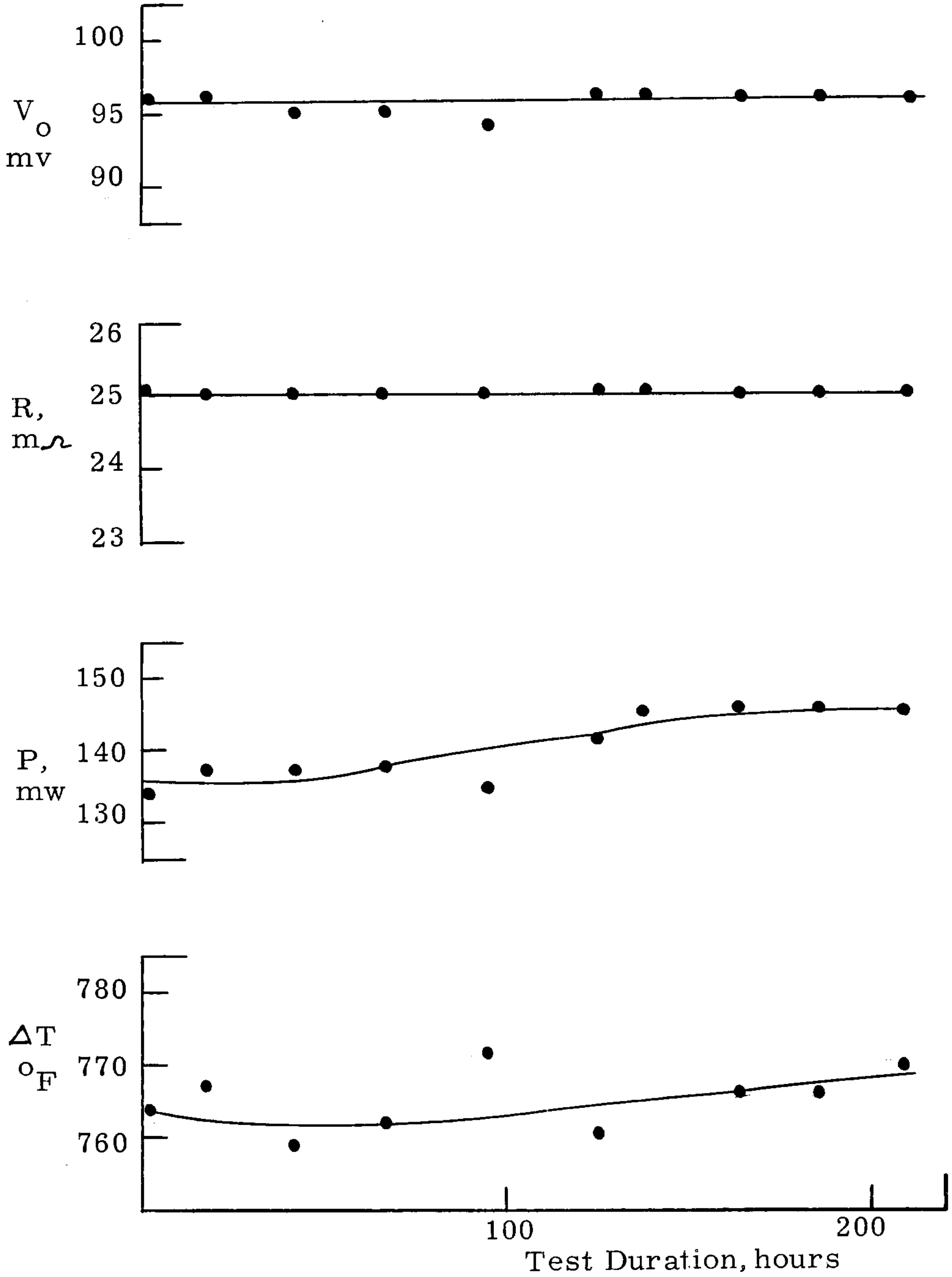


Figure 27. Performance of PbTe Element No. 180A During 200 Hour Test (n- type)

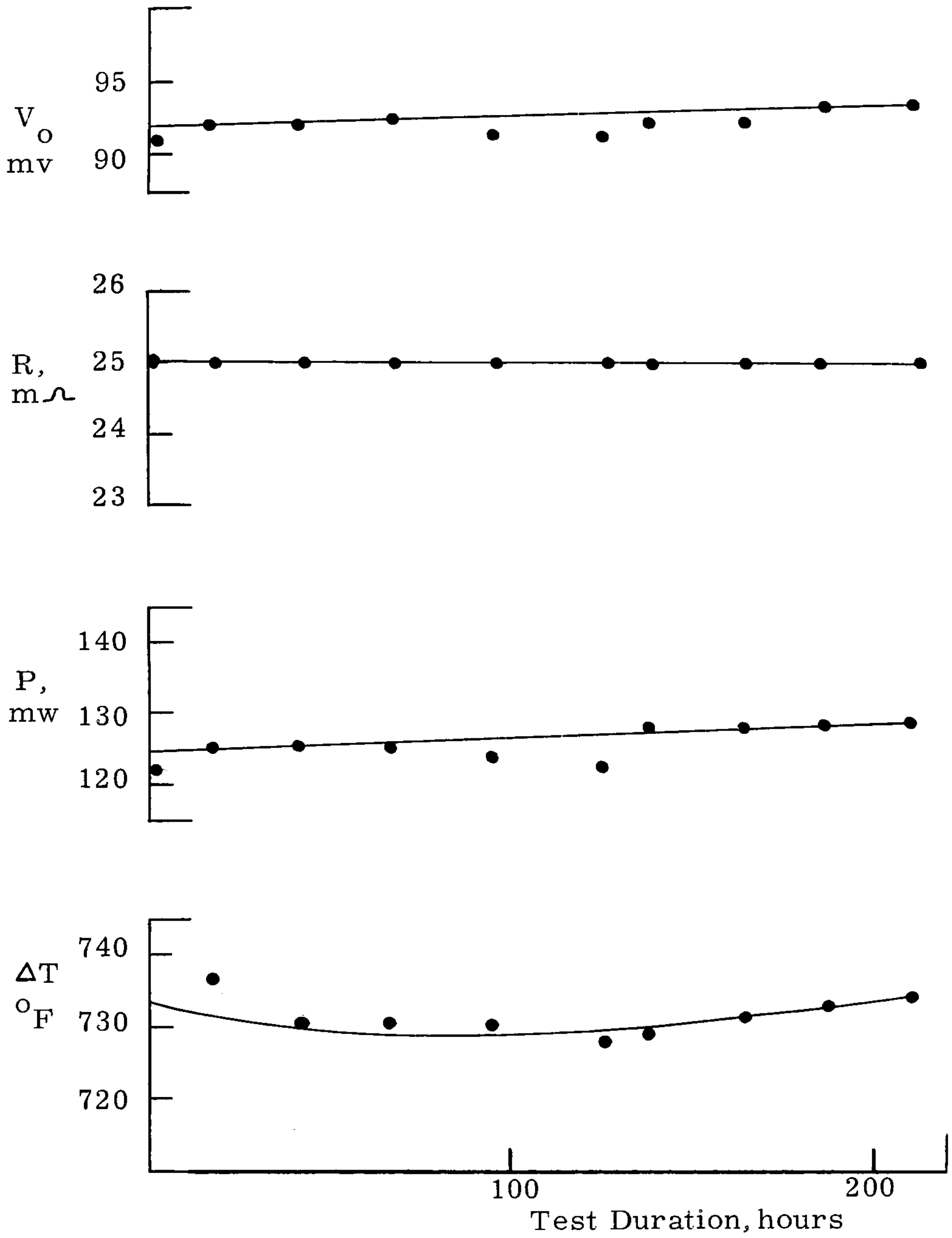


Figure 28. Performance of PbTe Element No. 182A During 200 Hour Test
(n- type)

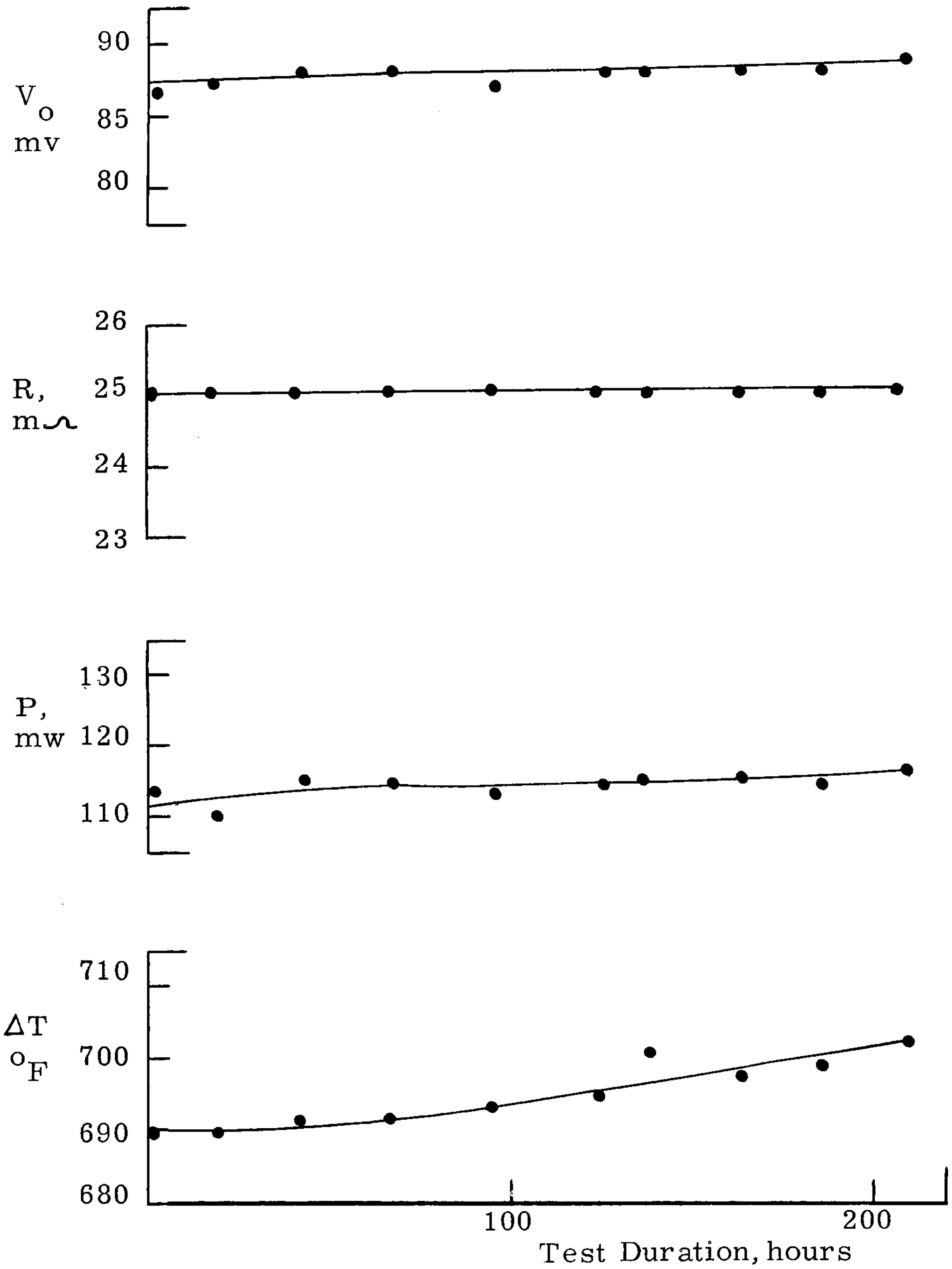


Figure 29. Performance of PbTe Element No. 184A During 200 Hour Test (n- type)

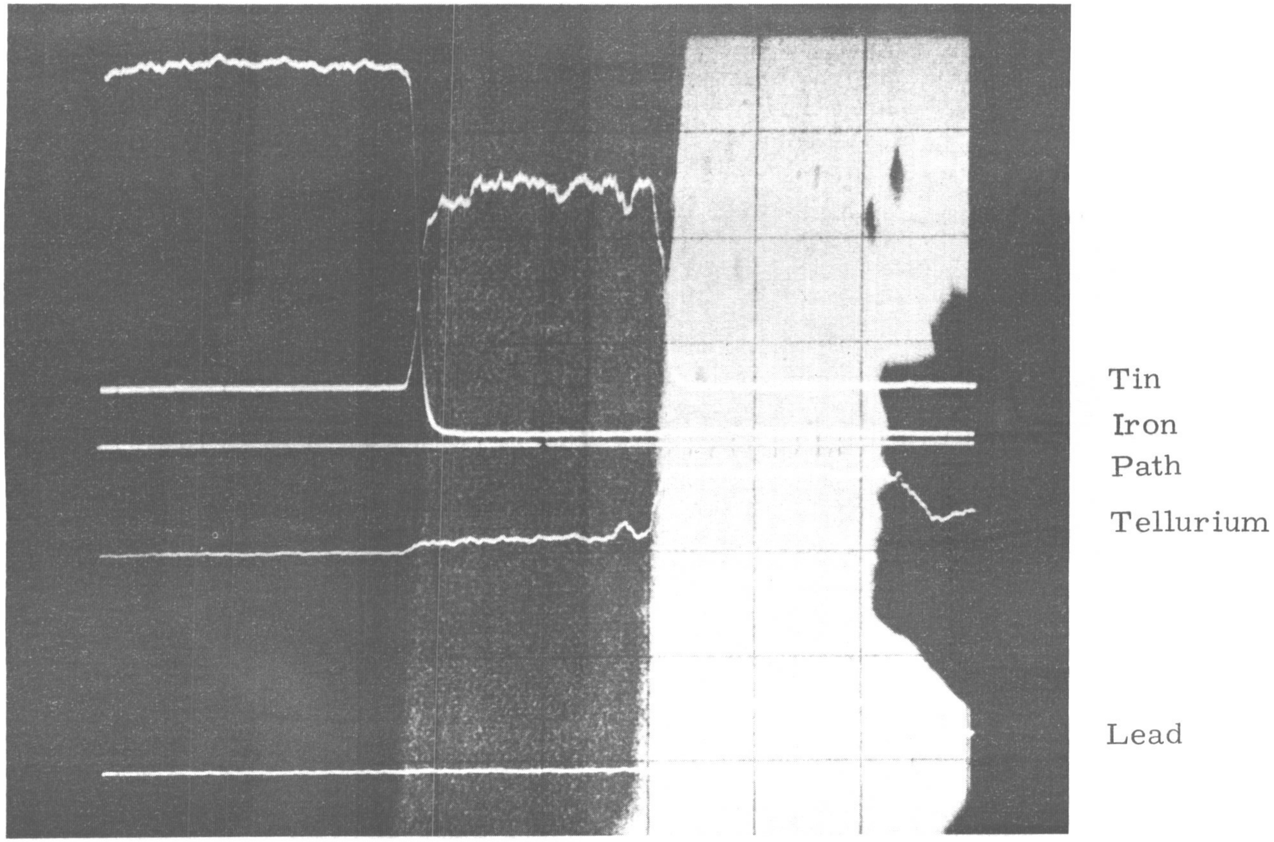


Figure 30. Electron Microprobe Traverse of Cold Junction of n-PbTe Thermoelectric Element After 200 Hour Life Test

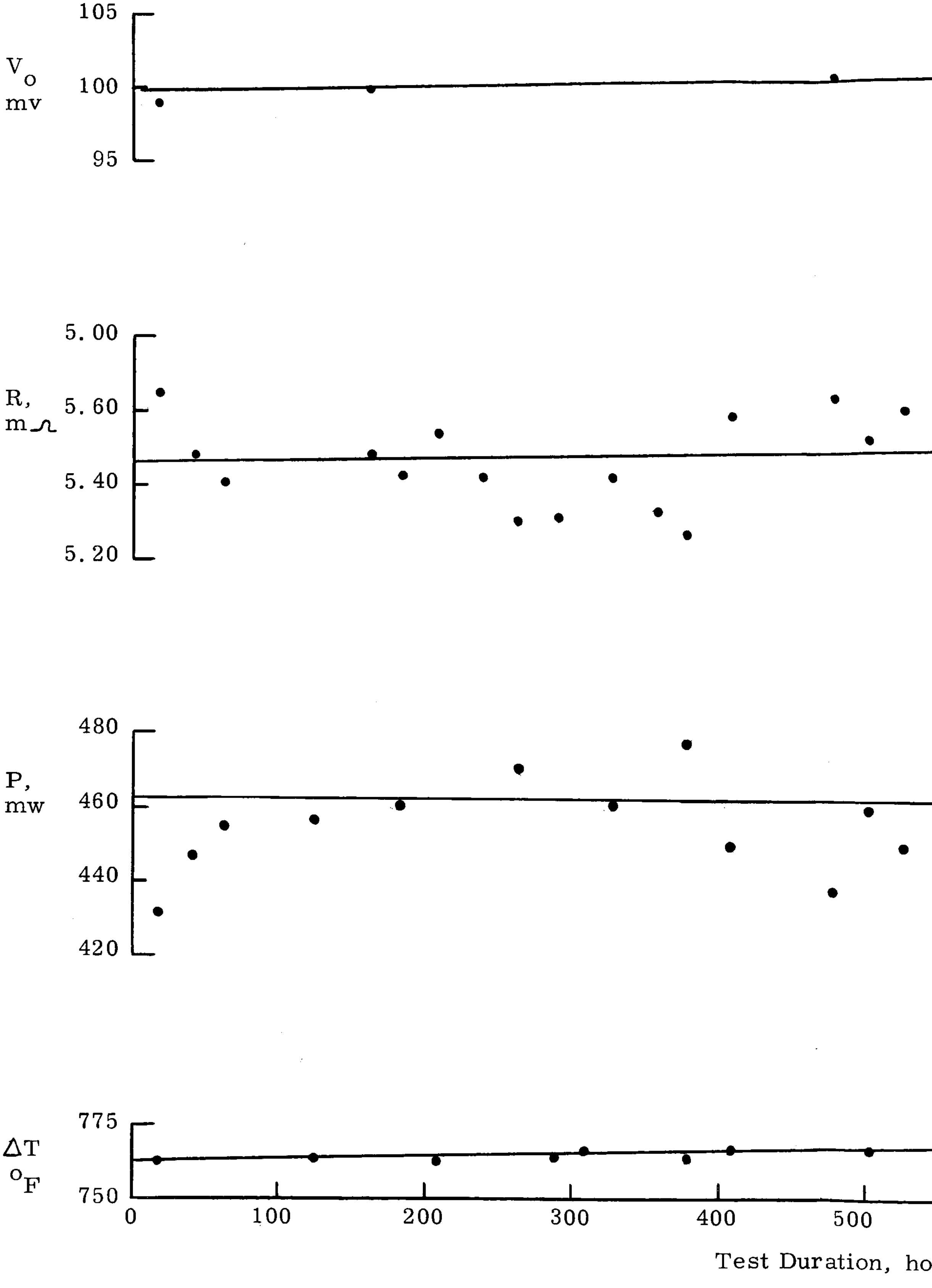
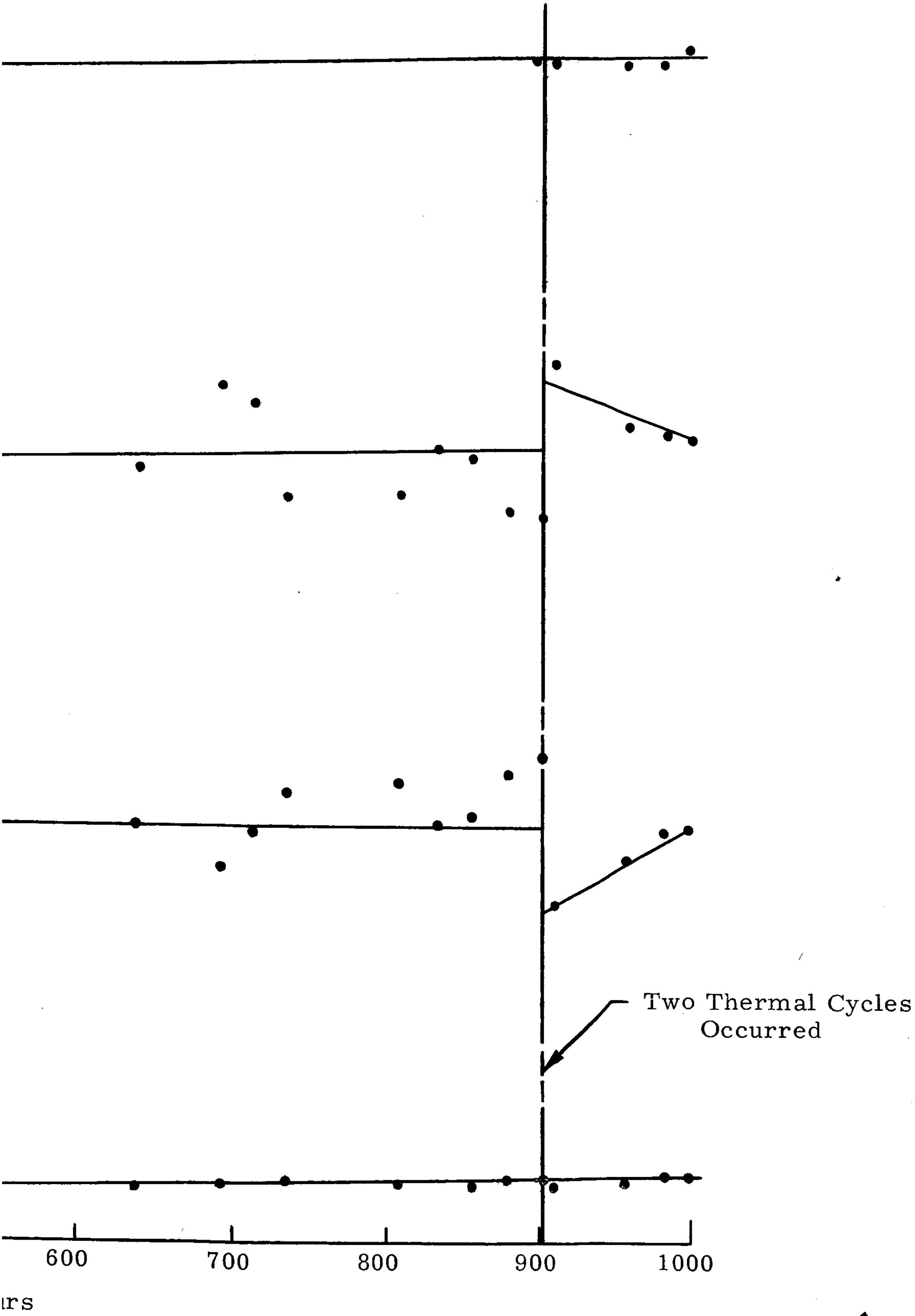


Figure 31. Performance of n-PbTe Element Numbe

V1-26-1



Two Thermal Cycles Occurred

213A During 1000 Hour Life Test

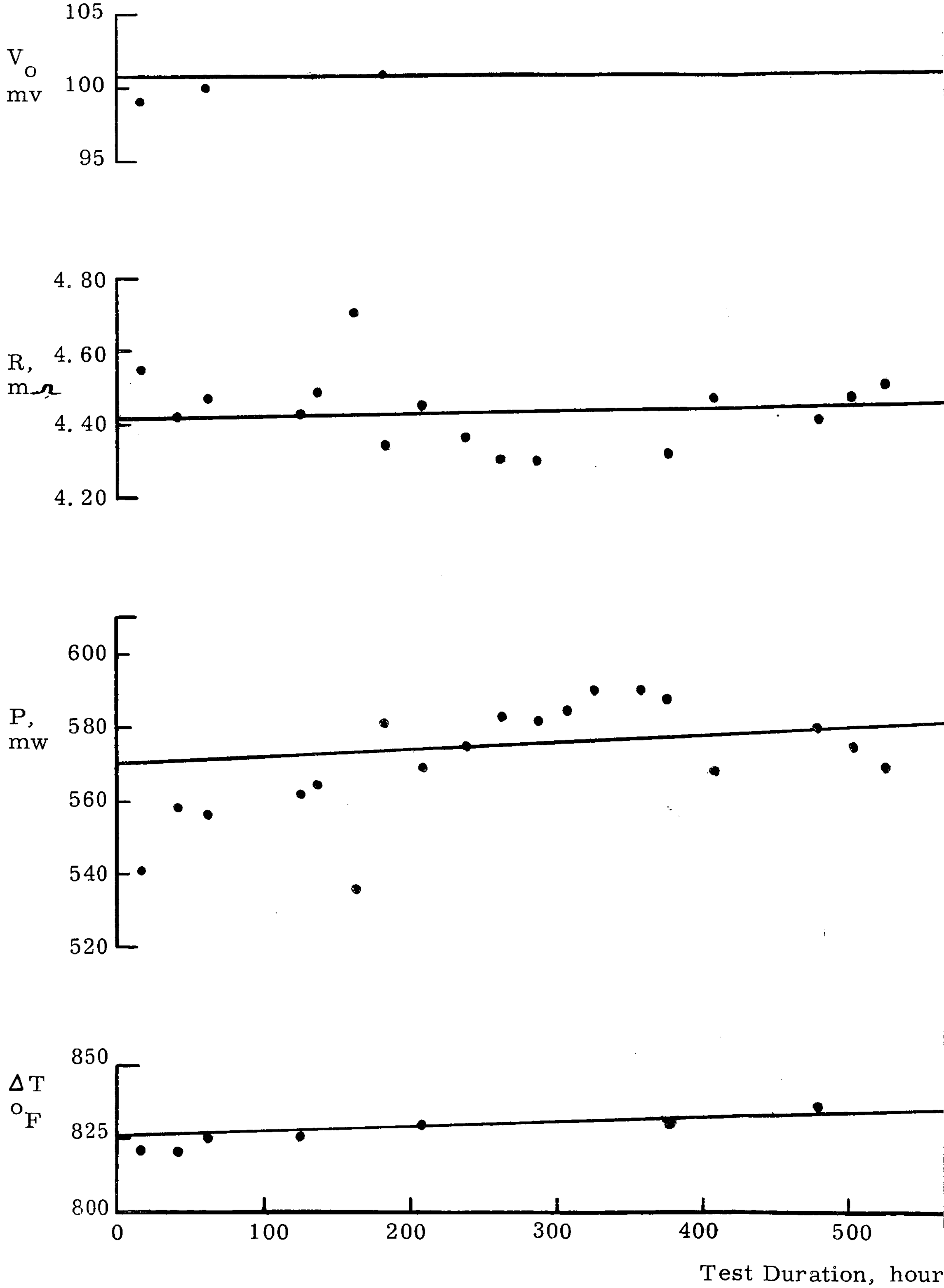
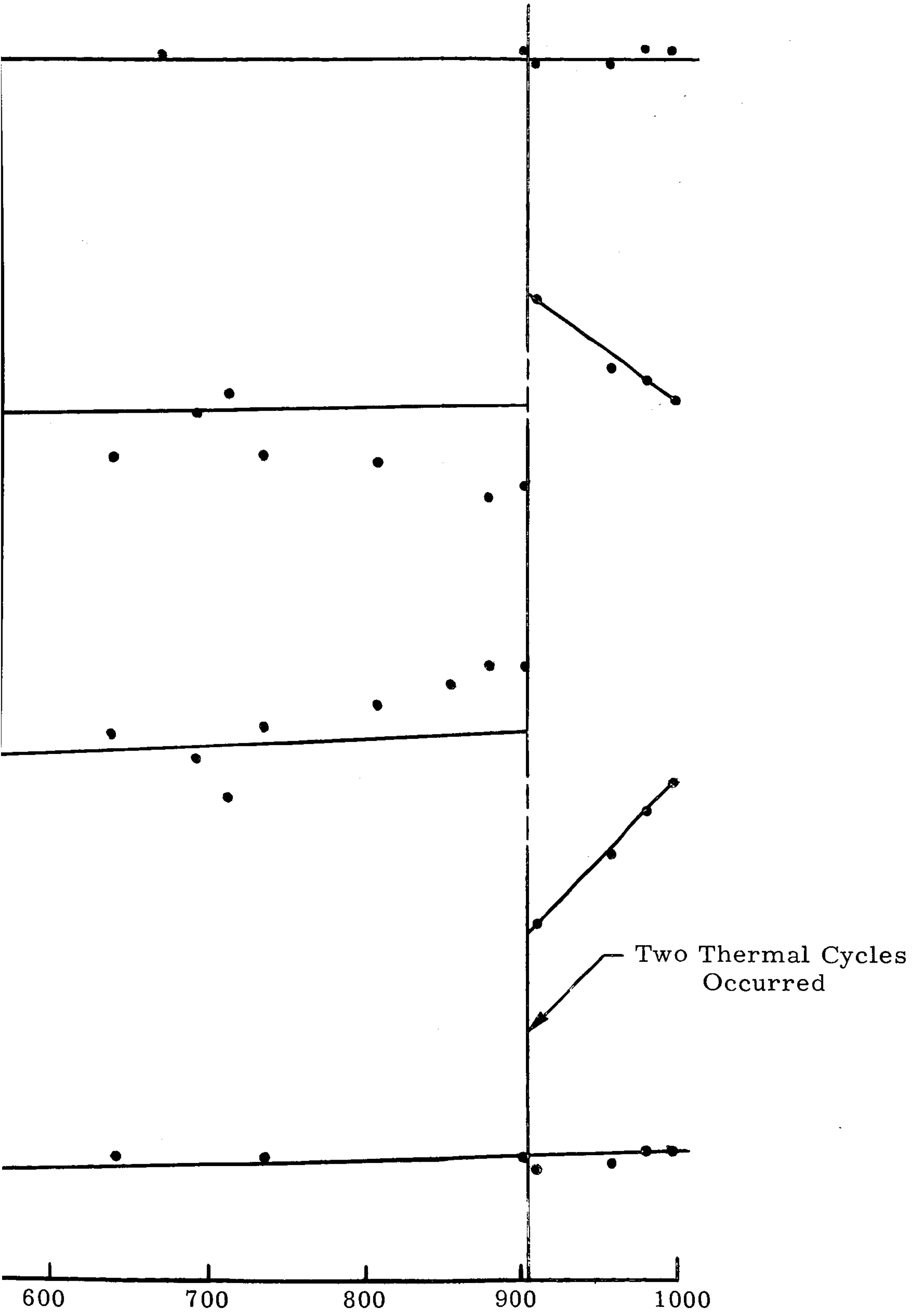


Figure 32. Performance of n-PbTe Element Number 2

V1-27-1



s

2A During 1000 Hour Life Test

VI-24-2

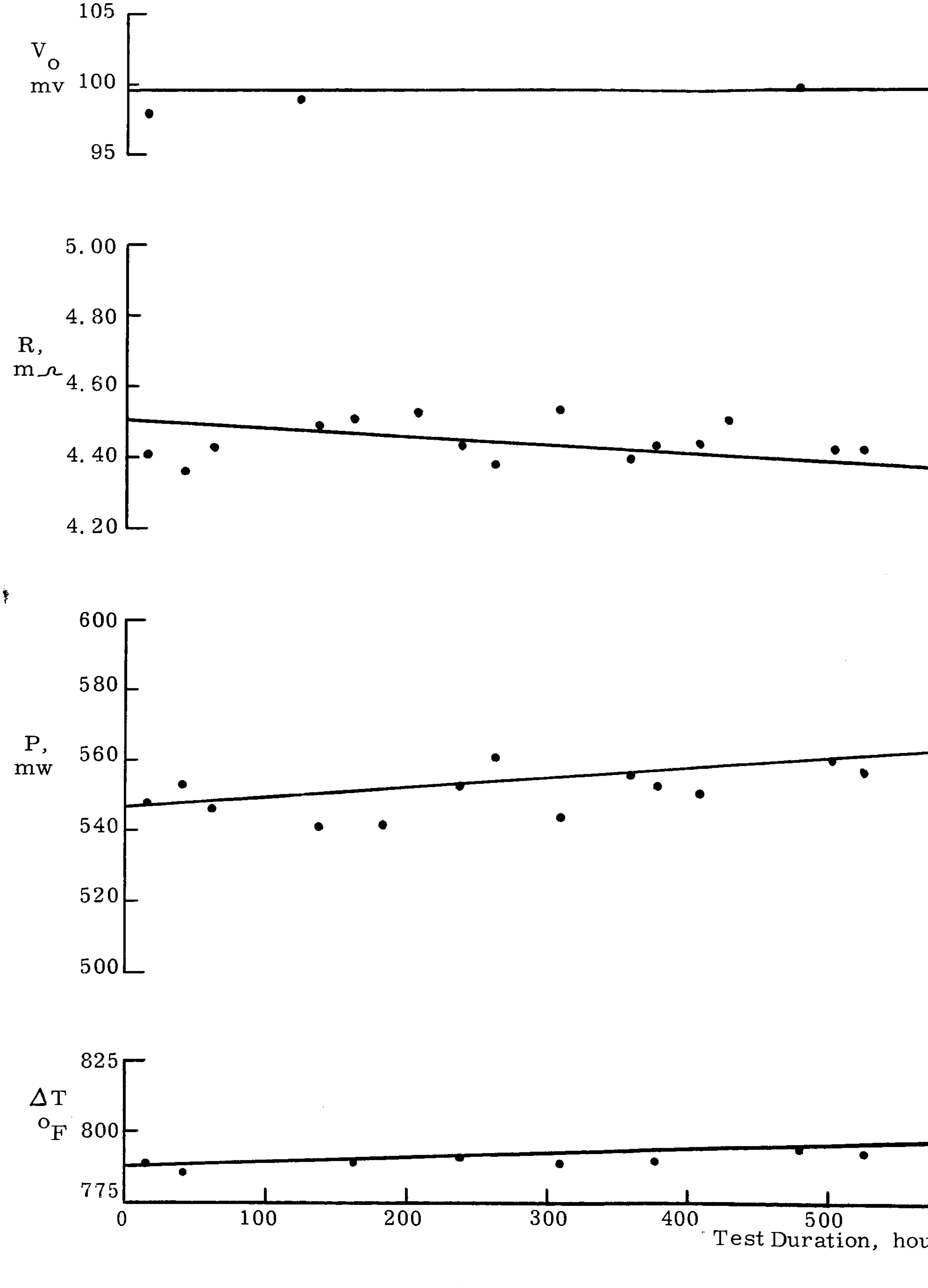
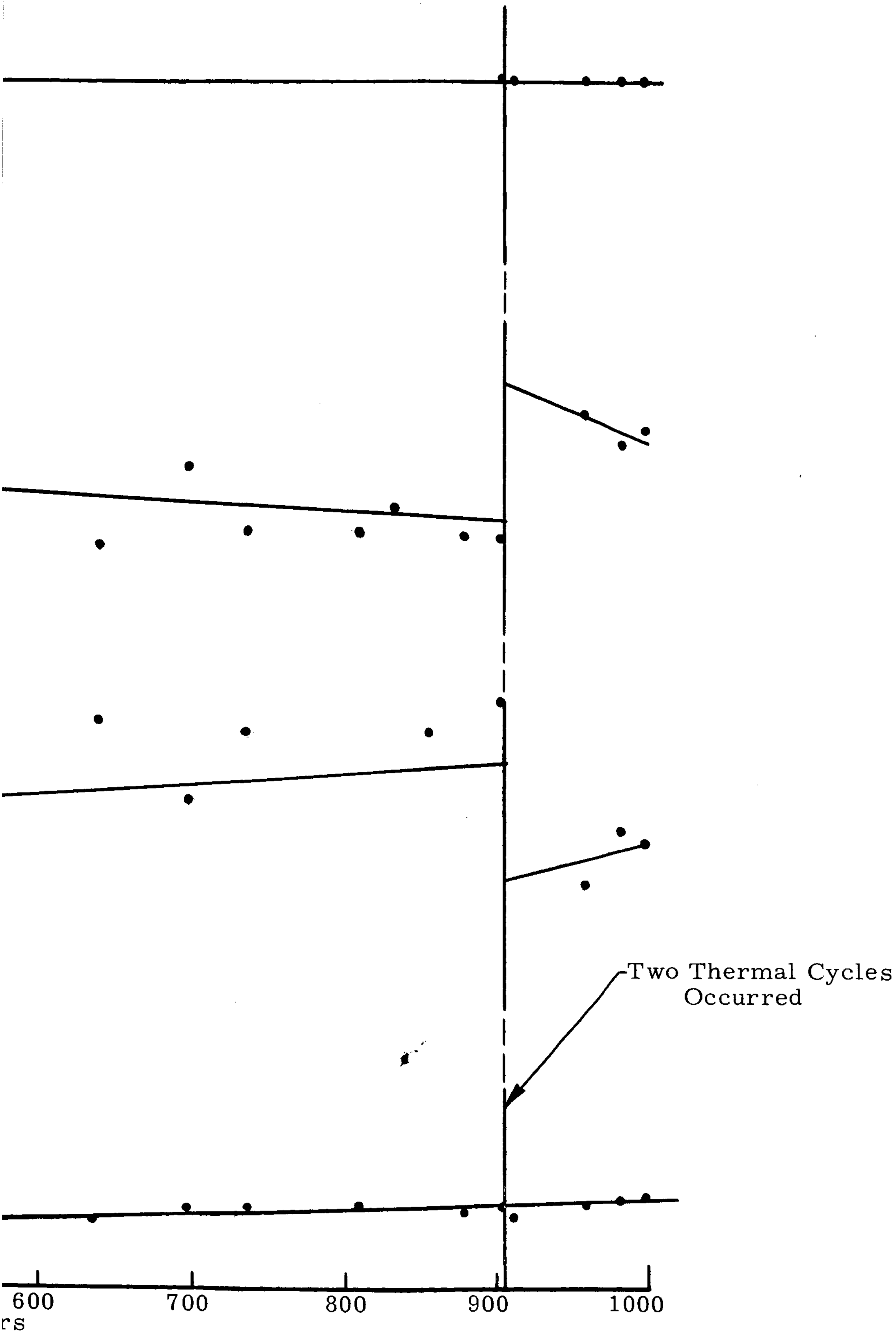


Figure 33. Performance of n-PbTe Element Number 3M



#1 During 1000 Hour Life Test

VI-28.2

However, this was largely recovered during the final 100 hours of testing. Measurement of resistivity and Seebeck coefficient before and after this test are included in Table VIII and Figure 21. As in the earlier tests changes in these parameters were minimal. No difference in performance between the Hittman and 3M Company elements was noted.

At the conclusion of the test all the hot shoes remained strongly bonded to the elements, but the cold shoe of one of the Hittman Associates produced samples had separated. Metallographic study of the remaining bonds showed them to be excellent in appearance with no cracks. (Note: these samples were prepared for metallography by the cold mounting process that minimizes stresses upon the bond during mounting.

An additional life test of n-PbTe elements is in progress. This group of samples which passed 4000 hours of operation on March 8, 1966 is continuing on test. These elements include three Hittman Associates produced TEG-2N thermoelements bonded to iron shoes, one 3M produced TEGS-2N element bonded at the hot end only, and two unbonded controls, one produced by Hittman Associates and the other purchased from 3M Company. Before the test was begun, several attempts were made to solder a cold shoe to the bonded 3M element. Considerable difficulty was encountered and, rather than delay the test, it was decided to proceed with the sample as described above. (The problem of attaching cold end contacts has not been circumvented by bonding both shoes in a single step as described earlier in this report).

Figures 34 through 36 show the performance to date of the bonded test elements. Over the first 2000 hours, power increased steadily due to a continued decline in resistance. At this point the utility failure mentioned in the previous discussion of the 1000 hour test caused two thermal cycles. An immediate increase in resistance and decline in power were largely recovered within the next 200 hours. A heater failure caused a thermal cycle and temporary shutdown of the system after 3100 hours of operation. During attempts to remove the failed heater, which had welded to the heater block, the elements were unintentionally stressed. Upon restart, this was manifested as a sharp rise in resistivity and accompanying decline in power. This has been only partially recovered in the succeeding time period. This test will be continued until 10,000 hours are accumulated or significant degradation not associated with test equipment malfunction is observed.

C. Tests of p-PbTe Thermoelectric Elements

Two life tests of p-PbTe elements have been completed and two others continue in operation. The first test was a 500 hour run of four elements, two bonded and two unbonded, tested at hot junction temperatures of 970° to 1000°F. The bonded elements were a 3M produced TEGS-2P p-PbTe sample and a Hittman Associates sample, hot pressed from TEG-2P powder but containing, in addition, one weight percent molybdenum fibers. The unbonded elements were produced at Hittman Associates, one being p-PbTe with no additive and the second containing one percent molybdenum fibers.

Figure 37 through 40 show the performance of these elements during the life test. It can be seen that open circuit voltage either increased slightly or remained constant during the 500 hour test. Power output of the two bonded

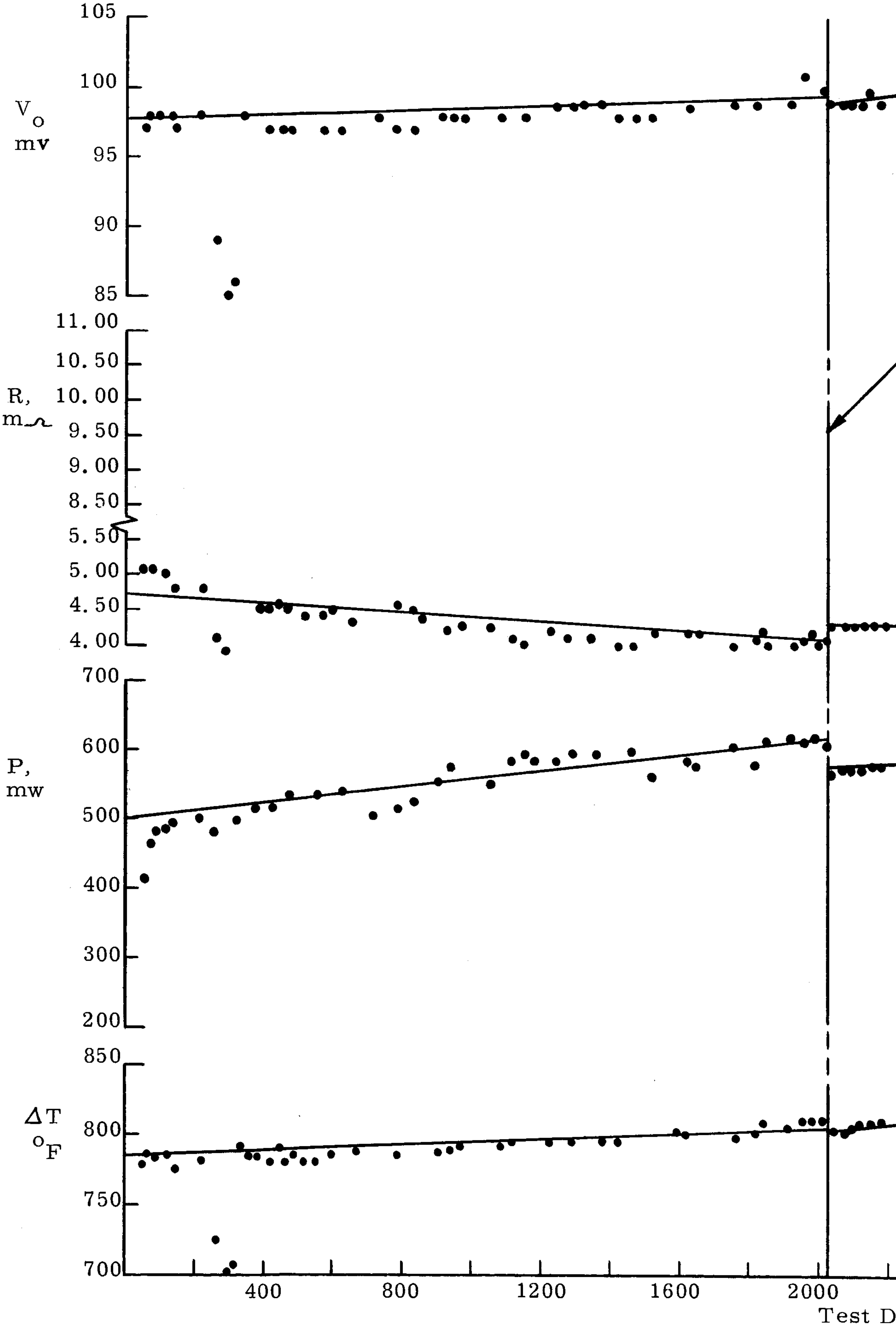
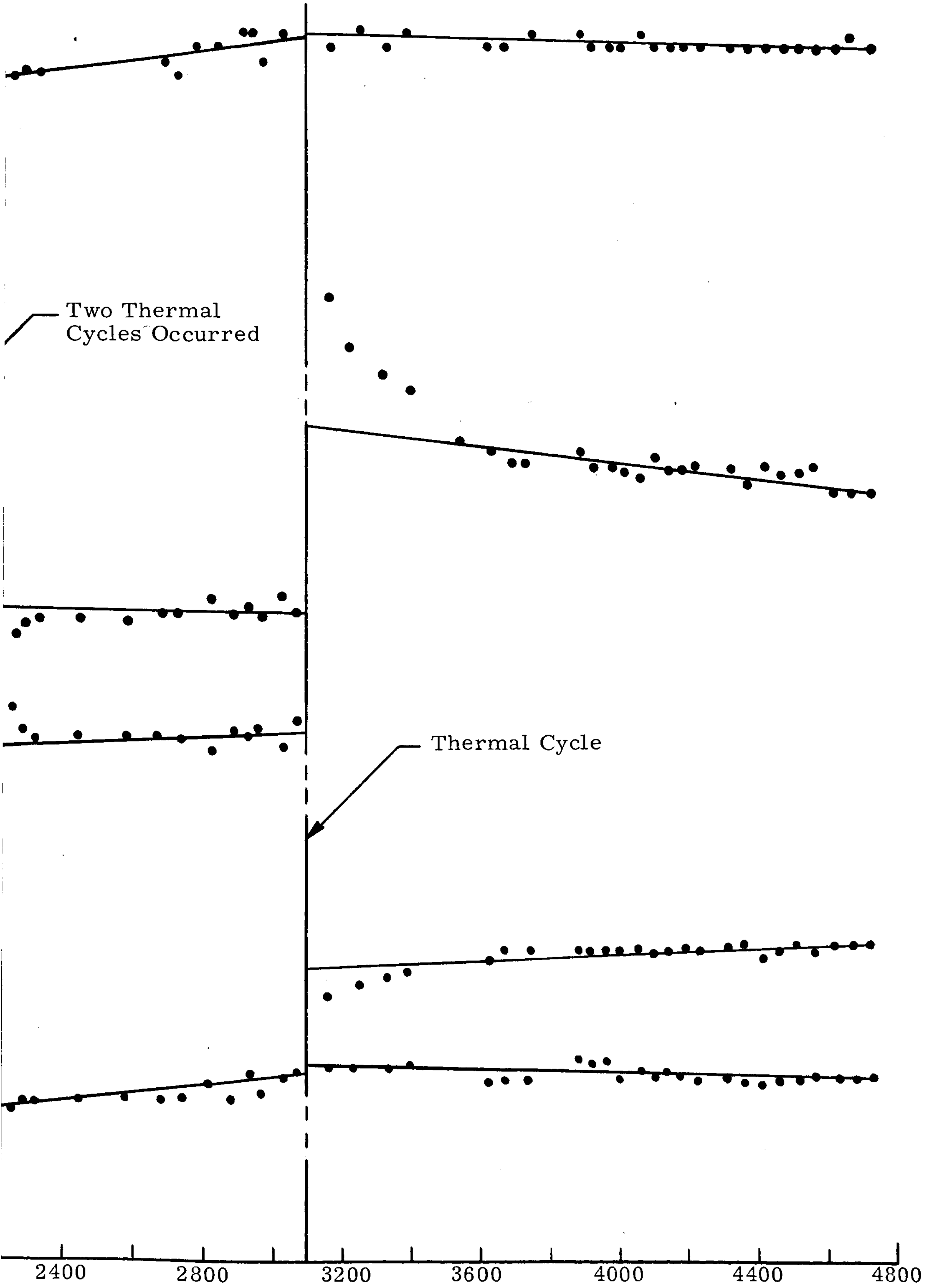


Figure 34. Performance to



Date of n-PbTe Element Number 197A

VI-30-2

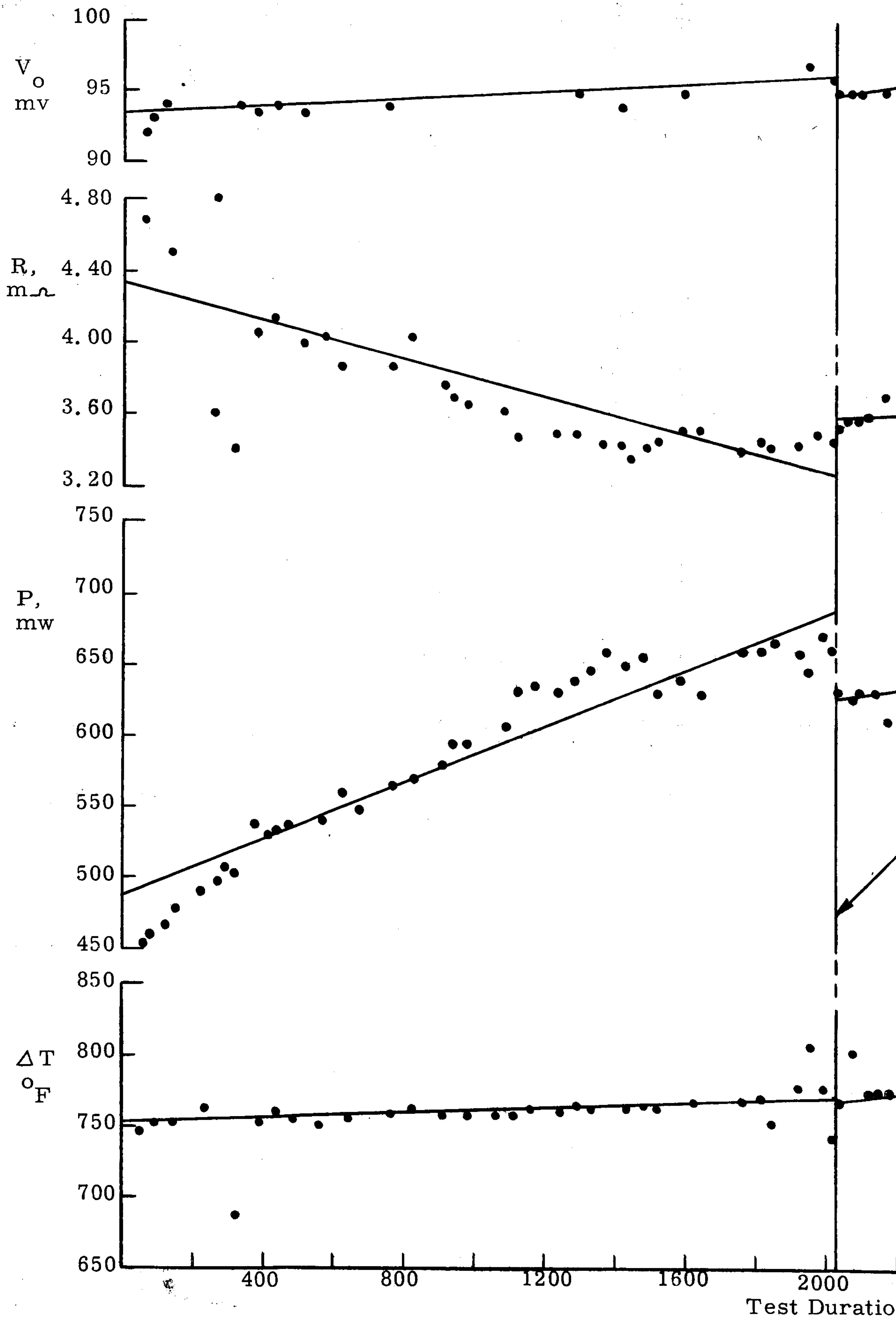
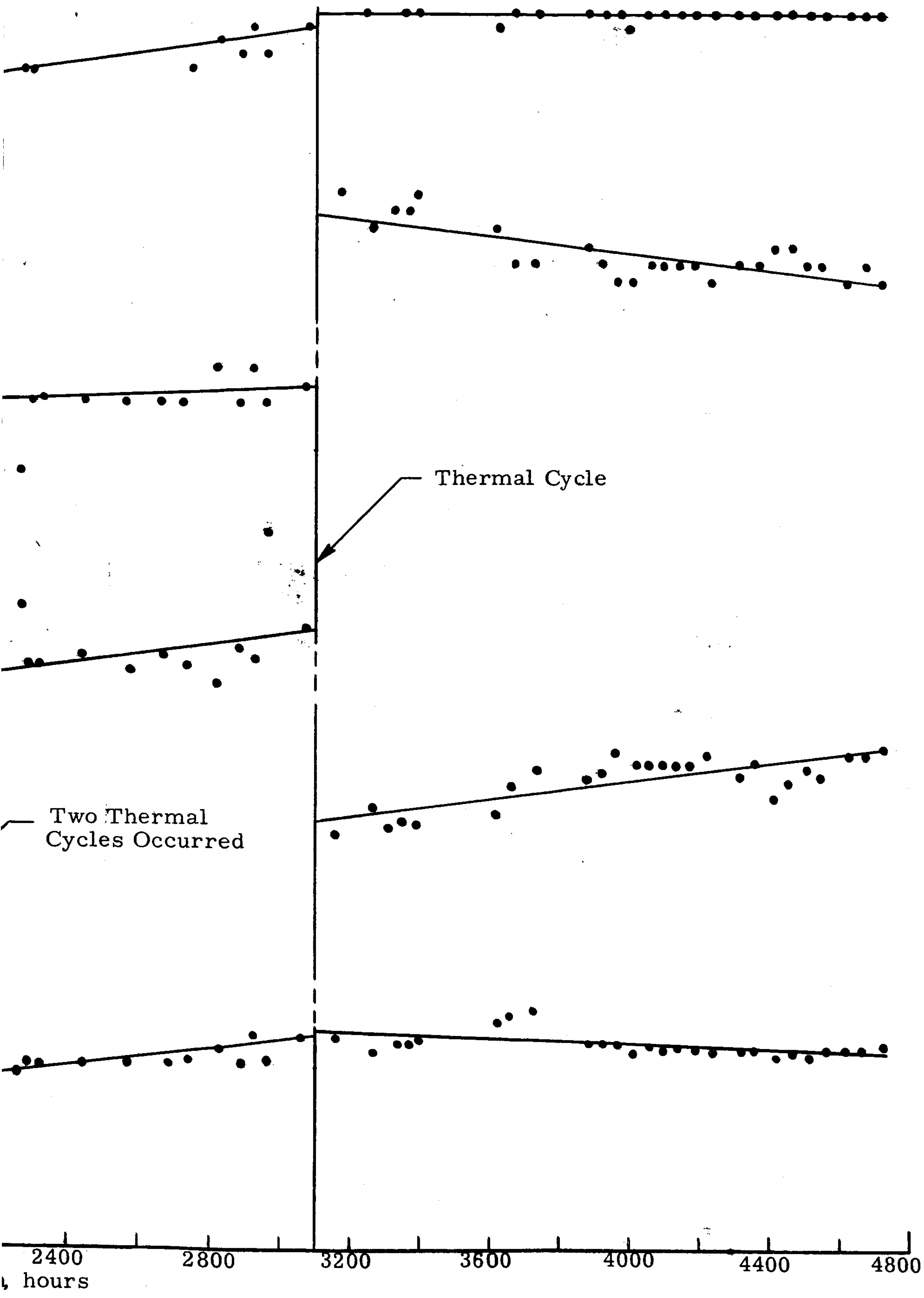


Figure 35. Performance to Da



te of n-PbTe Element Number 186A

VI-31-2

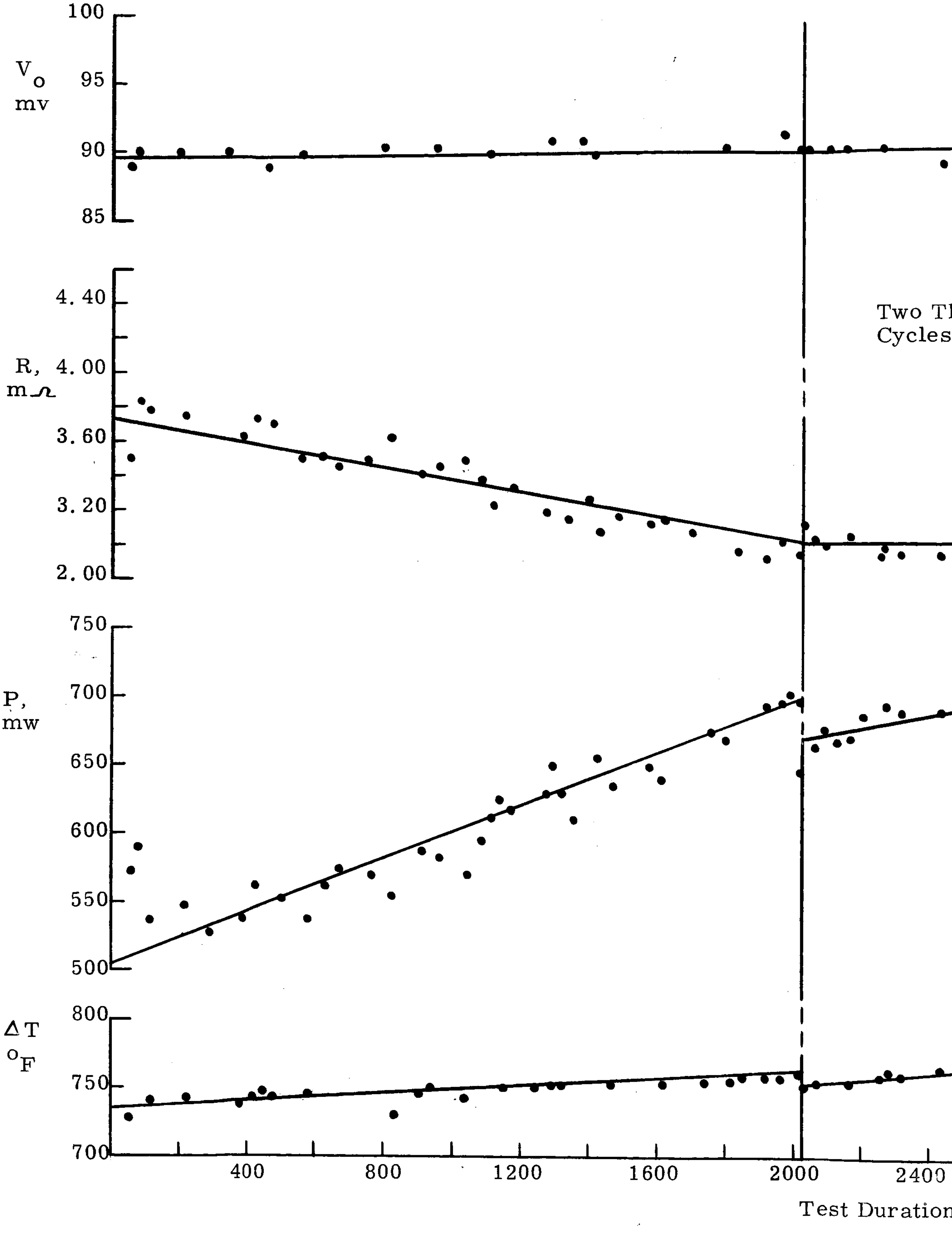
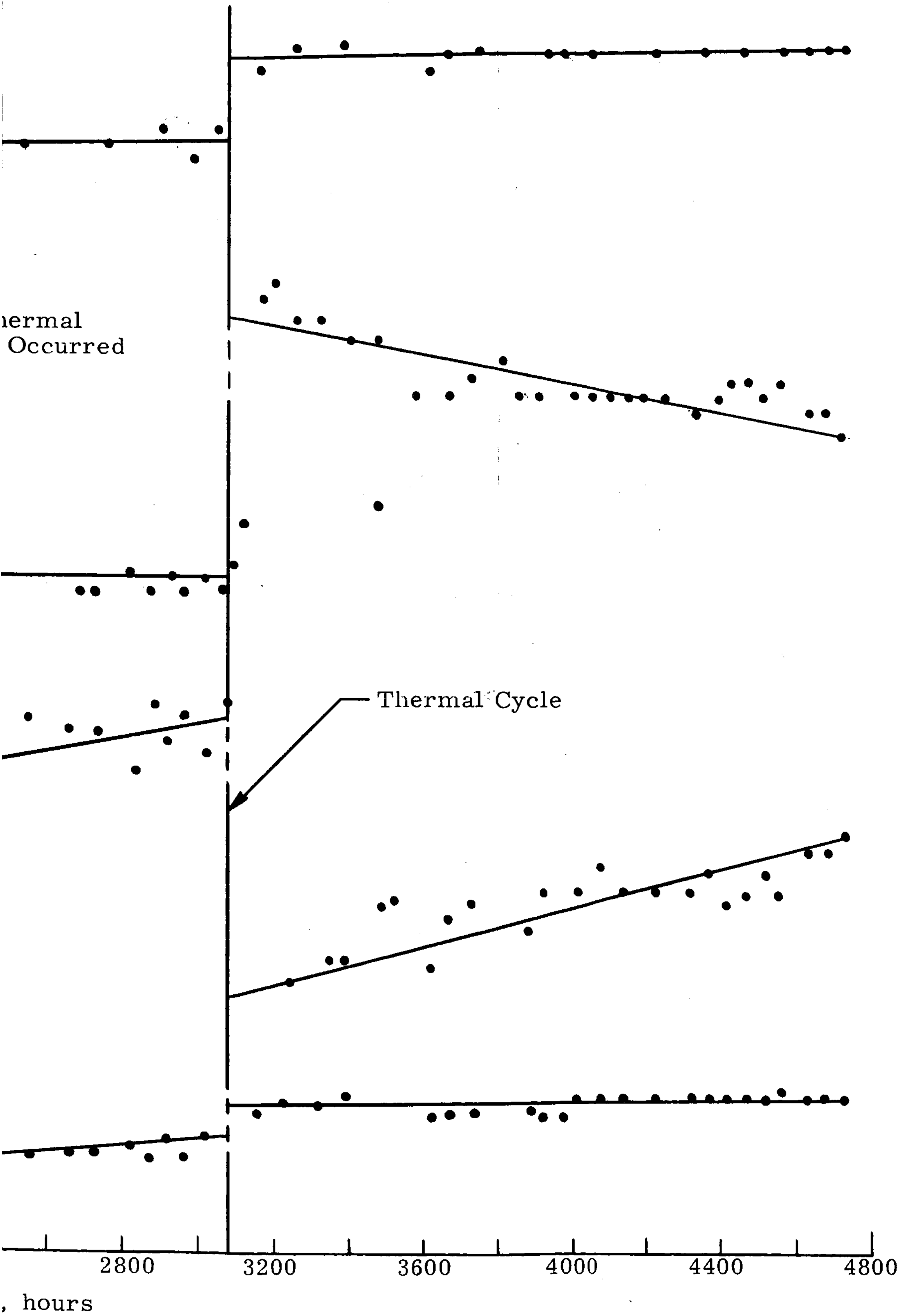


Figure 36. Performance to Date of n-



PbTe Element Number 189A

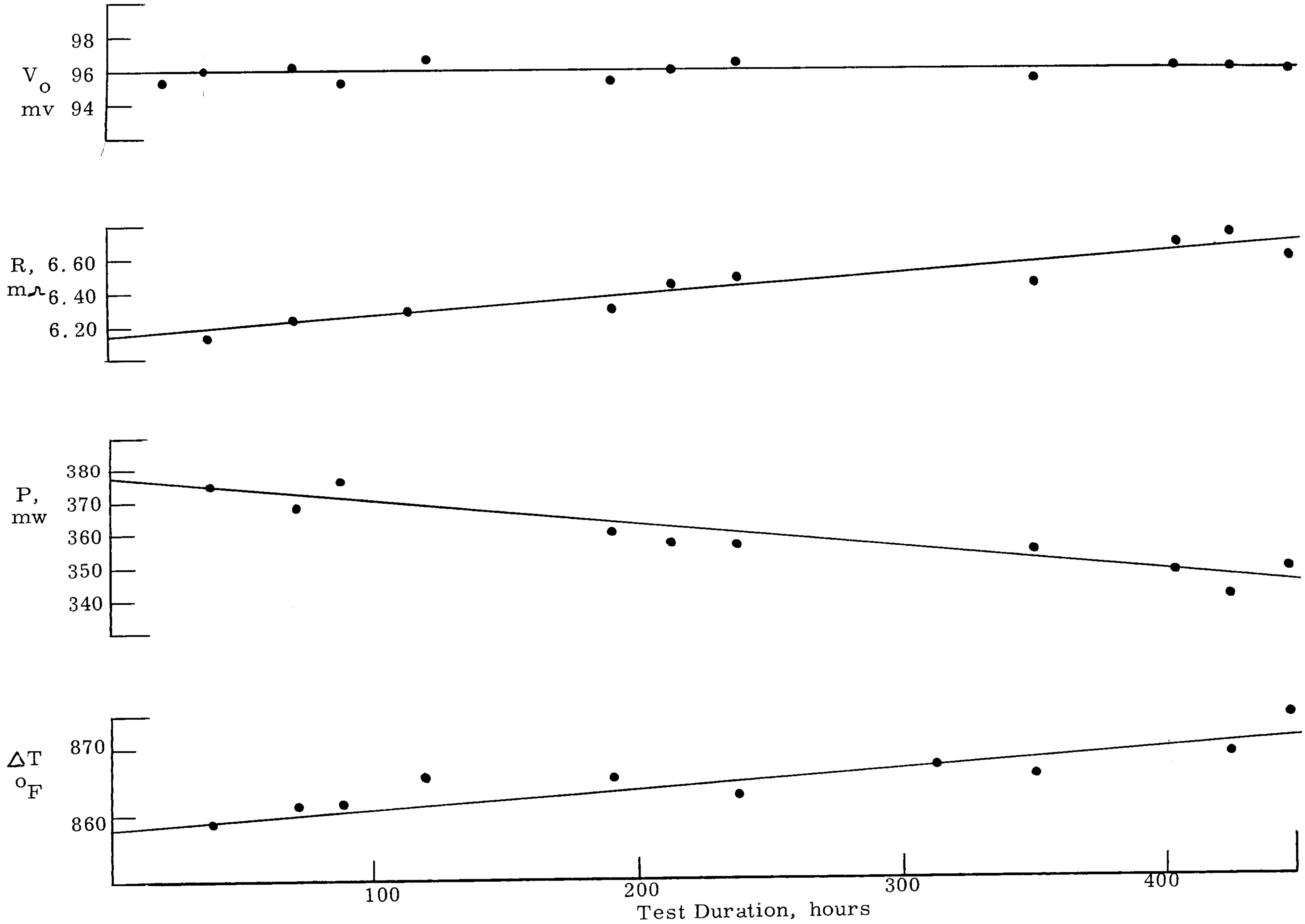


Figure 37. Performance of p-PbTe Element No. 253A During 500 Hour Life Test

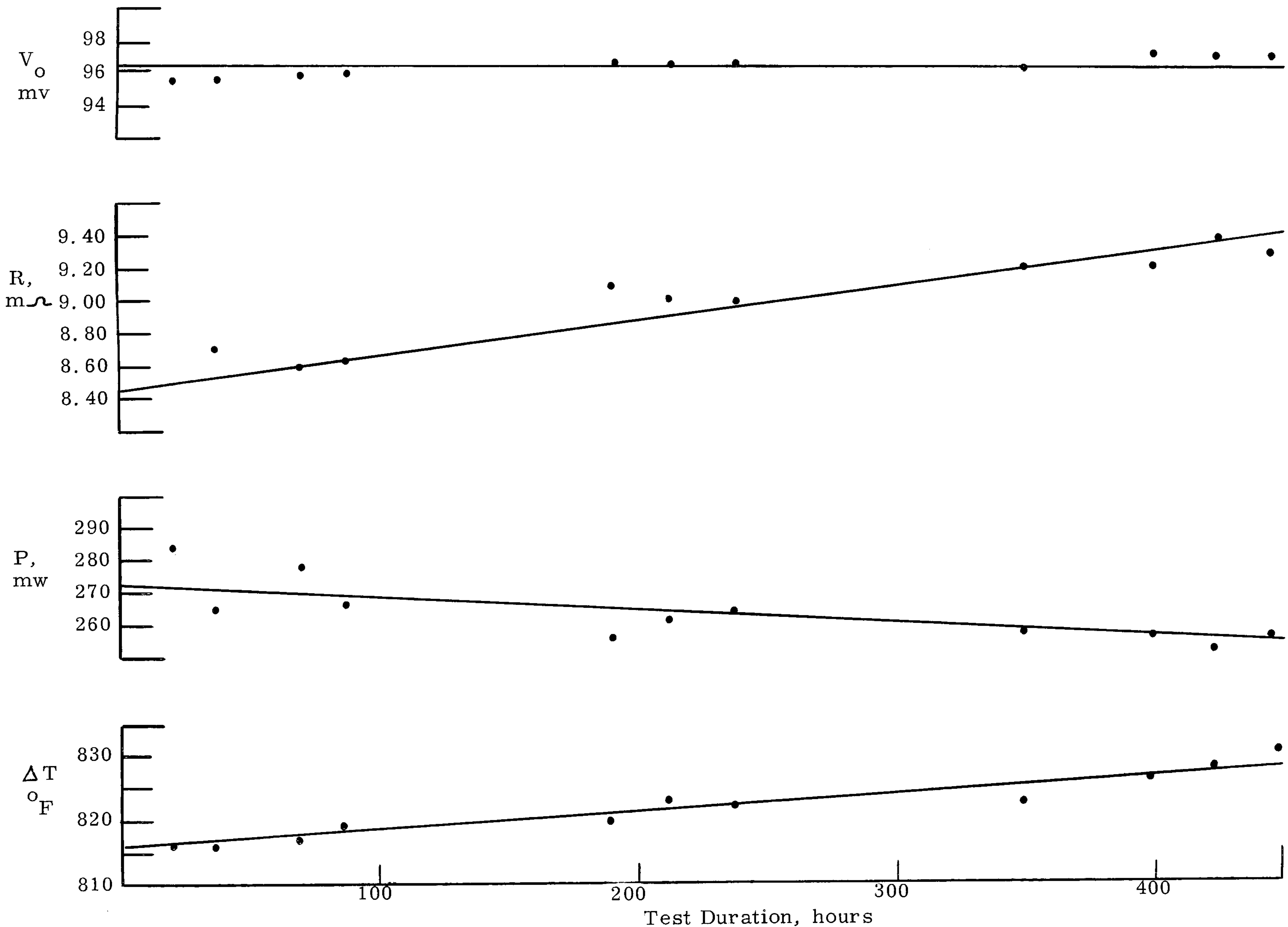


Figure 38. Performance of p-PbTe Element No. 3M - #2 During 500 Hour Life Test

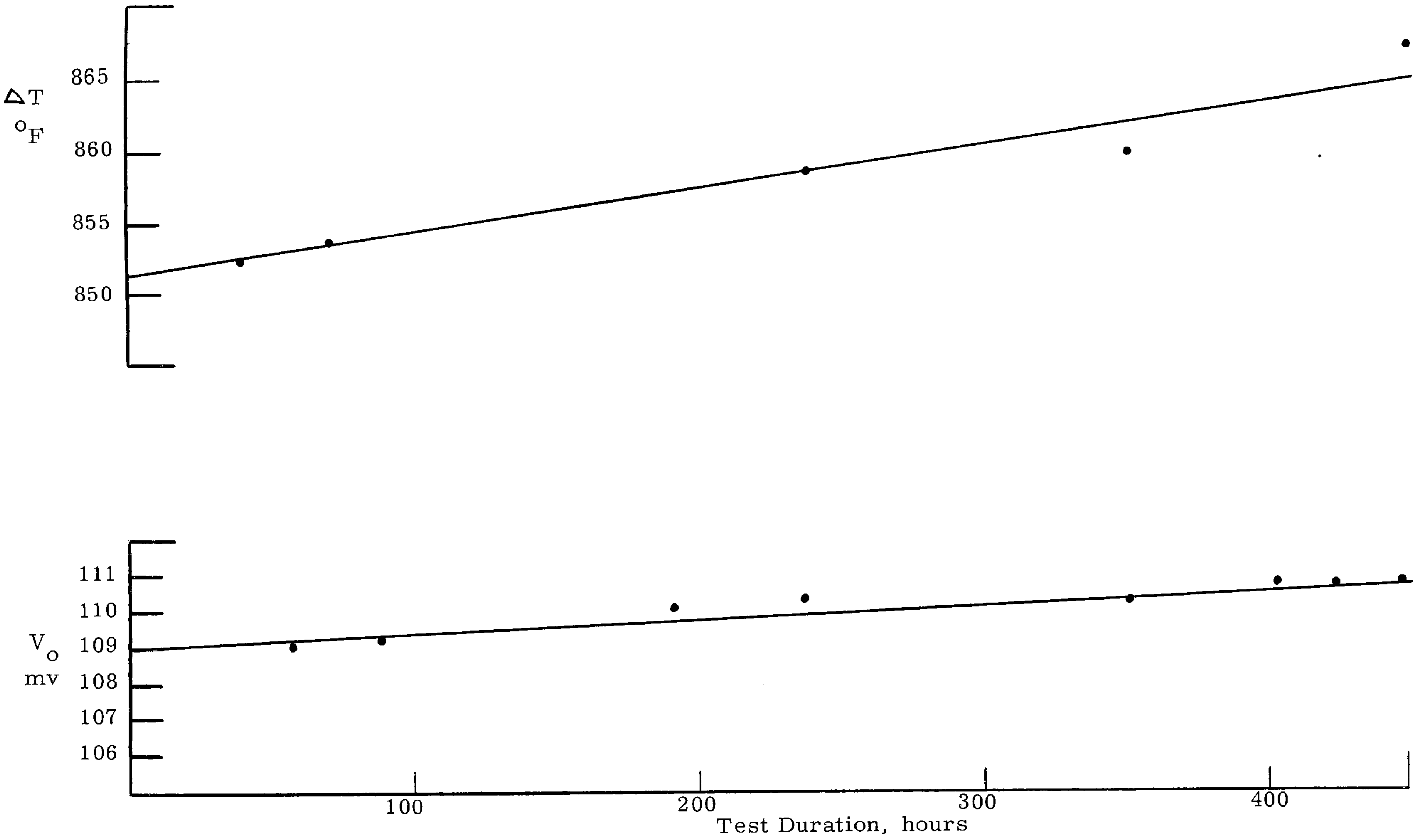


Figure 39. Performance of Unbonded p-PbTe Element No. 251A During 500 Hour Life Test

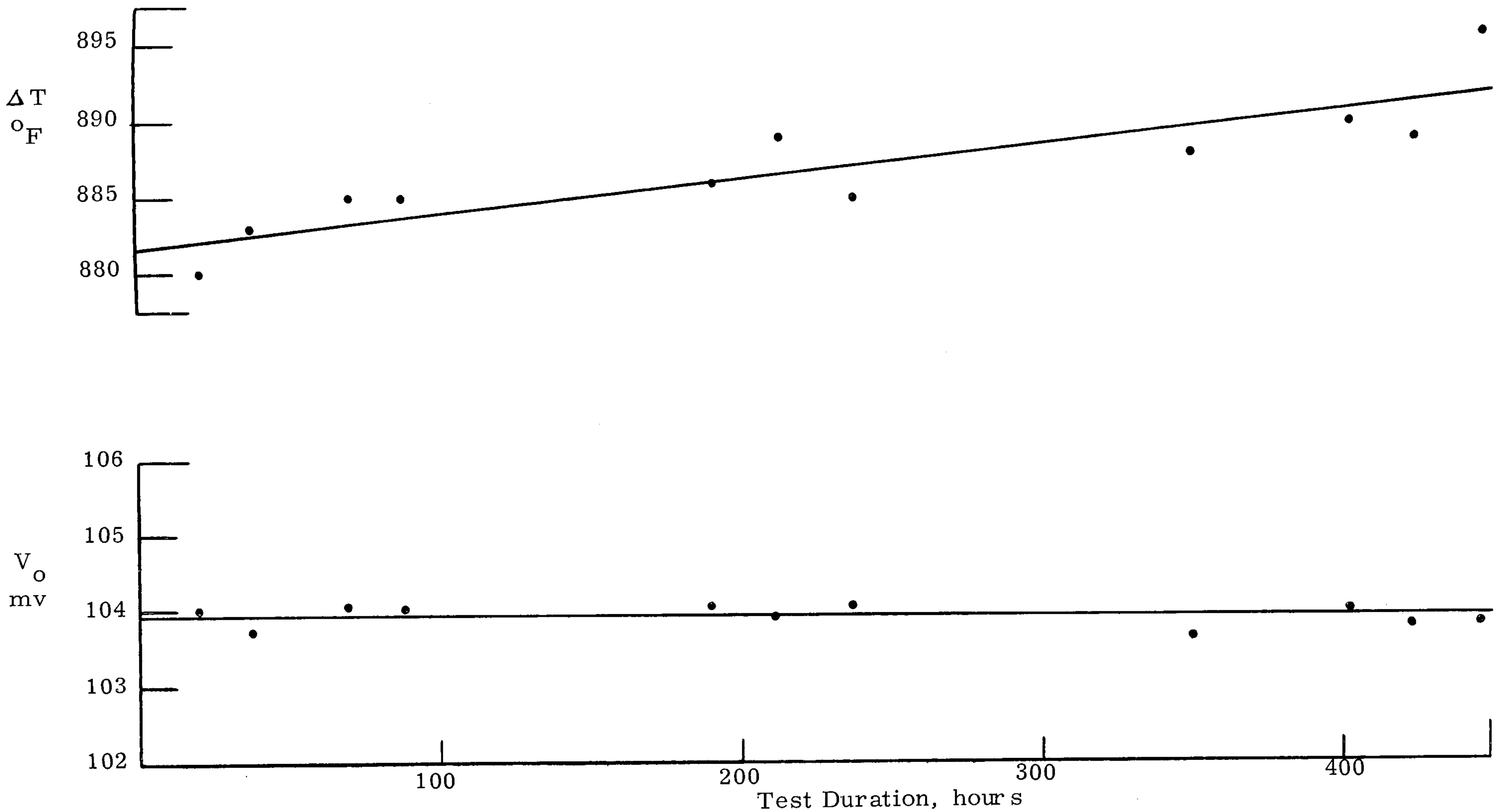


Figure 40. Performance of Unbonded p-PbTe Element No. 267A During 500 Hour Life Test

samples (the only ones for which power was measured) dropped about 7 to 10 percent. Table IX compares the properties of the test elements in the as-pressed, as-bonded, and post-life test conditions. Unlike the n-PbTe samples tested previously, in which measured property changes were within the error limits of the test equipment, substantial property changes were observed in the p-PbTe test samples. Resistivity of the bonded molybdenum containing element increased by 50 percent during bonding but both samples containing the additive had lower resistivity after the life test than before. The p-PbTe element, without additives, also had substantially lower resistivity after the test. The bonded 3M element, however, showed a 19 percent increase in resistivity. Seebeck test results also indicated changes. The Seebeck coefficient of the unbonded element, without additives, showed a substantial increase while the element containing molybdenum decreased somewhat. The bonded element containing molybdenum increased its Seebeck coefficient during bonding and may have increased it further during the life test, at least at lower temperatures. The Seebeck coefficient of the 3M element also increased during bonding, but decreased almost to the as-pressed value during life testing.

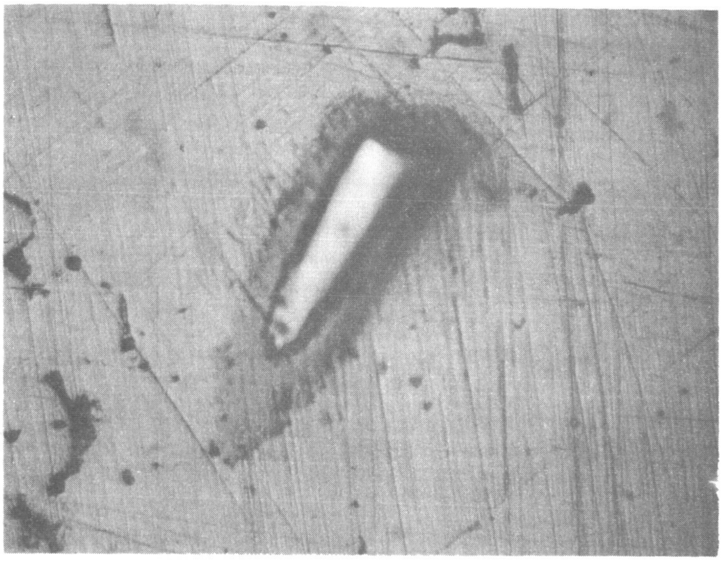
Metallographic examination of these samples following the life test disclosed the presence of a reaction zone around each molybdenum particle. The appearance of the bonded sample is shown in Figure 41a and 41b and the unbonded sample in Figure 42. The reaction appeared to be uniform through each sample and to be of greater extent in the bonded sample. If the reaction occurred during the life test, the reaction zone would be greater in those areas where the temperature was highest. Since this was not observed, it was concluded that the reaction is largely confined to the hot pressing and bonding operations when the element sees temperatures of approximately 1500°F. This is confirmed by the observation of greater reactions in the bond element.

The hot shoe bond zones appeared to be completely intact in both bonded samples. There was no evidence of cracking or extensive diffusion.

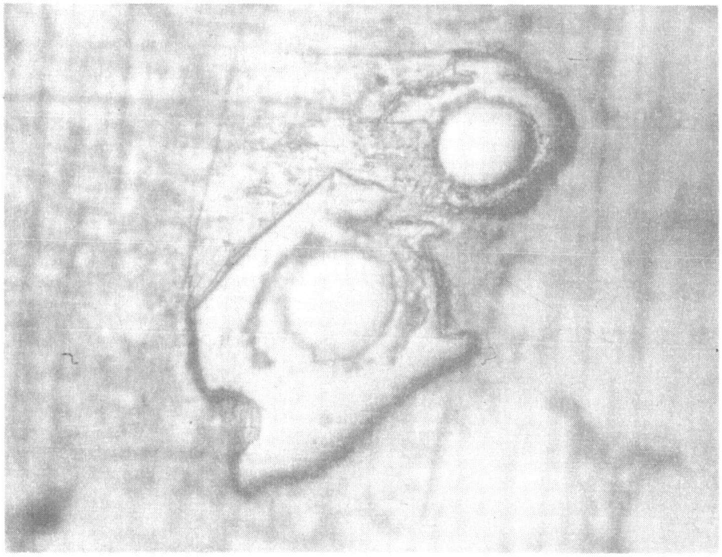
Results of the second test which ran 1745 hours were similarly erratic. Tested were three bonded TEG-2P elements each containing one weight percent molybdnum fibers and two unbonded elements, one being p-PbTe without additive and the other containing one weight percent molybdenum powders.

Performance curves for the three bonded elements are shown as Figures 43 through 45. The data are complicated by five thermal cycles, each of which resulted from a heater failure. However, the last 800 hours represent a continuous run typified by gradual but definite decline in power output for two of the elements and recovery from a sharp drop during the final thermal cycle for the third. Table IX includes the pre- and post-test thermoelectric properties of all five elements from this test. As with the 500 hour test property changes were erratic and were generally greater than can be explained by instrument variation. The only property that varied consistently was bond resistance which increased substantially in all elements.

All the hot side bonds were intact and appeared to be sound when examined metallographically. Two of the cold shoes bonds separated upon removal from the tester and when the third was examined metallographically cracks were observed within the lead telluride adjacent to the bond.



a) Near Hot Interface 520X



b) Near Cold Interface 520X

Figure 41. Bonded p-PbTe + 1% Mo Showing Reaction Zones After 500 Hour Life Test

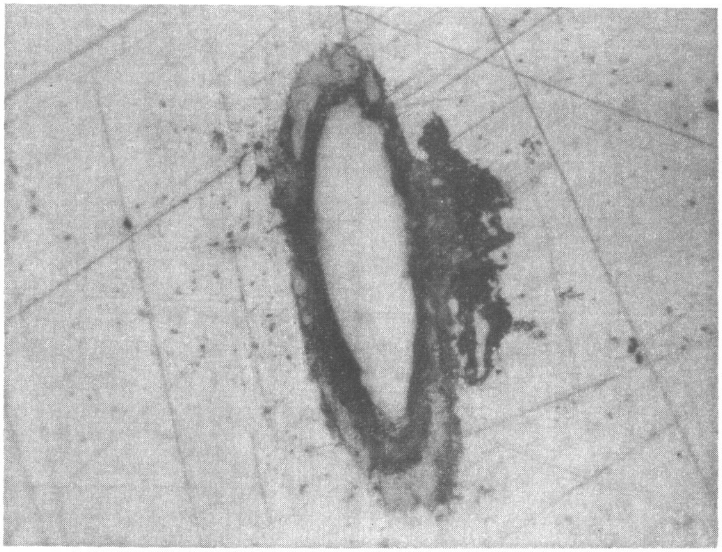


Figure 42. Unbonded p-PbTe + 1% Mo Element Showing Reaction Zone After 500 Hour Life Test (520X)

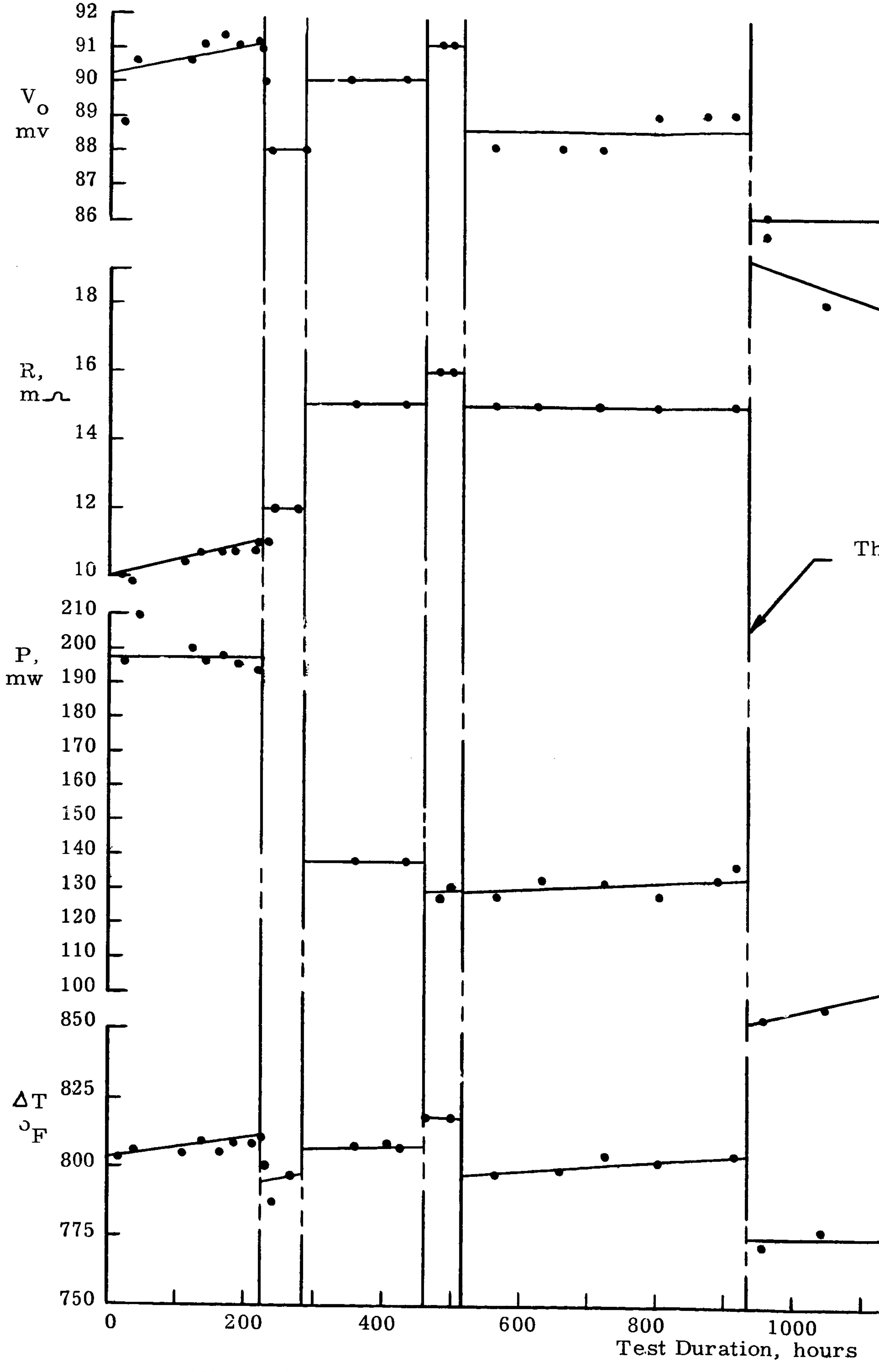
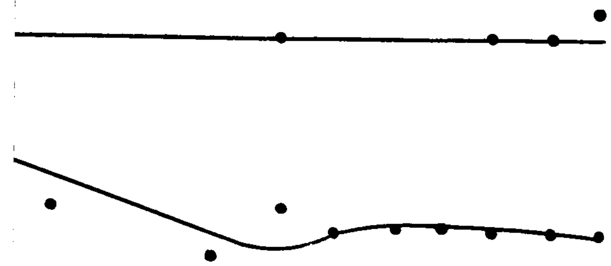
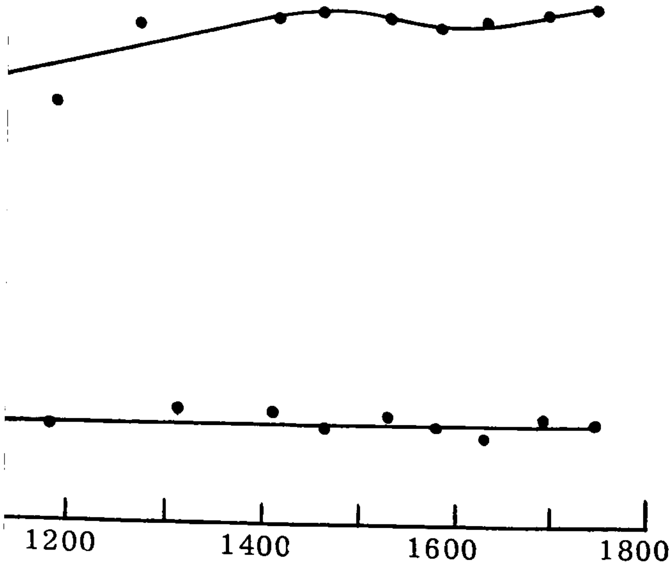


Figure 43. Performance of p-PbTe Element Number 269A



ermal Cycles
Typical



During 1745 Hour Life Test

VI-40-2

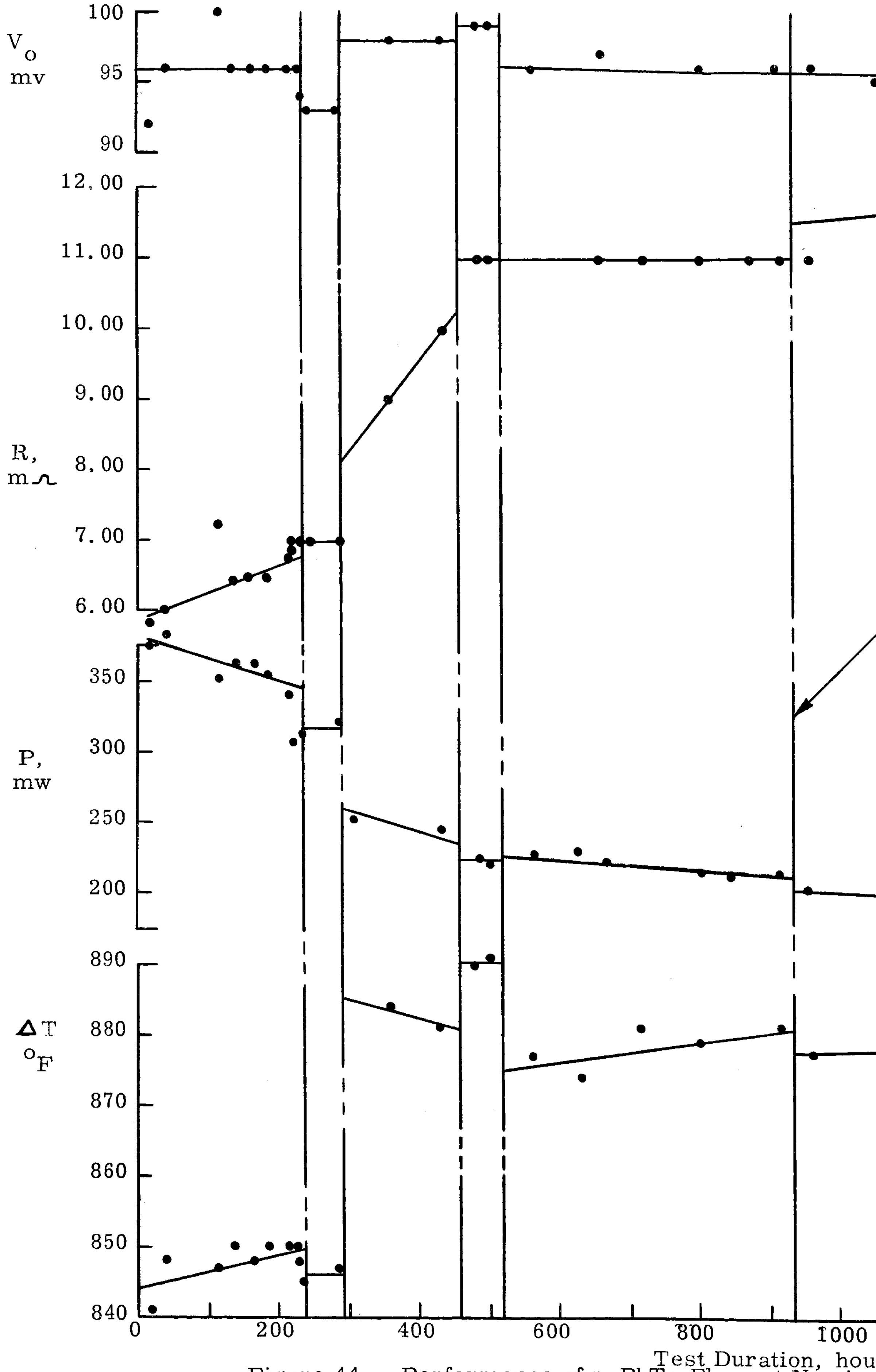
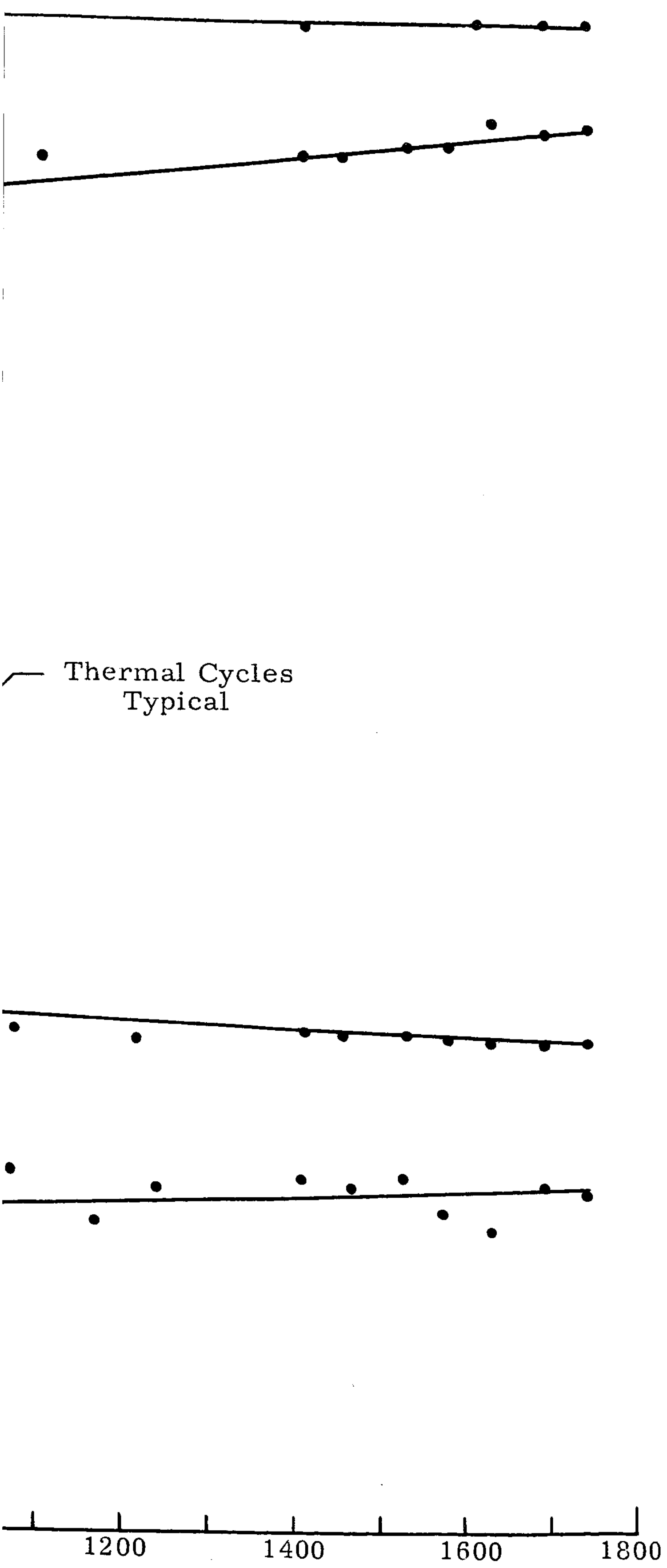


Figure 44. Performance of p-PbTe Element Number

VI-41-1



266A During 1745 Hour Life Test

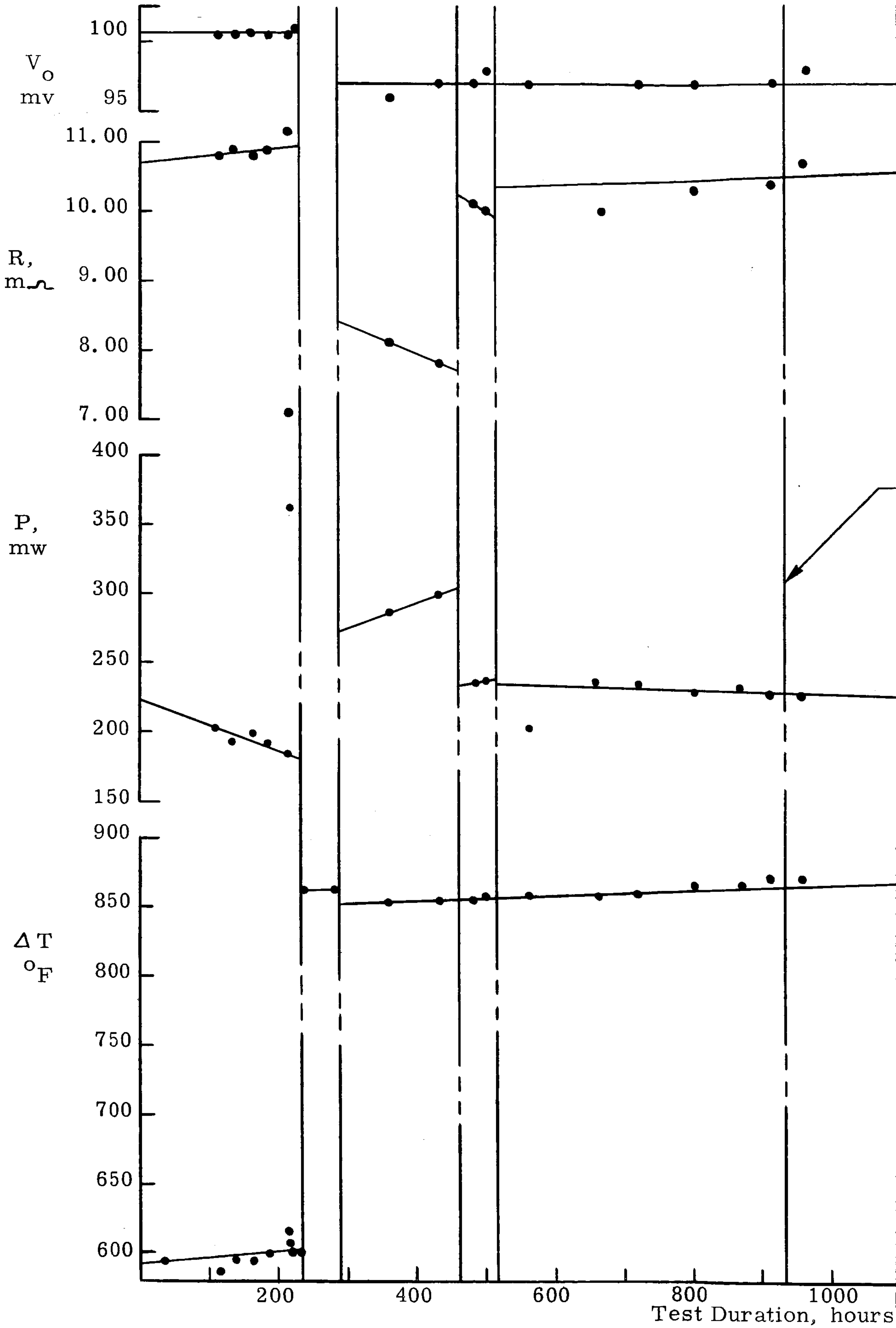
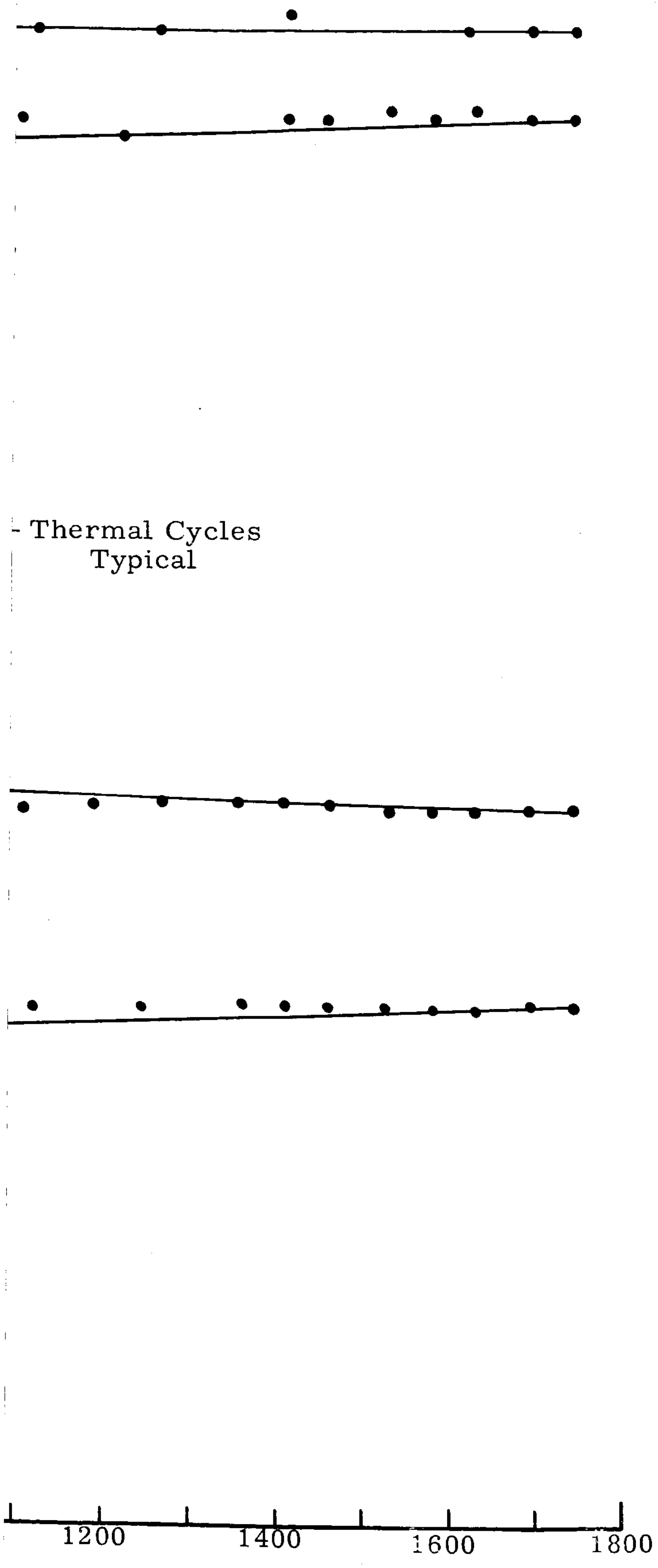


Figure 45. Performance of p-PbTe Element Number 26

VI 42-[redacted]-1



8A During 1745 Hour Life Test

VI-42-2

Sample No.	Composition	Bond Resistance μΩ			
		Before Test		After Test	
		Hot	Cold	Hot	Cold
500 Hour Test					
251	p-PbTe	-	-	-	-
253	p-PbTe + 1 w/o Mo fibers	105	115	210	1140
3M-2P-#2	TEGS-2P, p-PbTe	190	180	0	Separated
267	p-PbTe + 1 w/o Mo fibers	-	-	-	-
1745 Hour Test					
269	p-PbTe + 1 w/o Mo fibers	140	280	360	Separated
288	p-PbTe	-	-	-	-
266	p-PbTe + 1 w/o Mo fibers	90	70	1300	Separated
256	p-PbTe + 1 w/o Mo fibers	-	-	-	-
268	p-PbTe + 1 w/o Mo fibers	20	0	320	120

Table IX. Properties of p-PbTe Thermoelements Tested for 500 a

				Seel	
Room Temp. Resistivity μΩ in.			As Pressed		
As Pressed	As Bonded	After Life Test	Temp °C	S, μV/°C	% Deviation from 3M Values
148	-	116	94	95	-13.7
			153	140	-3.5
162	249	220	92	89	-14.4
			137	123	-8.2
163	162	192	96	82	-19.8
			150	123	-13.4
175	-	148	93	85	-18.2
			160	131	-12.1
244	244	198	87	91	-9.0
			148	127	-9.9
152	-	208	91	98	-4.9
			149	138	-2.8
208	267	276	81	84	-12.5
			144	124	-10.1
132	-	138	77	92	-2.1
			149	130	-8.5
190	275	389	81	90	-6.3
			138	126	-6.7

d 1745 Hours

eck Coefficient Data

As Bonded			After Life Test		
Temp°C	S, μV/°C	% Deviation from 3M Values	Temp°C	S, μV/°C	% Deviation 3M Values
-	-	-	98	118	+9.3
-	-	-	153	157	+9.0
80	97	+1.4	72	113	+25.6
124	127	+1.6	124	128	+2.4
69	87	-1.1	73	81	-11.0
121	122	-0.8	120	113	-7.4
-	-	-	103	96	-13.5
-	-	-	171	121	-22.4
77	88	-6.4	90	102	0
119	115	-5.7	147	148	+5.7
-	-	-	97	128	+19.7
-	-	-	148	176	+24.8
75	88	-4.4	102	81	-26.4
110	114	-0.8	153	112	-22.2
-	-	-	93	121	+16.4
-	-	-	155	160	+9.7
77	90	-4.2	79	93	-19.2
117	117	-2.5	119	128	+4.9

Two additional life tests are in operation. Of these, only one has accumulated sufficient time for the data to have significance. Three p-PbTe elements containing one weight percent molybdenum fibers and three containing no additive are included. During 1300 hours of steady operation power has declined at a fairly consistant rate to 5 to 25 percent below the initial figure. Power continues to decline but at a reduced rate of about 5 to 10 percent per 1000 hours. Initial power decline was somewhat greater in the elements containing additives, but at present all are behaving in a similar manner. This test and the other operating test of p-PbTe will be continued until at least 5000 hours are accumulated or a significant performance change indicates the advisability of termination.

VII. REFERENCES

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