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THERMOELECTRIC BONDING STUDY

Covering the Period from
1 June through 31 August 1965

September 30, 1965

Work Performed Under
NASA Contract NAS5-3973

Prepared for
National Aeronautics and Space Administration
Goddard Space Flight Center

HITTMAN ASSOCIATES, INC.
BALTIMORE, MARYLAND

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THERMOELECTRIC BONDING STUDY

Quarterly Progress Report
For the Period
1 June through 31 August 1965

I. INTRODUCTION

The objective of this program is to develop an understanding of the process by which lead telluride thermoelectric elements may be bonded to metal contacts. The nature and mechanisms of bond failures should be better understood if a successful, long-lived joint is to be achieved. In order for a thermoelectric generator to perform satisfactorily the element to shoe contacts, which are an integral part of the internal wiring and thermal path, must have low resistance to the flow of electricity and heat and must have reasonable mechanical strength. Further, these attributes must be maintained with minimal changes throughout the operating lifetime of the generator.

During the first phase of this program a systematic approach was applied to the selection of braze materials for use with p- and n-PbTe thermoelectric elements. Of the twenty or more braze alloys investigated only SnTe and titanium modified SnTe formed satisfactory bonds with little deleterious effect on the thermoelectric properties of the PbTe. Several shoe materials appeared useful and iron was chosen for continued study on the basis of its general acceptance for this application.

The above investigation demonstrated that two mechanisms are primarily responsible for the failure of PbTe to shoe braze joints. The first is poisoning of the thermoelectric element properties as a result of interdiffusion between the braze material and the PbTe. This may cause gross changes in electrical resistance and/or Seebeck coefficient of the thermoelectric and result in sharply decreased power output. The second mechanism of bond degradation is fracture caused by the thermal expansion mismatch between the thermoelectric and shoe materials. Unless these stresses are largely accommodated by deformation of a ductile braze in the interface, cracking of the weak PbTe at or near the braze joint will occur.

The current phase of the bonding study is continuing toward the achievement of a more complete understanding of the bonding of PbTe to metal shoes. The specific tasks include optimization of the process for bonding PbTe to iron contacts with a SnTe braze. The performance of bonded PbTe elements under typical generator operating conditions is being measured and comparisons made of degraded and failed samples with those that continue to perform without degradation. Evaluation includes electrical property measurements and metallographic study. Electron-probe microanalysis of samples is being performed in cooperation with NASA-GSFC.

Progress during the current quarter is reviewed in the following sections.

II. BRAZE PROCESS DEVELOPMENT

Braze process development during this quarter was concerned principally with n-PbTe. A number of bonds were made between Hittman produced p-PbSnTe (TEG-3P material) and iron shoes early in the period. It was found that successful joints could be made, but that fracture usually occurred in the PbSnTe near the bond interface. This is ascribed to the weakness of the material. A mechanically successful bond was made to a 3M produced PbSnTe element. Although the thermoelectric properties degraded significantly during the bonding operation, this element will be placed on life test.

The braze process described in the previous report (Reference 1) has continued to produce satisfactory results with n-PbTe. Experiments performed during this quarter show that braze wafer initial diameter has no significant effect on bond quality or element performance.

Several elements were bonded by the standard process 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. These elements were 3/8 inch in diameter. Braze wafers were 1/4 inch or 3/8 inch in diameter. In order to closely duplicate the configuration of our production element, the diameter of each shoe was reduced to the element diameter for a distance of about 1/4 inch along the length. One such element is shown in Figure 1. These elements were tested in torsion and the stress for failure was measured. All fractures occurred at the braze joint and, as can be seen from Table 1, the results were reasonably consistent for such brittle materials and very close to those reported in Reference 2 for 1/2 inch n-PbTe elements.

Two series of tests were performed in which bonded elements sealed in vycor capsules under argon atmosphere were held at 920°F for 100 hours. The changes in thermoelectric properties resulting from the test were small and were probably within the experimental variations of the test equipment. Resistance data are shown in Table 2 and Seebeck coefficient changes are given in Figure 2. There was no difference between samples brazed with 1/4 inch or 3/8 inch braze wafers so all data are reported together. Metallographic examination showed some cracks present in the PbTe and/or the braze zone. These did not appear to affect the element performance during the short time test.

Reference 1: Thermoelectric Bonding Study - Quarterly Progress Report, Covering the Period from 1 March through 31 May 1965. HIT-170

Reference 2: Thermoelectric Bonding Study - Summary Report. HIT-163 (March 1965)

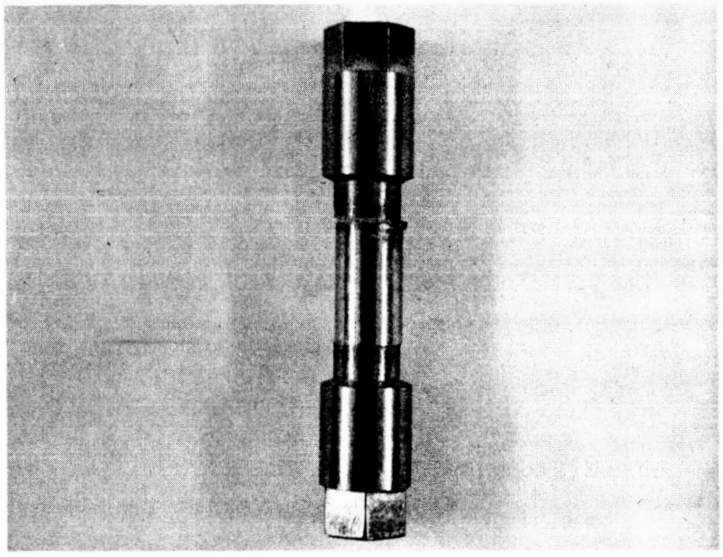


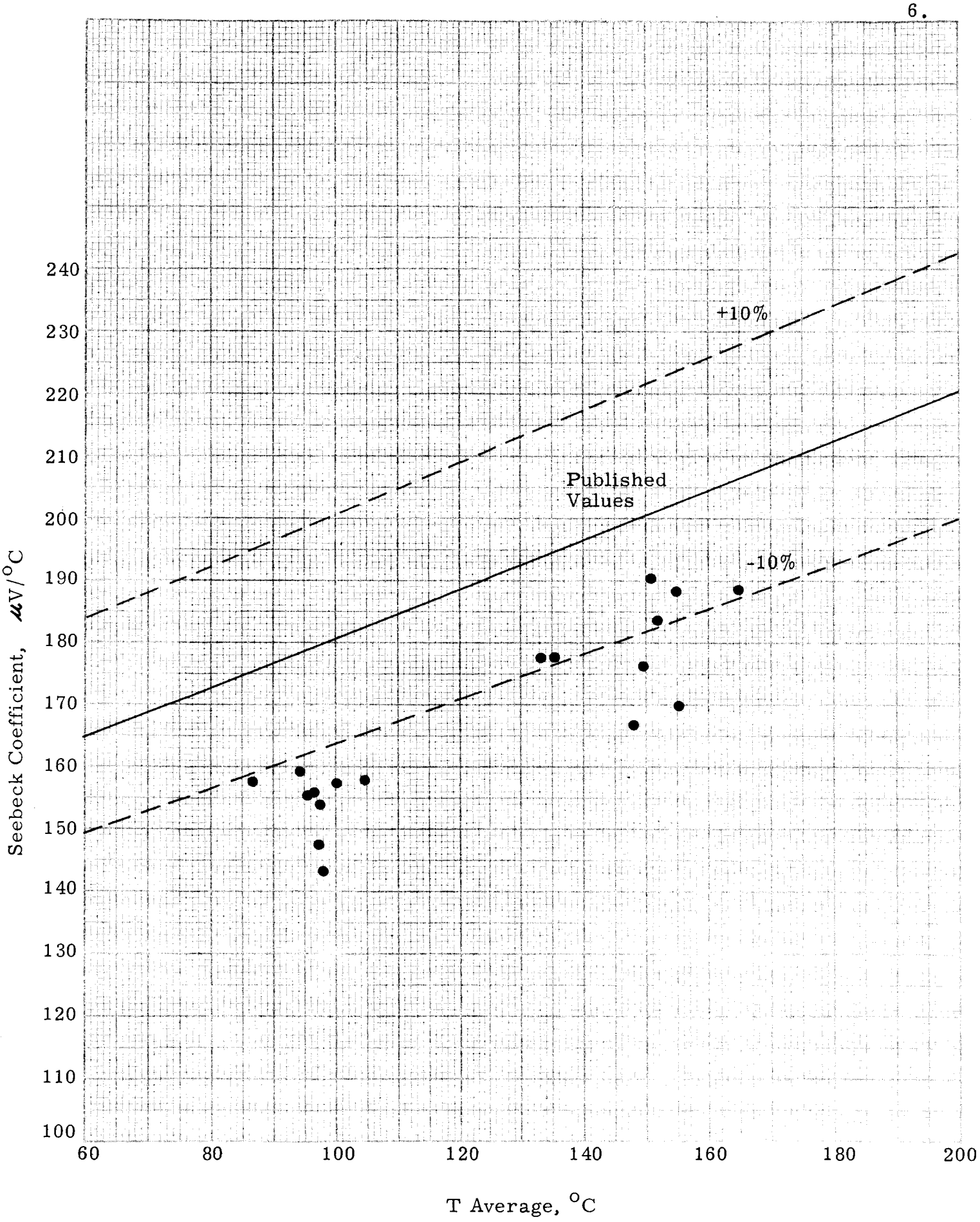
Figure 1 Torsion Test Specimen of PbTe Bonded to Iron Shoes

Table 1 - Results of Torsion Tests on n-PbTe

Braze Wafer Diameter (inches)	Bond Resistance ($\mu\Omega$)	Torsion Strength (psi)
1/4	230; 240	900
1/4	60; 40	1450
1/4	85; 230	800
1/4	130; 140	1150
3/8	70; 130	1150
3/8	160; 230	120 (poor bond)

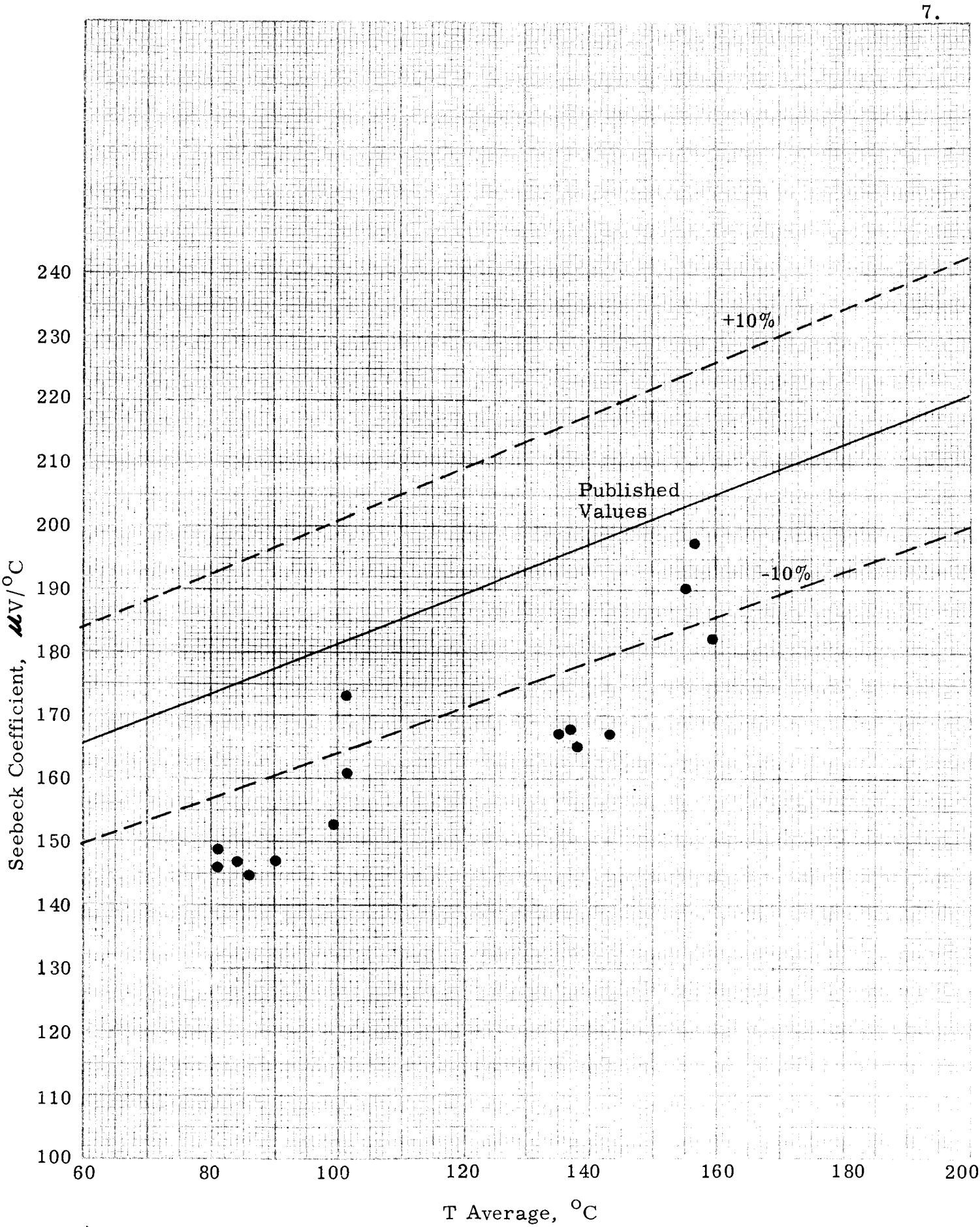
Table 2 - Change in Resistivity of n-PbTe After 100 Hours at 920°F

Sample #	Initial Resistivity, $\mu\Omega$-in	Final Resistivity, $\mu\Omega$-in	Percent Change
157	195	184	-5.6
150	190	175	-7.9
149	187	176	-5.9
141	183	194	+6.0
148	162	179	+10.5
162	159	187	+11.3
164	168	168	0
165	190	187	-1.6
Average	179	181	+1.1



a) As Bonded

Figure 2. Effect of 100 Hour Isothermal Test on the Seebeck Coefficient of Bonded n-PbTe



b) After Test

Figure 2. Continued

III. SAMPLE FABRICATION

Thermoelectric element production continued during the quarter in order to provide samples for bonding and life tests. The hot pressing procedure employed was described in detail in Reference 1. About one-hundred PbTe thermoelectric elements, mostly n-type, were fabricated during the period. TEG-2N and TEG-3P powders purchased from 3M Company were the raw materials.

The room temperature electrical resistivity and low temperature Seebeck coefficient of each element was measured. The results are shown in Figure 3 which plots the deviation from the published property values for each element. In general the properties obtained are about ten percent below the published values for both parameters. This is consistent with the test results obtained by other investigators (Reference 3) with 3M supplied materials.

The few p-type PbSnTe samples produced during the quarter had the same poor thermoelectric properties obtained earlier in the program. 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 more recently and demonstrated the degraded properties typical of our most recent 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 recently produced sample. The tentative conclusion drawn from this test is that the poor properties observed in recent production is the result of micro-scale 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.

Reference 3: Discussion with M. Weinstein, Tyco Labs, and J. Mueller, BMI August 1965.

Turn page for Figure 3.

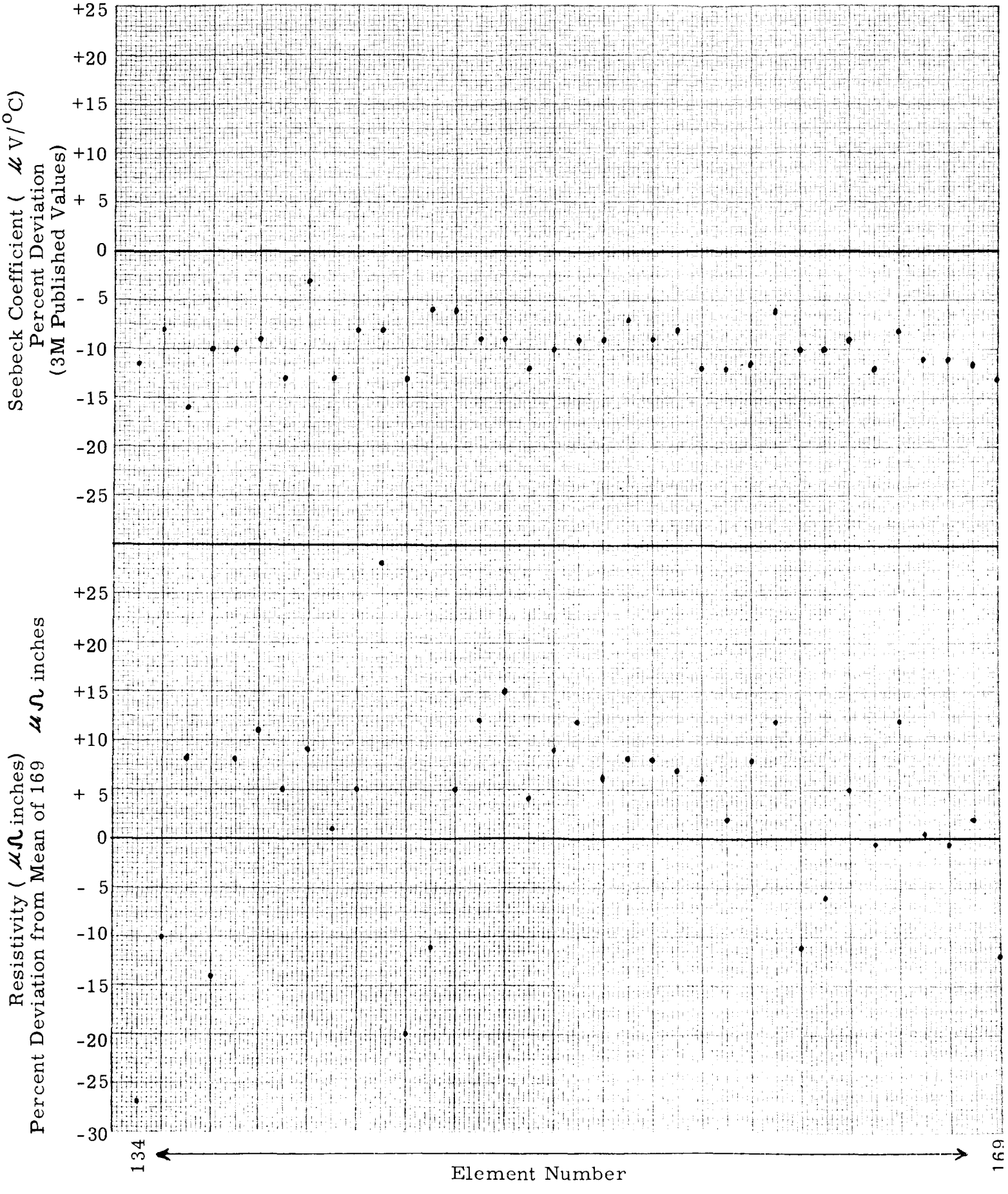
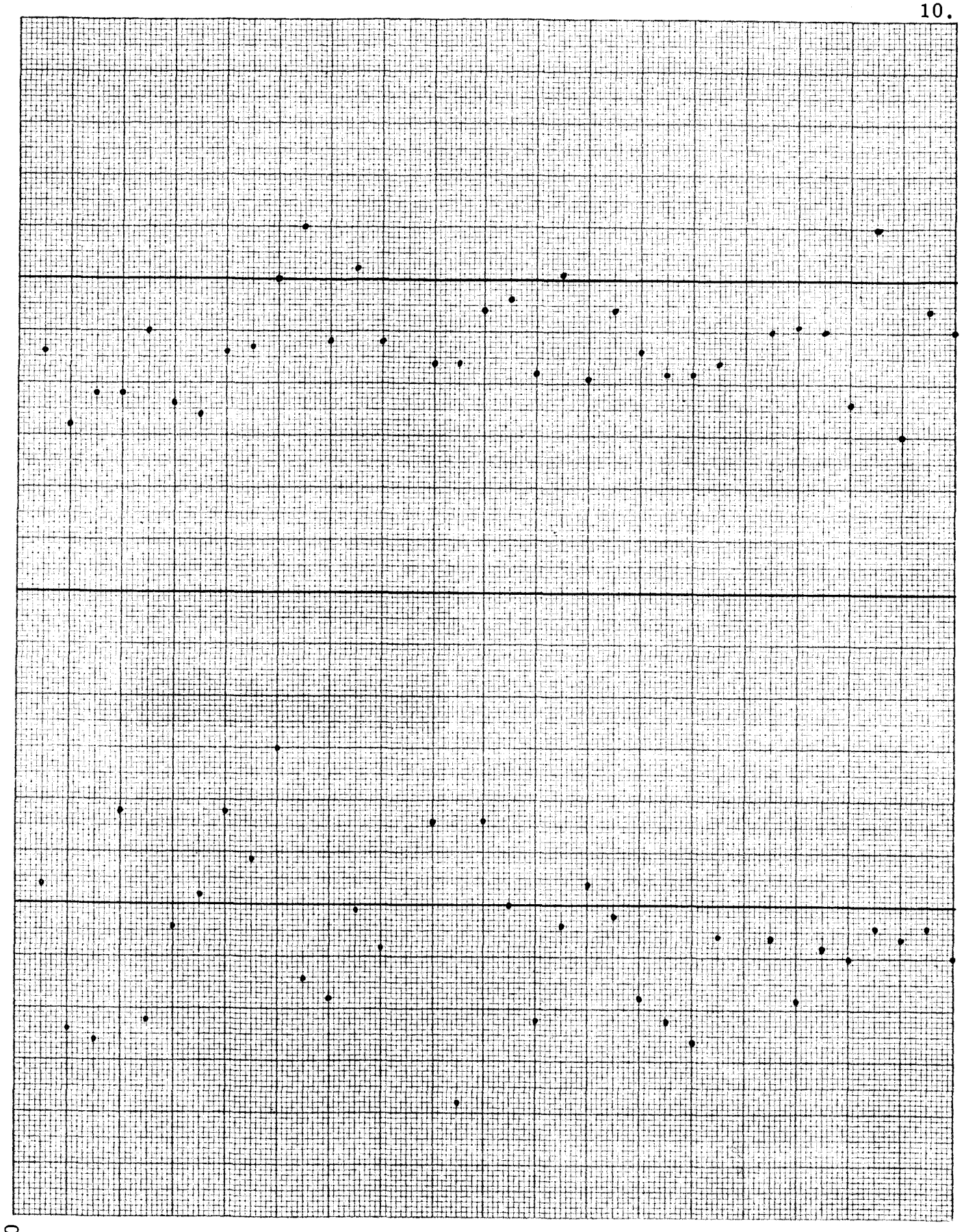


Figure 3. Seebeck Coefficient and Resistivity of n-PbTe Thermoelement Produced During June - August, 1965



170 ← Element Number → 206

IV. LIFE TEST EQUIPMENT

The thermoelectric element life testing device has been completed and placed in operation. This device, which is described in detail in the preceeding report in this series, (Reference 1) can test twenty-four individual thermoelectric elements at hot junction temperatures up to 1000°F and ΔT of approximately 700°F.

Three tests were carried out during the quarter of one hundred, two hundred, and five hundred hours duration. These experiments served several purposes. First, they were used to shake down and evaluate the testing device and procedures. Second, they served as a qualification test for the braze process and third, they enabled us to acquire data on the performance of bonded thermoelectric elements.

The equipment performed satisfactorily during the above tests. The only problem was encountered in measuring the resistance of the test elements. It was found that the resistance of the measuring circuit was slightly greater than that of the element making exact measurement impossible. Approximate measurements were made and are reported along with other life test data in the following section. The equipment has been modified to correct the problem in the future.

V. LIFE TESTS OF THERMOELECTRIC ELEMENTS

During the quarter, three tests were made in the life test apparatus. These are discussed in this section.

All elements tested were 3/8 inch diameter n-PbTe made at Hittman Associates from 3M type TEG-2N powder. The elements, one of which is pictured in Figure 4, were bonded to iron shoes. The hot shoe bond was made with SnTe-Ti by the process described in Reference 1. The long extension on this shoe passes through a hole in the heater block and allows connections to copper conductor wire to be made at some distance from the thermoelectric material. The cold shoe was soldered to the PbTe with pure tin.

The first test was a ninety-six hour shakedown run for the test apparatus. Three n-PbTe elements were placed in test chamber No. 1 under argon atmosphere. The heater block temperature was controlled at 1000°F. Hot shoe temperatures ranged from 957° to 1006°F. A greater temperature 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 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 the observed degradation. Subsequently, the outlet valves were replaced with a new type that permits gas flow only in one direction.

The principal objective of the other two tests was to obtain operating data on thermoelectric elements while increasing our familiarity with the test equipment and procedures. These tests were a 500 hour run of six elements in Unit No. 1 and a 200 hour run of five elements in Unit No. 2. In both cases, the tests ran smoothly. The hot junction temperature was not uniform across all elements. With the heater block temperature controlled at 1000°F, the temperature varied from about 890° to 970°F in Unit No. 1 and 890° to 950°F in Unit No. 2. Figure 5 shows the hot junction temperature profiles for these units. The cold junction temperatures were relatively uniform, but were lower in Unit No. 2, largely because of the greater care taken to assure good thermal contact between the cold shoes and the water cooled contacts.

Figures 6 through 11 record the performance of the elements tested for 500 hours. A gradual increase in T, due both to increases in T_h and decreases in T_c, was observed over the first 200 to 300 hours which resulted in increases in voltage and power. The cause of this change in temperature is not clear. The results of the 200 hour test are shown in Figures 12 through 16. Temperature and voltage were more uniform. The power measurements on all elements were made near, but not at, matched load conditions. No apparent degradation was observed on any samples. 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 3 and the Seebeck coefficient data in Figure 17.

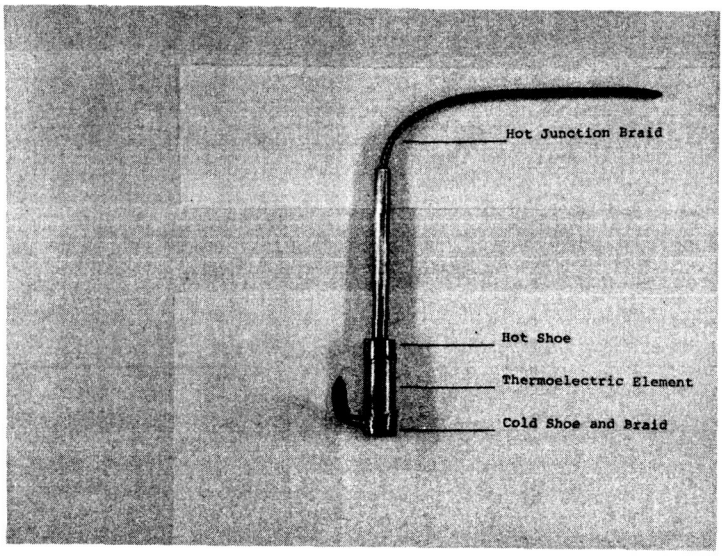


Figure 4 Lead Telluride Thermoelectric element for use in Life Test Apparatus

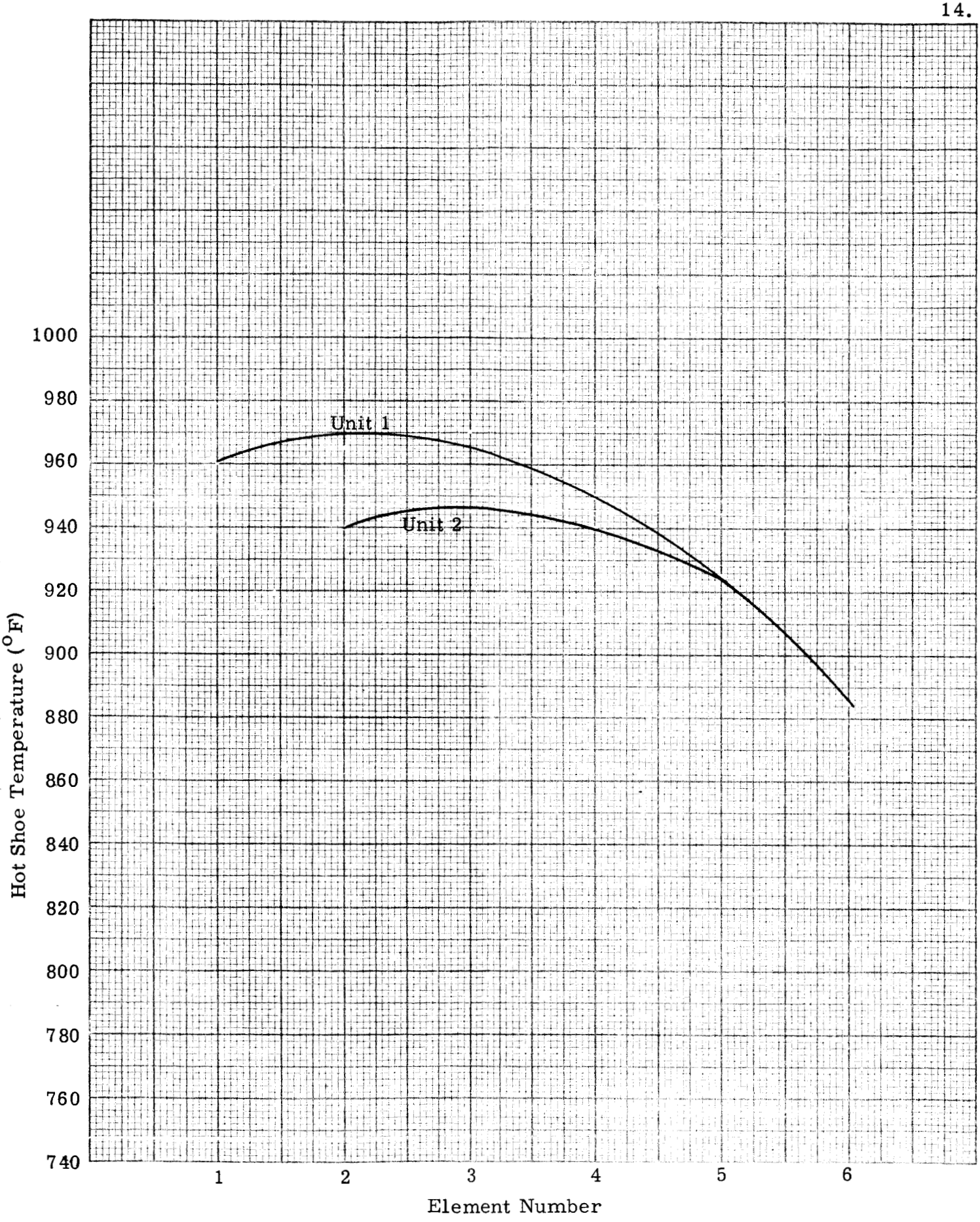


Figure 5. Hot Junction Temperature in Tester Units 1 and 2
(Controller set at 1000°F)

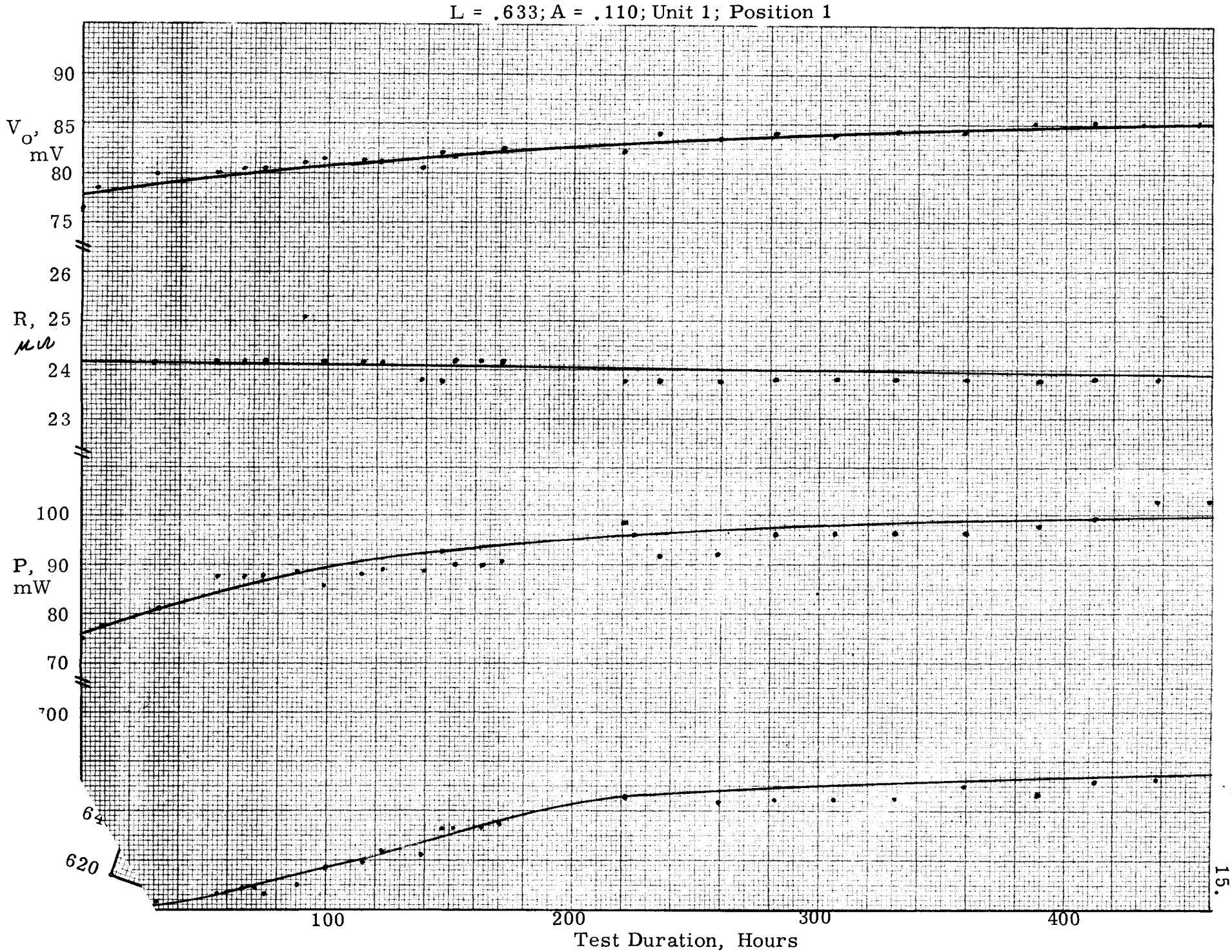


Figure 6. Peformance of PbTe Element No. 90B During 500 Hour Test

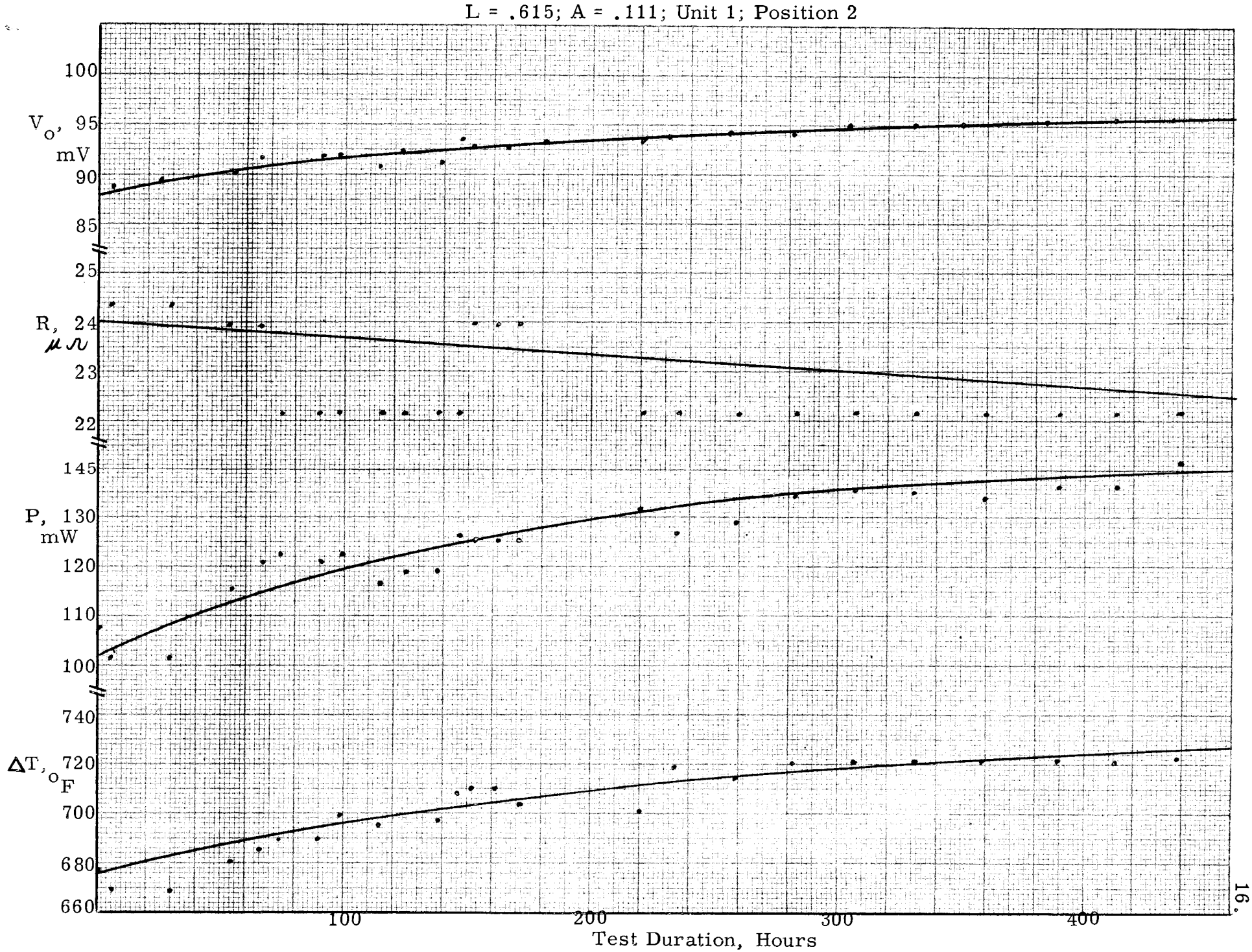


Figure 7. Performance of PbTe Element No. 93B During 500 Hour Test

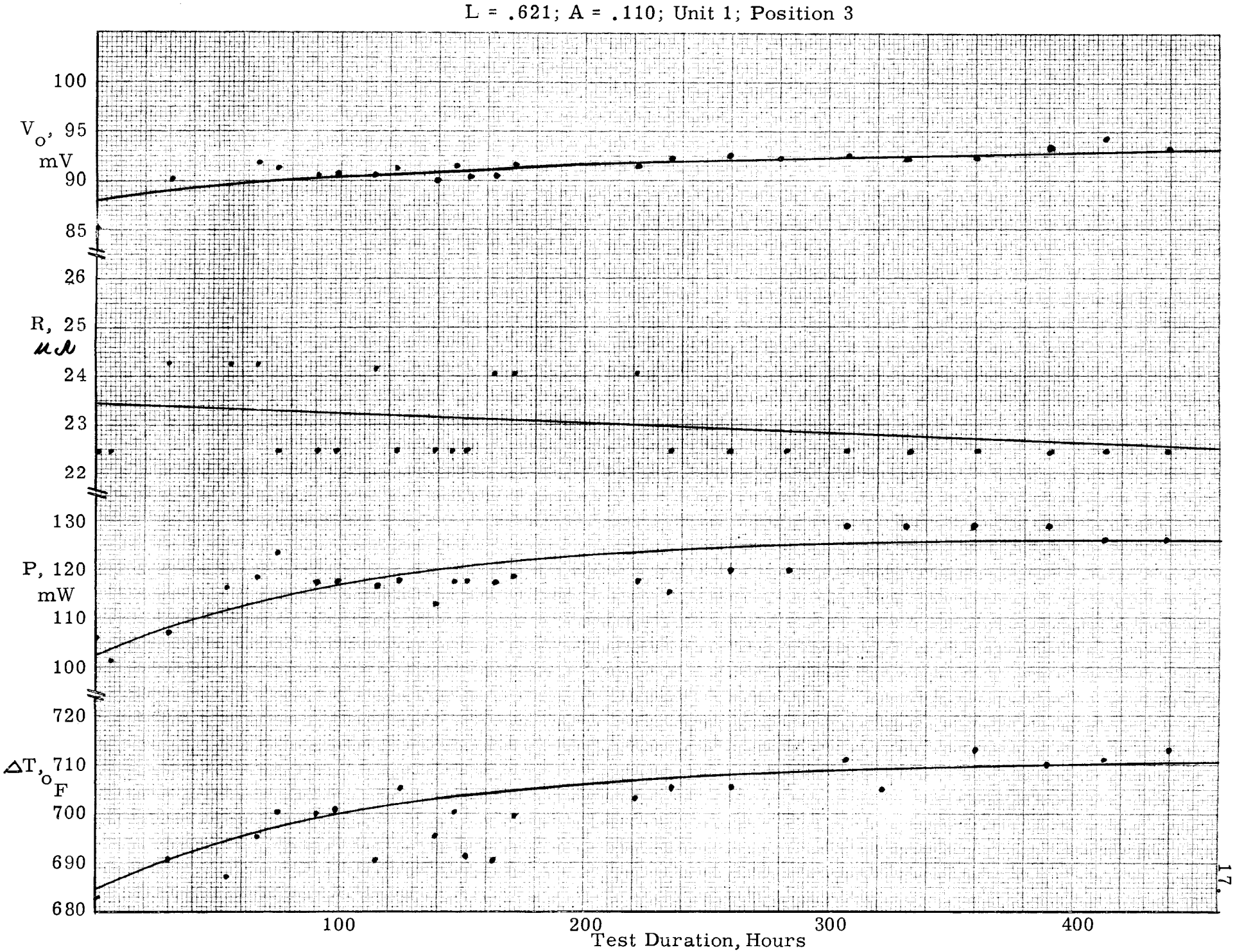


Figure 8. Performance of PbTe Element No. 82B During 500 Hour Test

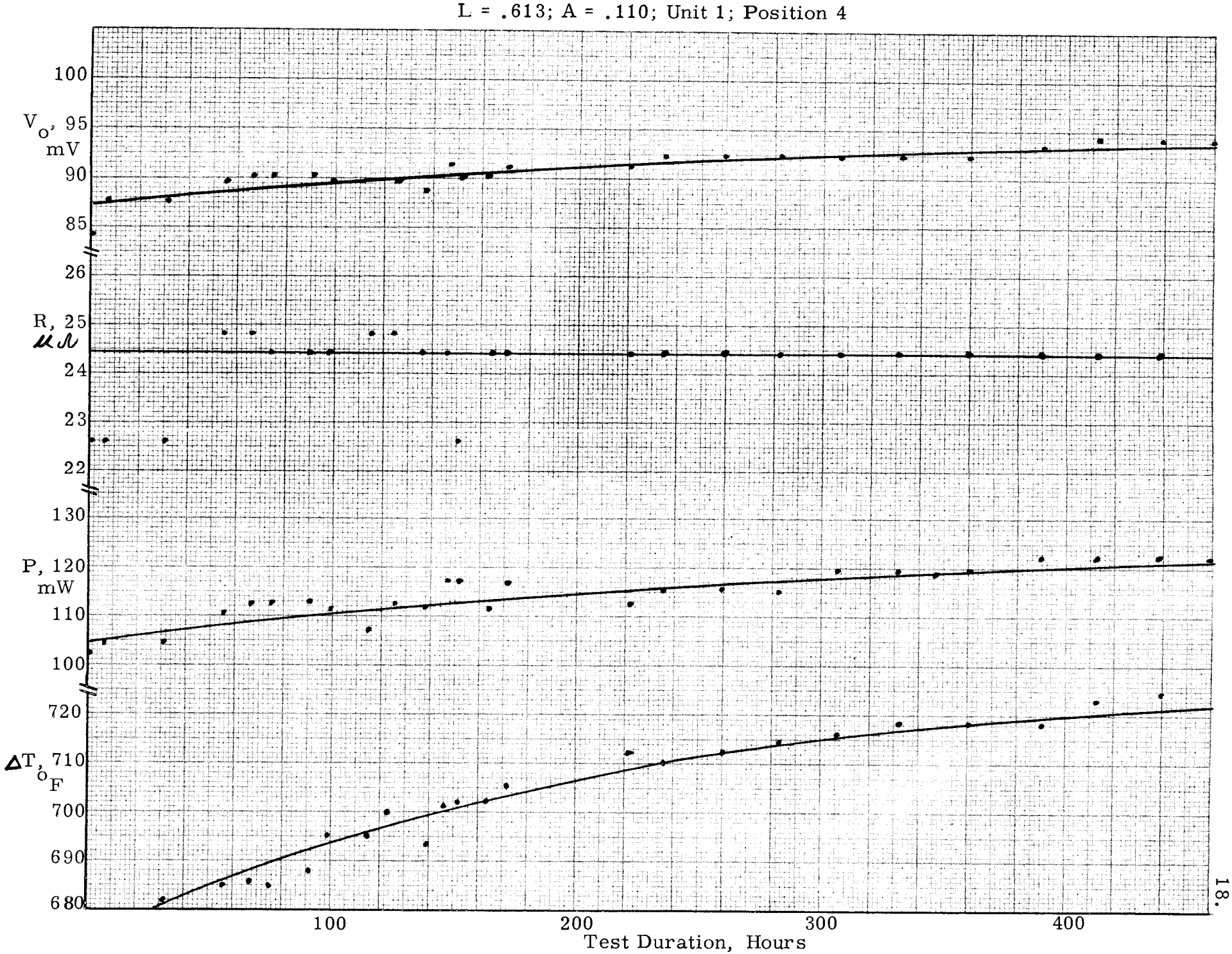


Figure 9. Performance of PbTe Element No. 84B During 500 Hour Test

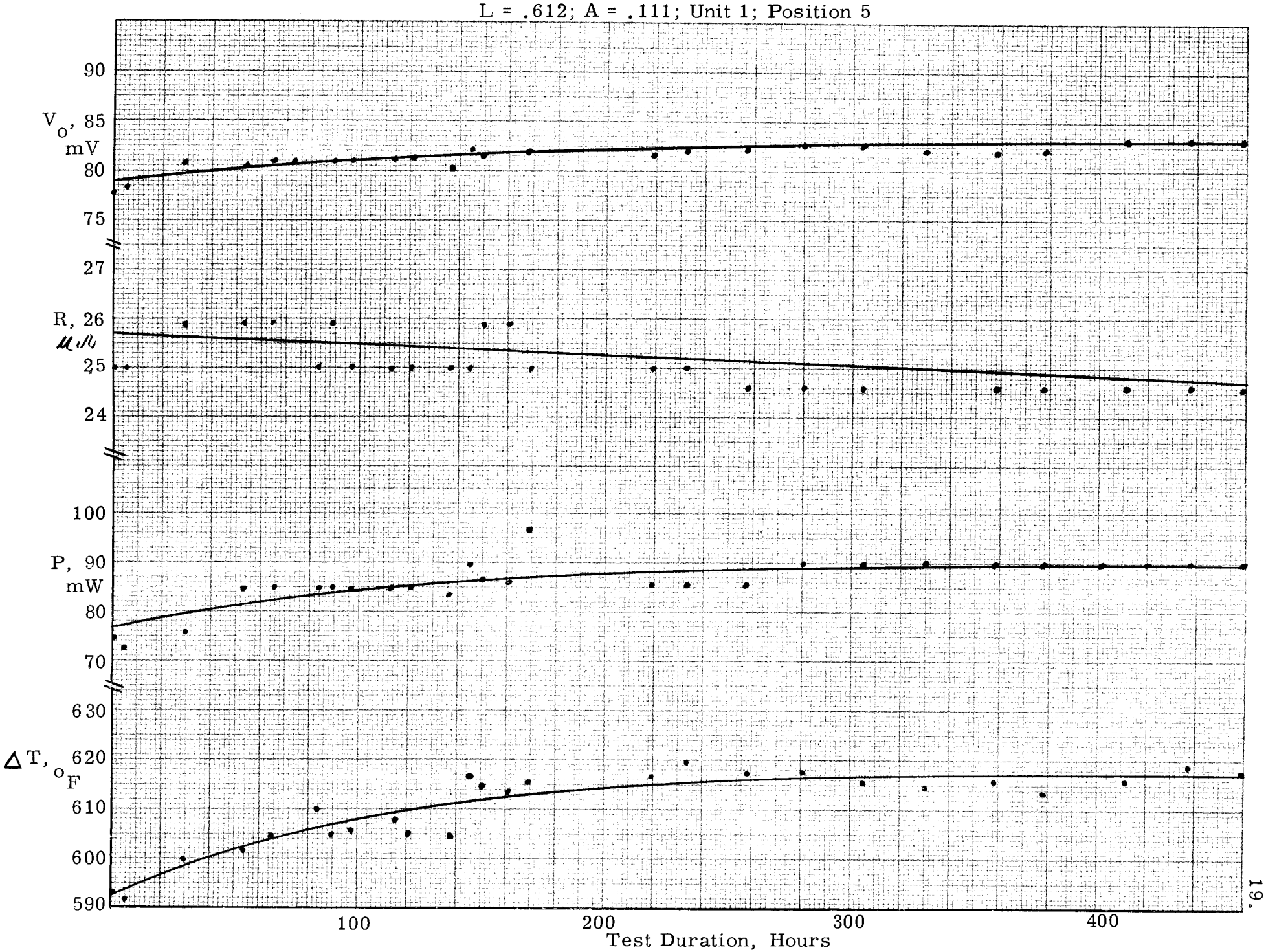


Figure 10. Performance of PbTe Element No. 85B During 500 Hour Test

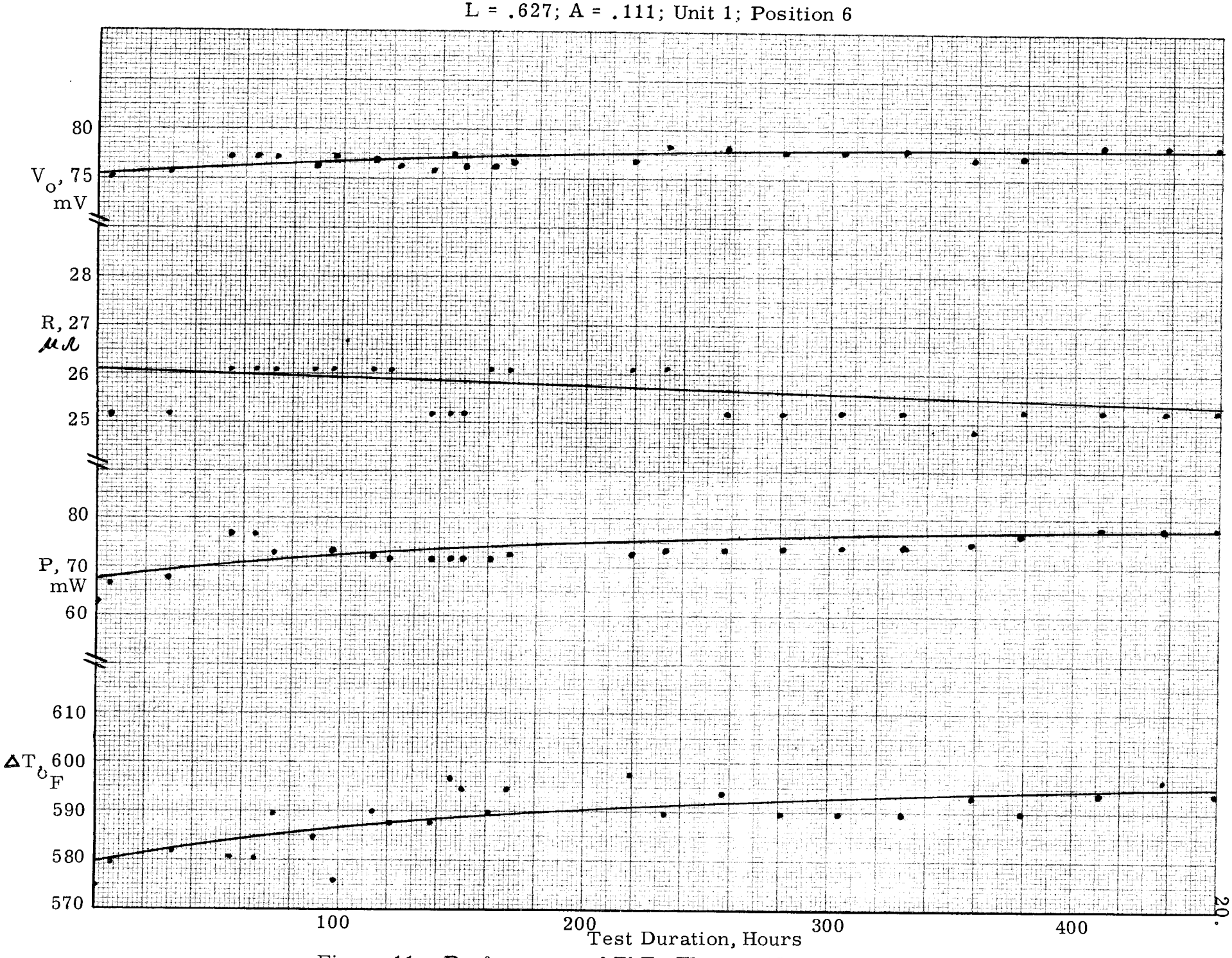


Figure 11. Performance of PbTe Element No. 87B During 500 Hour Test

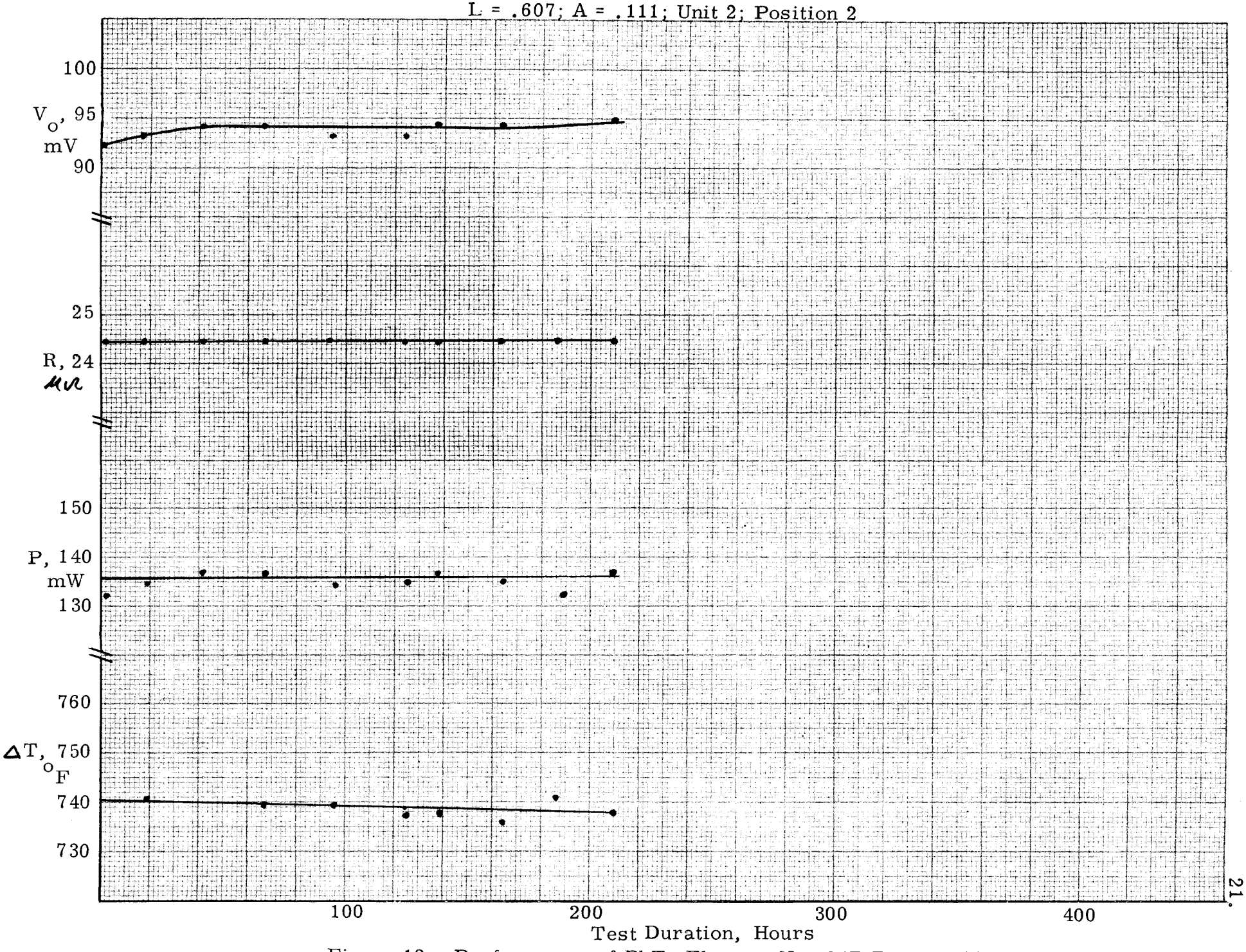


Figure 12. Performance of PbTe Element No. 94B During 200 Hour Test

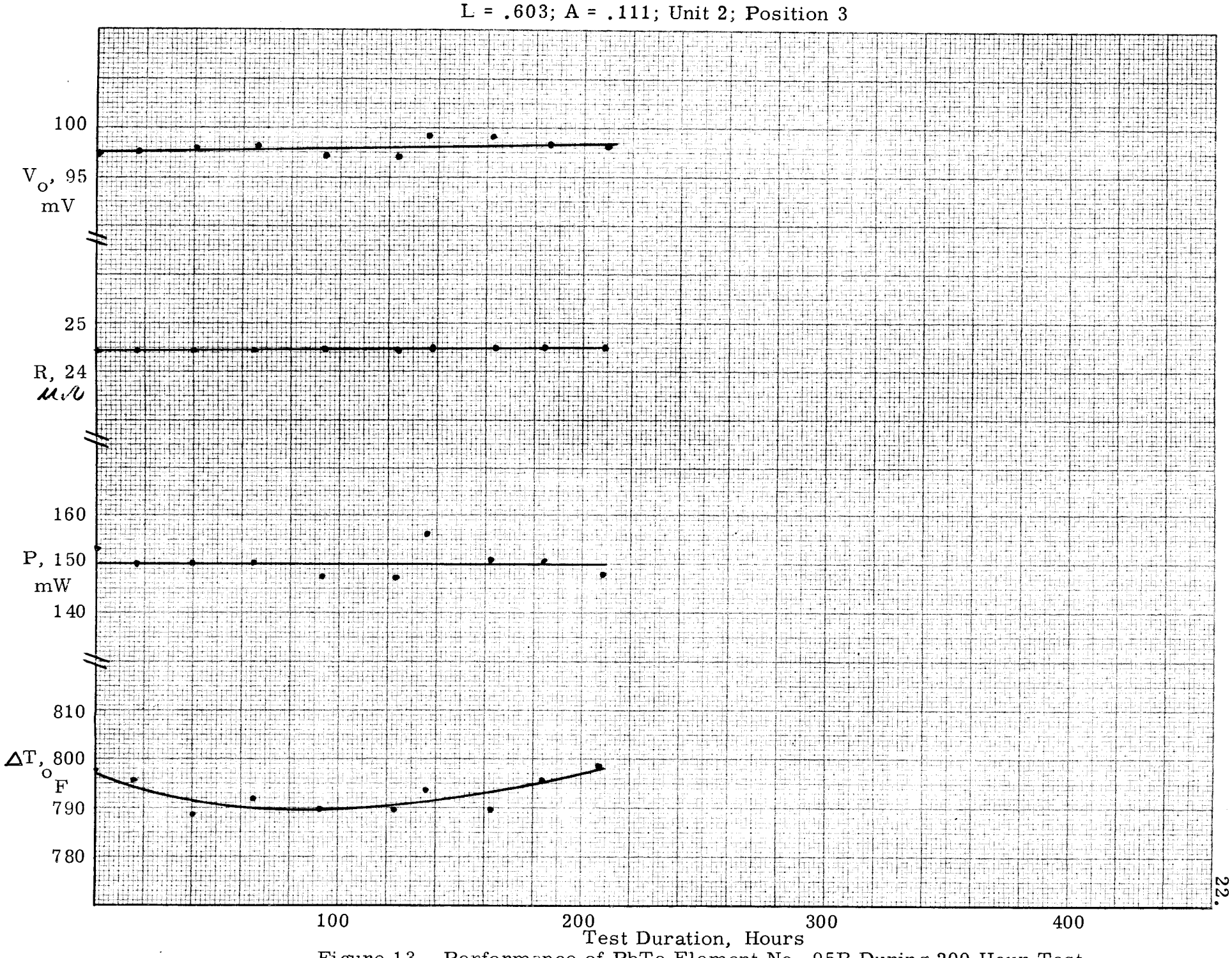


Figure 13. Performance of PbTe Element No. 95B During 200 Hour Test

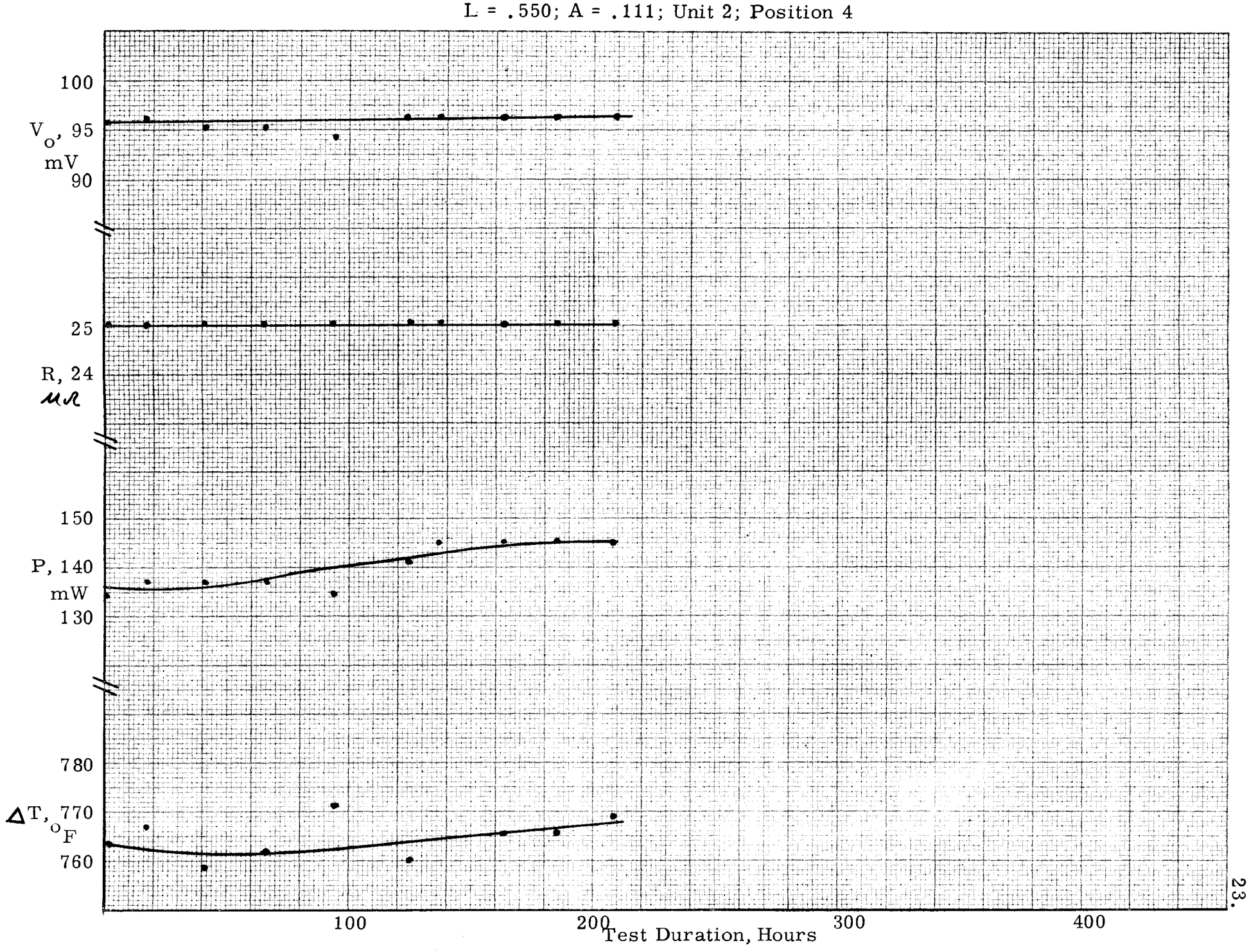


Figure 14. Performance of PbTe Element No. 97B During 200 Hour Test

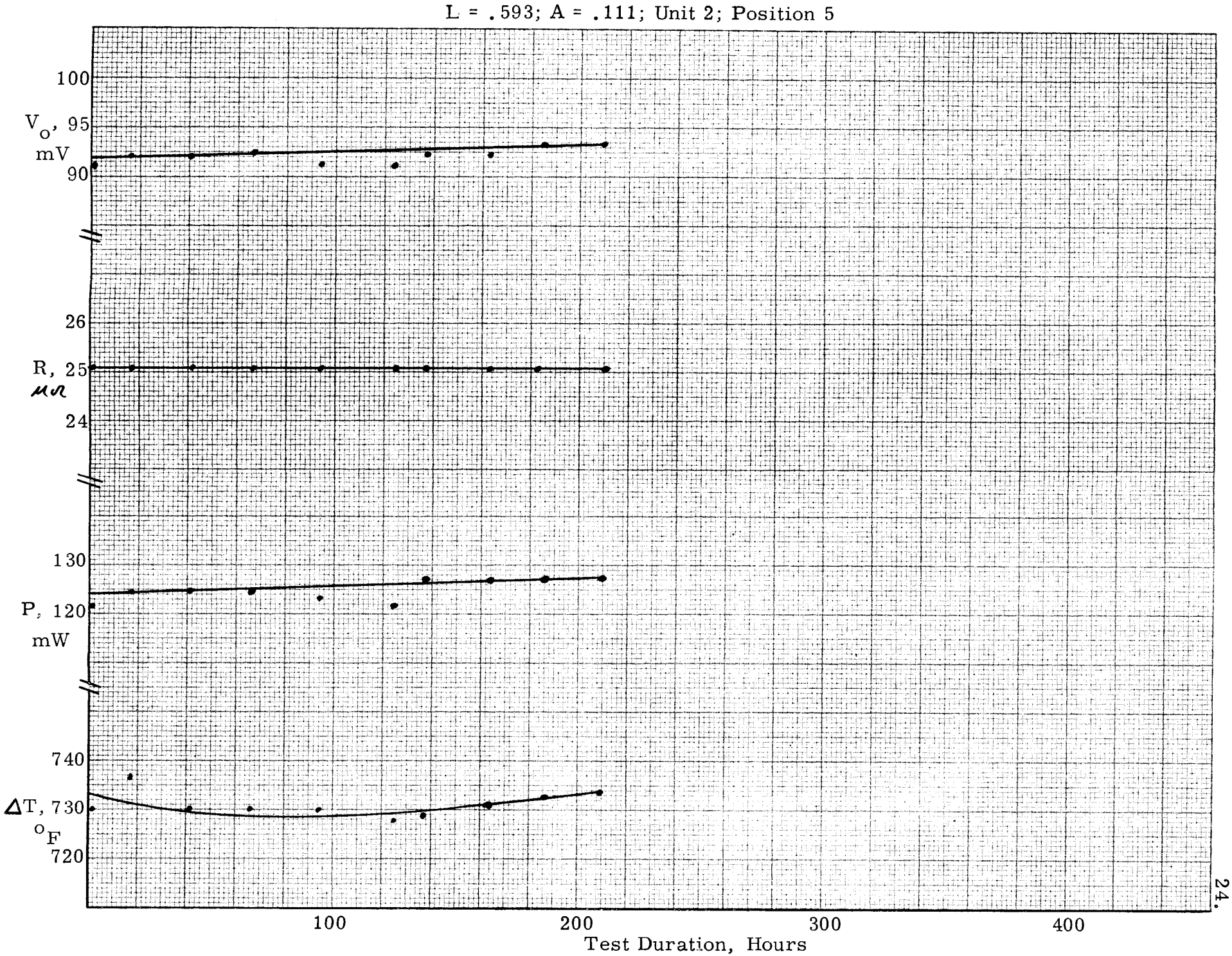


Figure 15. Performance of PbTe Element No. 98B During 200 Hour Test

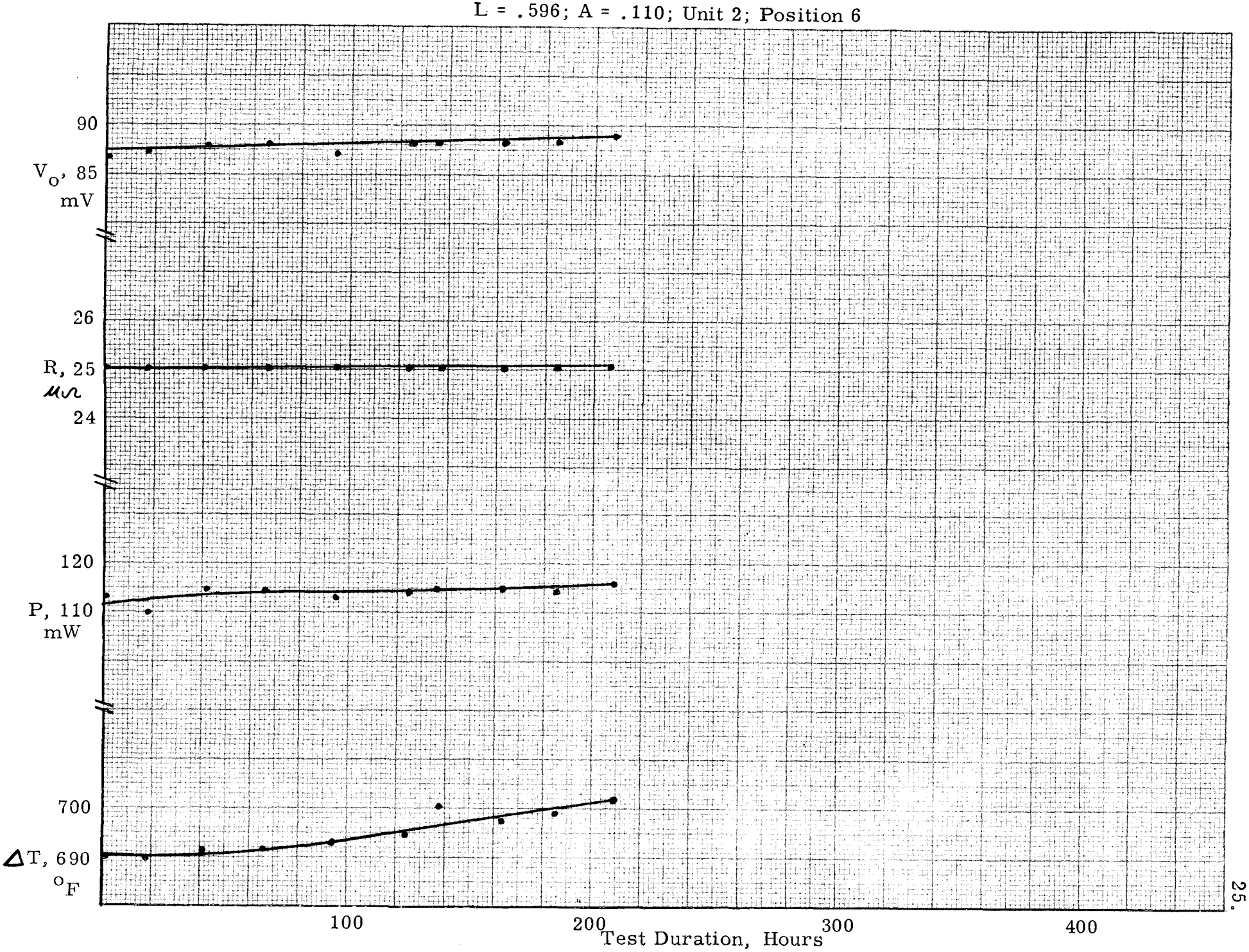
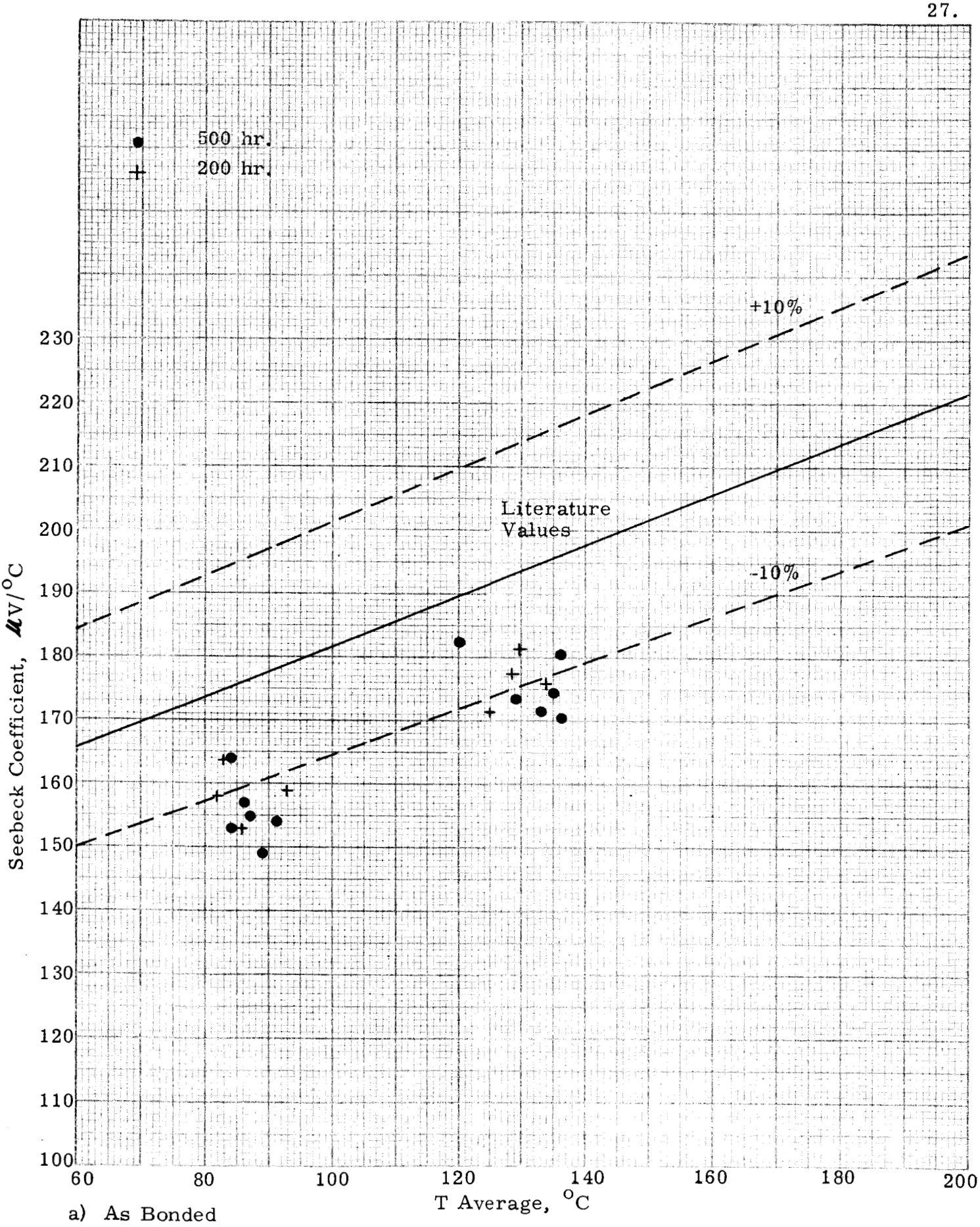


Figure 16. Performance of PbTe Element No. 100B During 200 Hour Test

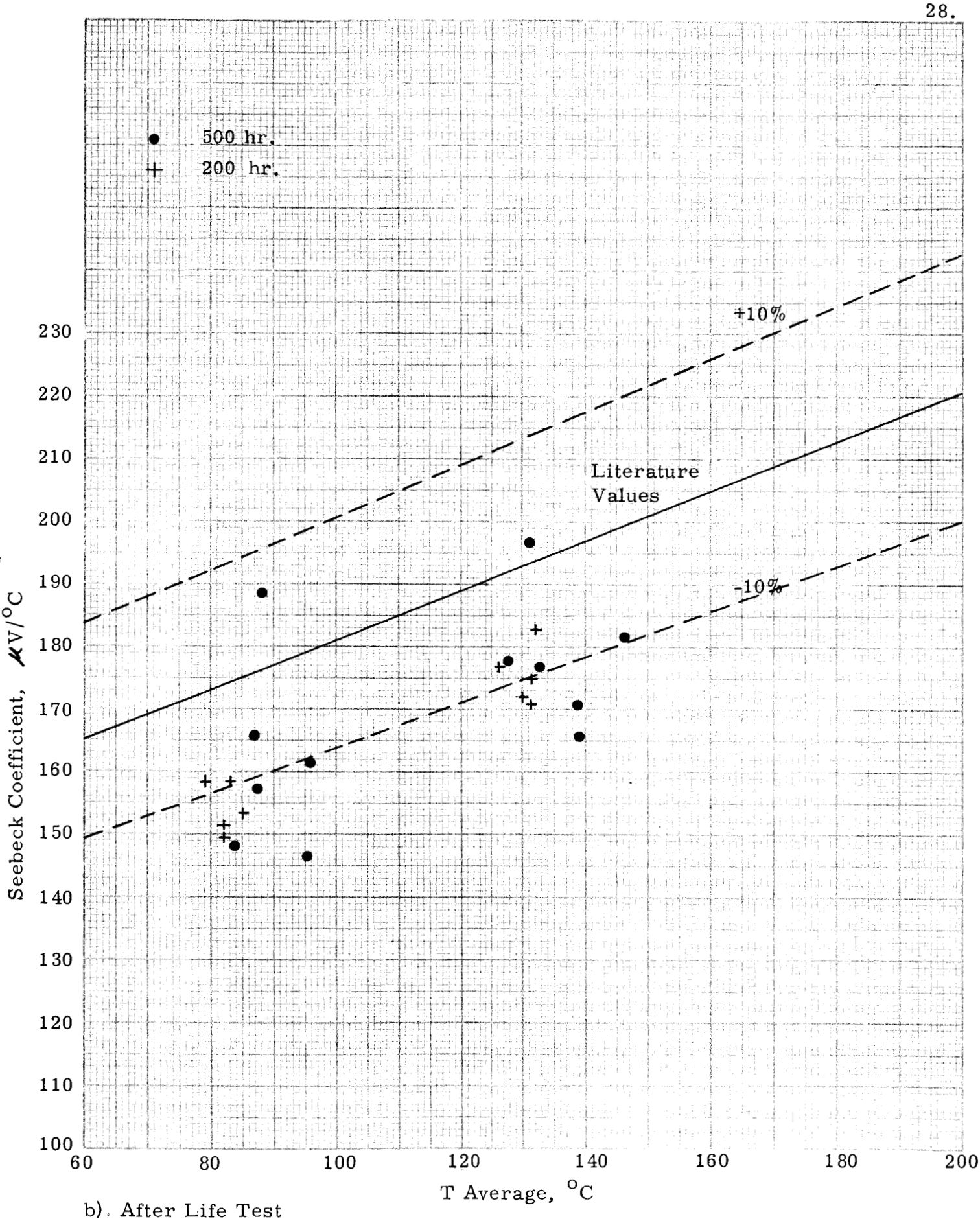
Table 3. Effect of 200 and 500 Hour Life Tests on Electrical Resistivity of n-PbTe

Sample No.	Test Time Hr.	Hot Shoe Bond Resistance, μΩ Before Test	Hot Shoe Bond Resistance, μΩ After Test	PbTe Electrical Resistivity Before Test μΩ in.	PbTe Electrical Resistivity After Test μΩ in.	% Change
82B	500	75	0	169	166	-1.8
84B	500	0	60	175	182	+4.0
85B	500	0	0	179	197	+10.1
87B	500	0	195	176	170	-3.4
90B	500	38	50	180	190	+5.6
93B	500	80	40	171	176	+2.9
Average				175	180	+2.9
94B	200	110	190	177	178	+0.6
94B	200	120	Broke	167	174	+4.2
97B	200	290	260	181	174	-3.9
98B	200	50	60	173	171	-1.2
100B	200	110	65	170	176	+3.5
Average				174	175	+0.6



a) As Bonded

Figure 17. Effect of the 200 Hour and 500 Hour Life Test on the Seebeck Coefficient of Bonded n-PbTe

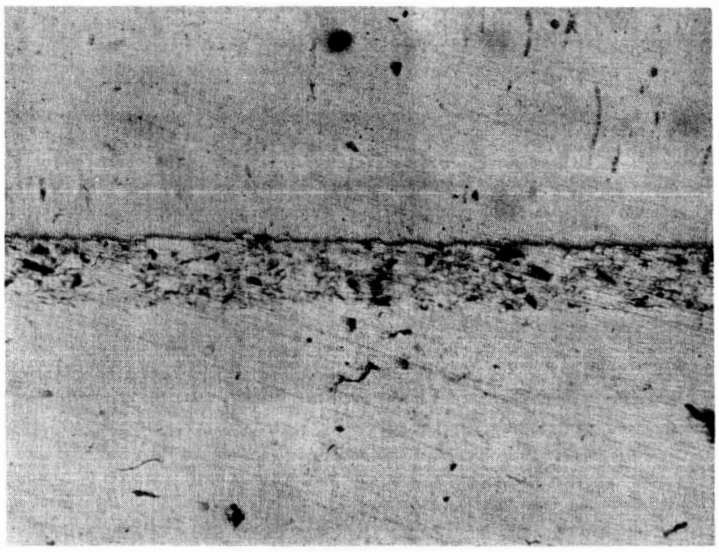


b). After Life Test

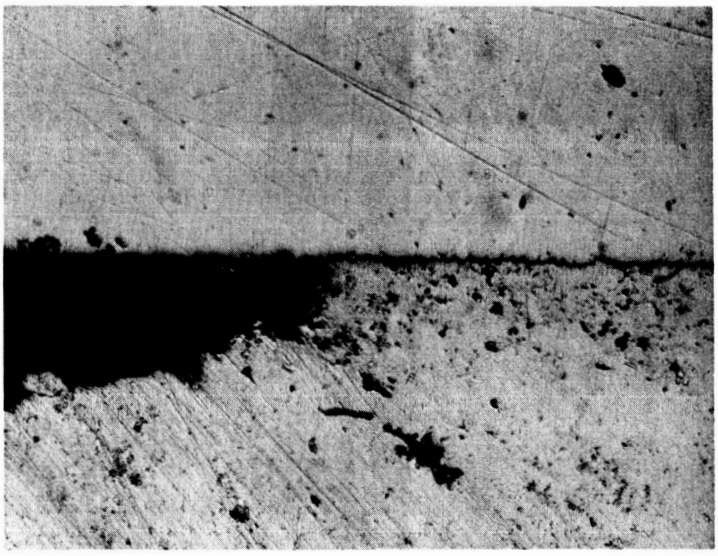
Figure 17. Continued

All the hot shoe bonds were strong and none broke during removal from the tester, although one bond from the 200 hour test separated during later handling. Four cold shoe bonds from the 500 hour test did separate upon removal from the tester. These bonds may have been exposed to temperatures in excess of their operating limit. No cold shoe separation occurred in Unit No. 2 in which the temperature was lower.

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 18a and 18b respectively.



a) Typical Good Bond 130X



b) Poor Bond Area 130X

Figure 18 - Bond Areas After 500 hour Life Test

VI. DISCUSSION OF RESULTS

Considerable progress has been made in developing a reliable bond for n-PbTe. Indications from thermoelectric measurements, metallography, and life tests up to 500 hours are quite favorable. Torsion tests have shown that bonds are of consistent, reproducible strength, During the next quarter greater emphasis will be placed on the development of metallographic standards and improved metallographic sample preparation, so that more definitive post-life test evaluation can be performed. Life tests for periods up to 5000 hours shall be initiated.

The lack of success with p-PbSnTe is consistent with results obtained elsewhere. A decision has been made to resume work with p-PbTe (TEG-2P) and to concentrate on improving its properties, particularly its poor strength. Earlier work in this program has indicated that small additions of refractory metal such as molybdenum and columbium will strengthen p-PbTe without serious effect on the as-hot-pressed thermoelectric properties. Our effort will, therefore, be focused on further defining and exploring this dispersion strengthening effect. Metal and ceramic additions in the form of powder and fibers will be investigated.