

NBSIR 74-553

Preparation and Calibration of Phosphor Standards

M. L. Greenough

Electronic-Optical Development Section
Measurement Engineering Division

and

H. K. Hammond, III

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Final Report

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U. S. Postal Service

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

Preface

This report, together with its associated "Technical manual for phosphor standards calibrator, NBS Report 74-552 and the Drawing Package, constitute the final report on the project sponsored by the US Postal Service, Luminescence Calibration Equipment and Standards.

The authors wish to acknowledge the participation and contributions of H. S. Parker, R. A. Forman and C. A. Harding in the preparation of the luminescent wafers used in the phosphor standards, and of J. Cohen in the conduct of tests on phosphor standards.

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1.0 Introduction

1.1 Scope

This report covers the fabrication and test of a group of standards which are employed as the basic calibrating elements in the U.S. Postal Service Model 4A Phosphormeter.

1.2 Background

In the Model 4A Phosphormeter, readings of phosphorescent activity of stamps, test cards or other material are derived from comparison with the measured luminescent emission of designated phosphor standards. In operation the electrical gain of the instrument is adjusted so that the indicated reading agrees with the value marked on the standard. Since effective operating levels of luminescent activity (phosphorescent and fluorescent) are thereby established throughout the entire USPS system, it is essential that the phosphor standards provide a high degree of permanence in terms of short and long term stability. Stabilization is accomplished through:

- 1) Fabrication procedures which optimize the probability of stability, and
- 2) Periodic recalibration, particularly using the NBS Standard Calibrator, an instrument which refers luminescent activity to the calibration from a standardized source of radiant energy at NBS.

The work program for the project called for the fabrication and test of approximately 60 phosphor standards. While the primary USPS goal was the acquisition of these standards, there was also the secondary objective of testing out the specified fabrication procedure. This procedure had been prepared by the previous, commercial source, and was supplied to NBS by the USPS. The expectation was that deficiencies in the specifications would be noted and corrected by NBS, and that improvements might also be introduced. However the authorization was strictly limited to standards prepared by mixing the designated phosphorescent materials with a listed ceramic slip, firing at an elevated temperature, and mounting the polished wafers behind quartz windows in aluminum holders of specified dimensions. While it later became evident that further research would be desirable on the choice of the ceramic, because of an intrinsic phosphorescence in the ceramic itself, such exploration was outside the scope of the presently reported project.

Concurrently with the preparation of phosphor standards, the development of a laboratory calibration instrument for the phosphor standards was also sponsored by the USPS. This has resulted in the completion of the NBS Phosphor Standards Calibrator, which is covered in a separate report entitled "Technical Manual for Phosphor Standards Calibrator, NBS Report 74-552". This instrument responds to the luminescent emission from the phosphor standards in basically the same manner as the Model 4A Phosphormeter. There is however one point of difference, in that the NBS instrument is designed to reject the emission from the intrinsic phosphorescence of the ceramic base. This rejection of an essentially unwanted phenomenon is obtained by confining the spectral acceptance to the visible portion of the spectrum, so as to avoid dependence upon the primarily infrared intrinsic phosphorescence of the ceramic. The result of the difference between the measurement systems is that an additive correction constant is required to supplement the normal scaling for conversion of values between the systems.

2.0 Fabrication technique

This section covers the process by which phosphor standards were made at the National Bureau of Standards. It includes a general outline and an instructional step-by-step procedure for wafer fabrication, concluding with notes, precautions and suggestions for modifications for future workers.

2.1 Fabrication, general

The important steps in the fabrication process are:

- a) Machining of holders
- b) Fabrication of wafers
 - 1) Preparation of the ingredients of wafers for mixing to obtain the desired level of phosphorescence
 - 2) Mixing, ball milling
 - 3) Firing in a high-temperature furnace
 - 4) Surface finishing and dimensioning of the fired ceramic wafer
- c) Assembly of windows and wafers into the aluminum body of the standard holder

Testing and evaluation of the finished phosphor standards are discussed later in Sections 3.0 and 4.0 of this report.

The complete fabrication procedure was followed for green and red phosphorescent wafers. For fluorescent standards the modified project authorization called for the procurement of unmounted finished wafers. Other standards were prepared from black glass windows and from zero-phosphor wafers. All of these materials were mounted into aluminum holders which were made in the NBS shops using numerical-control tapes for automatic milling machinery. These tapes were prepared from the sponsor-supplied drawings.

Drawings were supplied by the USPS covering the mechanical dimensions and composition of the wafers for phosphor standards.

1. The complete drawing list is given below in Table

<u>USPS Drawing No.</u>	<u>Title</u>	<u>Corrections</u>
<u>Assembly</u>		
D39665	Standard Assembly-Phosphormeter	Section 2.2
<u>Body</u>		
C39652	Base Plate - Standard	Fig. 2
C39653	Back Plate - Standard	Figs. 3,4
C39676	Base Plate - Standard	Fig. 1
<u>Windows</u>		
A39658	Window - Standard	Commercial grade and finish
A39657	Window - Zero Adjust	No change
<u>Wafers</u>		
C39656	Wafer, Photoluminescent	Thickness 0.11 +0.01 (2.8+0.25mm) inch
<u>Small</u>		
A39654	Gasket - Standard	Not used
A39655	Back-up Plate	Not used
B39659	Plate - I.D.	Fig. 5
A39660	Tab Blank - PMU	Not used

2.2 Fabrication, detailed

2.2a Machining of holders

Certain modifications were made to the original machining plan indicated in the USPS-supplied drawings. Since these changes are essentially minor, they are given in the form of correction drawings, with notations in the Drawing List to show the updated portions. Except as noted the basic assembly drawing D-39665 remains applicable.

For an improved seal of the base and back plates of the standards, and for demountability, an 0-

ring gasket was installed around the wafer in the holder. This necessitated the machining of an accommodating groove in the base plate, plus re-positioning of the screws which clamp the back plate. The resultant changes are shown in Figure 1 (phosphorescent, small window) and Figure 2 (fluorescent, large window). relocation of the holes in the plates is shown in Figures 3 and 4 respectively. Drawing A-39654 is no longer needed.

2.2b Fabrication of wafers

The following is the step-by-step instructional procedure for producing phosphorescent wafers. As needed, additional explanatory material will be found in Section 2.4 - Notes on fabrication procedure.

2.2b(1) Preparation

(1.1) Dry the white body material

Spread out the contents of the container of white slip as received onto an evaporating dish. Allow to air-dry for several weeks if necessary. Stir occasionally and break up clumps as needed. Cover as needed to keep atmospheric dust from settling out on the material.

(1.2) Weigh the dry white body and the phosphor

Using the proportion of phosphor to total dry ingredients (white body plus phosphor) indicated below according to the level of phosphorescence desired, make up a batch of 1400 grams.

<u>Phosphor Color & Nominal PMU</u>	<u>Phosphor Concentration* (% by weight)</u>
G 22	4.0
44	8.0
88	12.5
R 22	3.0
44	6.0
88	13.0

*Note - Per cent by weight is computed from ratio of weight of phosphor divided by weight of white body plus phosphor. This total is always 1400 grams.

While these concentrations were used in wafers fabricated at NBS, modification may be necessary for specific conditions of manufacture such as surface roughness and firing temperature.

(1.3) Add measured amount of distilled water
Add 600 ml of water.

(1.4) Load ball mill
Add the moistened batch and about 4200 grams of grinding media, high-density alumina (burundum) cylinders approximately 20 mm diameter and 22 mm long, in a 4.5 litre, high-alumina jar made for use on a ball mill.

(1.5) Ball mill for four hours
Operate mill at 64 rpm, or at equivalent speed and time to accumulate 15,000 revolutions.

2.2b(2) Wafer formation

(2.1) Pour out slip on plaster bat
Use a large flat plaster bat, such as one foot (300mm) square, with 3/16 (5mm) inch raised border. Level slip at this thickness.

(2.2) Allow slip to dry slightly
Wait for a few minutes (maximum 15) until the slip is sufficiently stiff to allow cutting of the wafers in 2.3 below.

(2.3) Cut out wafers
Use cookie-like cutter whose inside dimensions are 15/16 x 1 3/16 inches (24 x 30 mm) with 1/8 (3mm) inch

radius at the corners. Press cutter nearly to bottom of wafer (1/64 to 1/32 inch) (0.4 to 0.8 mm) and then remove cutter carefully. If clay is sufficiently stiff and cutter is not pressed too deep, wafer will remain on bat and cut will not be filled in by flow of clay.

(2.4) Dry the wafers

Permit sheet to dry on bat for 24 hours, then lift off sheet and break off excess material from wafers.

2.2b(3) Firing of wafers

(3.1) Load wafers in furnace

Place wafers on flat sheets of 80% platinum and 20% rhodium and insert into furnace. The furnace used at NBS is an electrically-heated tube-type, 2-1/2 inches (63mm) and 14 inches (350mm) long, with programmable heat control.

(3.2) Fire wafers

Raise temperature in furnace at rate of 100°C per hour to a peak temperature of 920°C for green and 1000°C for red phosphor wafers. Soak 15 minutes at peak temperature. Return to room temperature at rate of 155°C per hour. Heat must be uniform within 5°C in firing zone if phosphorescence of fired wafer is to be acceptably uniform.

2.2b(4) Finishing to size

(4.1) Grind faces of wafer

Grind wafer face down on aluminum oxide abrasive paper placed face up on a sheet of plate glass. Hold wafer at edges with thumb and fingers. Using a random circular motion, grind first

with 240 grit paper. Then use finer grit, 23 μ m on plastic sheet with the same motion until scratches from the coarser grinding have been removed. Grind the back of the wafer with 150 or 240 grit paper so that the thickness is $0.11 \pm .01$ inch (2.8 ± 0.25 mm).

(4.2) Clean off the front face of wafer

Dust off the ground surface with a camel's hair brush, using separate brushes for green and red phosphors. Drop wafer from height of 6 inches (150mm) onto glass plate three times to insure absence of cracks. Blow off surface with compressed air (oil-less) or gas jet with pressure of 30 psi (20 N/cm²).

(4.3) Visual examination

Examine wafer carefully for uniformity of fluorescence under shortwave ultraviolet radiation.

2.2b(5) Evaluation of phosphorescence

(5.1) Measurement of PMU

Place the wafer temporarily in a holder with an installed quartz window and measure on a phosphometer. If the PMU value is within acceptable tolerance omit the next step and go on with (5.3) below.

(5.2) Trimming of PMU value

If the wafer is not within tolerance, but for example is too high in PMU value, it may be reduced by grinding the surface with a finer grit, such as 8 μ m plastic sheet. PMU values may alternatively be raised by grinding with a coarser grit. After each grinding operation, perform steps

(4.2) and (4.3) before remeasurement in (5.1) above.

(5.3) Test for uniformity

Mask off the lower half of a phosphor standard holder and load temporarily with the wafer. Measure on phosphormeter. Reverse the wafer and measure the previously-masked half. If difference is more than 10%, discard wafer

2.2b(6) Storage

(6.1) Label wafer

Identify wafer on back by marking with lead pencil. Prefix green wafers with letter G, and red with letter R. Follow with the nominal percentage of phosphor in the wafer, then the serial number of the wafer for the given phosphor concentration.

(6.2) Storage condition

Keep fingers off finished surface of wafer. Place accepted wafers face down in clear plastic compartmented parts boxes until ready for mounting in standard holders.

2.2c Assembly of standards

Quartz windows were cemented into the anodized aluminum holders by first coating the edges of each window and holder bezel with the prescribed primer, a clear red liquid that dries relatively quickly. The prescribed silicone adhesive sealant was placed in the metal bezel in sufficient quantity to over flow both inside and out when the window was inserted. Each holder was placed on a flat metal jig having four screws protruding to a height such that the window was held exactly 0.010 in. (0.25mm) above the bezel while the sealant cured. Use of a jig is imperative if the window is to be positioned parallel

to face of holder and at a prescribed distance from it.

The silicone adhesive cures without heat by absorption of moisture. After curing for at least a day in a room with 50% relative humidity, the excess cement was removed with a laboratory knife. Windows were cleaned mechanically with a section of a razor blade. They were then washed with a laboratory detergent to which a small amount of ammonium hydroxide had been added. A piece of lens tissue was used as a scrubber. The windows were rinsed with hot water and dried with lens tissue. Each window was examined visually for cleanliness in a darkroom by observing light scattered at the surface when a beam from a flashlight was incident on the window. Windows were washed three times to remove all traces of smear.

Wafers and windows were dusted with a camel's hair brush before assembly. The wafer was then placed in its holder, in the case of phosphorescent standards, the one it had previously occupied. Holders were placed, three or four at a time, on the top shelf of a laboratory oven operated at 107°C (225°F) where they remained for at least 30 minutes. Air in the oven was moved rapidly by means of a fan provided with the oven. The wafers were placed in the holders to prevent the possibility of dust collecting on their surfaces while moisture was being driven off in the oven. On removal from the oven, wafers were immediately sealed in the holder bases with silicone sealant worked in around all four edges and covering the back of the wafer. After curing at least overnight, excess sealant was removed with a microtome knife. The O-ring seal was inserted, the wafer back covered with a small amount of fresh sealant and the back screwed in place to complete the assembly.

2.3 Mechanical modifications

In addition to the revised sealing technique for the standard holders as mentioned in Section 2.2a above, several other minor changes were incorporated. These are described below and referenced in the Drawing List, Table 1.

For simplicity, the wafers were not cemented to the stainless steel back plate as indicated in drawing no. A39655. Instead the wafer was made thicker, by not

removing as much material during grinding. Therefore the wafer thickness shown in drawing no. C39656 should be revised to 0.11 ± 0.01 inch, (2.8 ± 0.25 mm) and drawing no. A39655 is no longer needed.

As an economy measure the quartz windows purchased for these standards were specified to be of commercial grade and finish, as being entirely adequate in our opinion for the intended service. This revised specification applies to drawing no. A-39658.

In order to provide an enlarged area for the calibration labels on the phosphor standard, the previous arrangement was modified to include a larger window, relocated at the bottom of the label. The resultant changes, together with minor textual revisions on the labels, are shown in Figure 5, which replaces drawing no. B-39659 completely. The new style features a thin bottom plate carrying the calibration data regarding PMU(T) and the date, which is visible through the window in the superimposed top plate. This top plate contains the fixed information (Red Phosphor Standard, etc.) plus the engraved serial number. Temporarily the bottom plate is a self-adhesive paper label with typewritten data and a lacquer protective lacquer over-coating. On the bottom plate, there is also marked the NBS-PMU value, to which is added the correction constant for phosphormeter response to surface reflectance and intrinsic phosphorescence. These markings may be seen when the top plate is removed, but with the latter in place, only the sum is visible. This is the reading to which the phosphormeter gain should be set. Ultimately it is planned that the bottom paper labels will be replaced with etched aluminum plates.

2.4 Notes on fabrication procedure

The following notes on the wafer fabrication procedure are referenced to the items listed in Section 2.2b - Fabrication of wafers. Comments and other explanatory material are included as experience has indicated.

- (1.3) The quantity of water specified, 600 ml, was found to be the correct amount which will produce a slip (after four hours of milling as in (1.5) that flows conveniently onto the plaster bat.

- (3.1) As a precaution to prevent contamination, the wafers when fired at NBS were placed in a completely covering structure. A folded-metal tiered assembly was constructed of 0.01 inch thick, (0.25mm) 80% platinum, 20% rhodium sheet. Wafers were placed inside the assembly, and fired in batches of six. Similar or equivalent measures may be necessary in order to pass the uniformity test as specified in step (5.3) of the procedure.
- (3.2) In the course of the work it has become evident that phosphorescent activity has a rather critical dependence upon the temperature of firing. A plot of measured PMU for green wafers fired at temperatures from 850 to 1000°C is shown in Figure 6. It can be seen that the resultant activity drops from 55 to 4 PMU over this region. In view of this steep function of temperature, it was felt desirable to revise the specified firing temperature from the original 1000° downward to 920°C. At this temperature, it was found that the required percentage of luminescent materials in the slip approximately matched those in the original specifications.

Because of this critical temperature dependence, uniformity of temperature inside the furnace is important. For this reason only a small number of wafers (six) were loaded at one time, with these placed in the center where the temperature was presumably most uniform.

- (5.2) Trimming of PMU value by means of surface finishing should not be used unless necessary to bring wafers within the acceptance range. Until more is known about the effects of surface finish, it appears desirable to perform final grinding with the 23 μ m grit paper, since the PMU characteristic seems to be relatively independent of grit size in this region. The results of a short investigation of the subject are given in Section 4.2- Effects of surface finish.

3.0 Specified test characteristics

In the authorizing Work Statement, as modified by mutual agreement, the following tests on phosphor standards are specified:

- 1) Accelerated aging
- 2) High temperature
- 3) Temperature coefficient
- 4) Immersion (substituted for humidity test)
- 5) Shock test

The specific procedures which were followed are given in detail below, together with the test results.

3.1 Accelerated aging tests

3.1a Procedure, phosphorescent standards

These tests were conducted in two categories, which were 1) aging exposure for approximately 100 hours on all standards with measurement every 24 hours, and 2) exposure up to approximately 800 hours on two sets with measurements every two hours for the first 24 hours, followed by less frequent measurement for the remainder of the time. The selected sets for the latter were the primary sets to be kept at NBS, which include wafers from both NBS and commercial sources.

Aging was conducted by mounting a bare mercury lamp of the type used in Postal Service equipment in a vertical position and then positioning standards around it at such a distance that the level of irradiation is comparable to the average level of a phosphormeter (approximately 2 mW per square centimeter). Two lamps were used and seven standards were positioned around each lamp. In addition to two phosphorescent standards for each of the three levels of intensity in both red and green there was one standard containing a ceramic wafer without phosphor and one standard of black glass. The standards were irradiated continuously except for the time required for periodic measurement. The quartz windows were

cleaned before start of aging tests but not during aging.

The detailed procedure was to read the reference standard, the control standard, the two aged standards, and then re-read the reference standard. The average value of the two readings on the reference standard was used as the reference. All green standards were evaluated in rapid succession by measuring their intensity relative to that of Green Standard No. 258 supplied with Phosphormeter 4A8 as reference. All red standards were similarly evaluated relative to Red Standard No. 458.

One control standard at each level containing a commercially procured (COM) wafer was not irradiated but was measured each time the irradiated standards of that level were measured.

Data from the aging tests were corrected by subtracting the reading for the blank ceramic wafer (mounted in a standard holder) from each reading for a phosphor standard.

Measurements on all standards were subsequently reduced to a percentage of the initial reading in order to illustrate most clearly any aging effect of ultraviolet radiation.

The data represent only one reading on each standard for each time interval except for the initial data (unexposed) which represent the average of two readings made by re-reading each standard in reverse order.

Each measurement on the NBS calibrator was followed by one on the phosphormeter.

3.1b Test results, phosphorescent standards

The relative aging effect of green and red phosphorescent standards is plotted in Figures 7 and 8 for data obtained from the NBS calibrator and in Figures 9 and 10 for data obtained from the phosphormeter. Readings on the unirradiated (control) standard at each level are plotted as points in circles. Irradiated standards containing wafers of commercial manufacture are plotted as points in

squares; standards containing wafers of NBS manufacture are shown as points in triangles.

Examination of the plots reveals the following: 1) Little change is observed in the relative intensity of green or red phosphor standards after the first few hours of aging. 2) Plots of data from the NBS calibrator (Figures 7 and 8) appear to be somewhat different than those for data from the phosphormeter (Figures 9 and 10). This difference may be due in part to the effect of subtraction of different amounts for the intrinsic phosphorescence of the ceramic wafer, which is particularly large for red standards measured on the phosphormeter.

Ultraviolet irradiation of the red and green phosphorescent standards previously aged for 100 hours was continued to determine how much exposure beyond 100 hours might be required to produce significant degradation in phosphorescence. Irradiation at a level equivalent to the average in a phosphormeter was continued to 760 hours for green standards and 828 hours for red. Measurements were made on irradiated standards and on a control standard of similar type relative to a reference standard for each color, using both the NBS calibrator and the phosphormeter.

Measurements on the green standards with increasing time of irradiation indicated that there was no certain change in the phosphorescence of the low, intermediate or high level standards. Measurements on the red standards however indicated that the phosphorescence of the two higher levels of standards increased slowly as irradiation was continued, the final values being about 5% higher than the values at the start of the aging test. While an increase in the indicated values of irradiated standards could be caused by a decrease in the phosphorescence of the reference standard, measurements made each time on an unirradiated control standard at each level indicated no changes in values of the control standards. Thus the indicated rise of 5% during the aging tests to 828 hours for red phosphor standards must be regarded as real.

From these data the precision of a single measurement for the NBS instrument as a comparator was shown to be of the order of 0.4%. When measurement

requirements are more stringent than this, it will be necessary to make multiple readings.

3.1c Procedure, fluorescent standards

Accelerated aging tests were conducted on the designated Red Fluorescent and Balance Adjust standards, using both the NBS calibrator and the phosphormeter. In the phosphormeter, evaluation involves simultaneous, two-color sensing of fluorescent activity, wherein the signal derived from a photocell with a yellow filter partially cancels out the main signal obtained from a photocell with a red filter. This procedure is used to minimize the effect of fluorescent whitened paper. To accomplish the desired degree of cancellation, a Balance Adjust standard is normally employed. With this standard in place, approximate equality is first set into the signal processing channels. Then introduction of the Red Fluorescent standard causes an up-scale reading on the red channel, with the magnitude of this reading being the indicator of PMU value. From our separate measurements of red and yellow fluorescent activity, it appears that the yellow channel is designed to cancel approximately 11 percent of the red activity on a nominally-rated standard of 22 PMU. Thus the true measure of the PMU scale for fluorescent evaluation requires measurement of both the Balance Adjust Standard and the fluorescent standard under test, plus a knowledge of the relative weighting assigned by the phosphormeter to the red and yellow sensing channels.

In view of this complex mode of operation we have chosen for completeness to measure both red and yellow output, on Balance Adjust as well as Red Fluorescent standards. All of these data may not be usable without further knowledge of the relative weighting given them in the phosphormeter. In the absence of specification information regarding weighting, we have elected to give primary attention to the major factor, the red-channel fluorescence. In the discussions which follow, it can be assumed that this is the parameter under consideration unless otherwise indicated.

3.1d Test results, fluorescent standards

Readings of overall PMU indicated by the phosphormeter are plotted in Figure 11, and of red-

channel fluorescent activity measured on the NBS calibrator, in Figure 12. Irradiation of a Red Fluorescent and a Balance Adjust (fluorescent) standard for 117 hours revealed no certain change due to radiation for either standard when measured on a phosphormeter and on the NBS calibrator relative to a corresponding non-irradiated control standard. Instrument readings on the irradiated red fluorescent standard suggest that during the first few hours of irradiation the fluorescent output was reduced and then as radiation was continued the output increased again to approximately the original value at the end of 117 hours. A phenomenon of this type has been previously encountered when a green phosphorescent (dummy) stamp was irradiated. In any case it must be assumed that the change took place, since it was observed with both instruments and was absent on the non-irradiated control standard.

3.2 High Temperature Test

The purposes of this test were to determine qualitatively the effect of elevated operating temperatures upon the phosphor standards, and to note any residual permanent changes in phosphorescent activity. This test was performed on phosphorescent standards only.

3.2a Procedure

Standards were placed in an oven at 50°C for about 2 hours and then removed for measurement of phosphorescence on a phosphormeter and the NBS calibrator. They were returned to the oven and heating was continued for 4 additional hours. The standards were again removed and measured for phosphorescence on the two instruments. Measurements were made within about one minute after removal from the oven.

Two standards at each of the three phosphor levels were tested. Initially standards were withdrawn from the oven in pairs, but the aluminum holders cooled quickly, especially while in contact with the metal head of the phosphormeter or the NBS calibrator. To minimize cooling, standards were subsequently withdrawn one at a time and measured first on the phosphormeter and then on the NBS calibrator. Readings on the phosphormeter could be made more quickly than on the NBS calibrator and so

these data should be more representative because the temperature of the standard has had less time to change.

For measurement control, a standard similar to each of the heated pairs was kept at room temperature and measured each time a pair of heated standards was measured. In addition, two standards with blank ceramic wafers were measured; one was heated, the other served as control. The instrument reading for the heated blank wafer standard was subtracted from the readings for the other heated standards. The reading for the blank standard kept at room temperature was subtracted from the readings on the control standards.

3.2b Test results

The data show that the percentage change in phosphorescence on heating is about the same for the six standards of a given color measured on a given instrument, but the change appears to be dependent on the time of heating. It is significantly larger for 4 hours than for 2 hours. Thus we conclude that equilibrium is not reached in 2 hours, as shown in Table 2.

Table 2

Average Percentage Change in Observed Phosphorescence
After 2 and 4 Hours at 50°C Relative to 24°C

Standard	<u>Measuring Instrument</u>			
	<u>NBS Calibrator</u>		<u>Phosphormeter 4A</u>	
	<u>Hours at 50°C</u>		<u>Hours at 50°C</u>	
	<u>2</u>	<u>4</u>	<u>2</u>	<u>4</u>
Green Phos.	-7.6	-8.7	-3.7	-5.9
Red Phos.	+1.7	+2.7	+0.7	+1.7

The percentage change also appears to be dependent on the instrument used. While the data agree in direction, it can be seen that there are consistently larger shifts on the NBS calibrator than on the phosphormeter.

It is possible that the source of difference lies in the intrinsic phosphorescence of the ceramic wafer, the effect of which has been subtracted before listing in Table 2. The question raised is whether simple subtraction of measured values on blank wafer standards is an adequate technique for the phosphormeter.

More important, however, is the fact that our data show that the phosphorescence of red standards increases with increase in temperature while the phosphorescence of green standards decreases and at a much faster rate.

Remeasurement of the standards after return to room temperature indicated that this heat treatment caused no change in the values of the standards at room temperature.

3.3 Temperature coefficient tests

Phosphorescent standards were tested to determine the extent to which PMU value are dependent upon ambient temperature.

3.3a Procedure

Details of the temperature coefficient tests were established as a result of the conference with the USPS project engineer on April 16, 1973.

In essence the standards were maintained at constant temperature for at least one hour, then withdrawn and measured as quickly as possible. The desired temperatures for measurement were 32, 50, 75, 100, 125, and 140°F. (0, 10, 24, 38, 52, 60°C).

It is recognized that the procedure introduces a degree of approximation in the derived temperature coefficient. The actual temperature at the instant of measurement is necessarily somewhat different from that in the oven, being influenced by the thermal conductivity of the aluminum holder, the temperature of the measuring head and the elapsed time between removal and measurement. To determine the temperature at the measurement time would require instrumentation of unjustifiably high sophistication.

These difficulties were evident during the tests. At high temperatures, the standard cooled rapidly during measurement when the hot aluminum case contacted the cooler metal of the optical head of the Phosphometer. The converse was true at low temperatures. At temperatures below the dew point for the laboratory atmosphere, water vapor condensed on the cold quartz windows. Even though the window was wiped with lens tissue immediately before measurement, it was impossible to be certain that no moisture had condensed on the window by the time the reading was made.

For measurements below room temperature, the standards were placed in a cardboard box in a refrigerator freezer with the bulb of a mercury thermometer centered in the box. After the prescribed time interval, the box was removed from the freezer and taken to the phosphometer where the standards were removed for measurement one at a time. The temperature in the box rose gradually during the 15 to 20 minutes required to measure all the standards on the two instruments. An attempt was made to obtain more precise temperature control near 0°C by placing standards in individual plastic envelopes and immersing them in ice water. Some of the plastic bags leaked however, and the standards had to be dried before measurement. In any case it appeared that temperatures of standards at time of measurement are probably no more accurately known when liquid cooled than when air cooled.

3.3a(1) Definition of temperature coefficient

The formula which has been adopted for expressing the phosphorescent activity at other than the reference temperature of 75°F (24°C) is

$$\text{PMU at desired operating temperature} = [\text{PMU at } 75^{\circ}\text{F}] \times [1 + \alpha(\Delta t)],$$

where:

Δt = temperature difference in °F between operating temperature and 75°F, and

α is the temperature coefficient for the phosphor (different each type)

A negative value for α signifies that phosphorescent activity decreases with elevation of temperature. When α is large, there is a large dependence upon the operating temperature of the standard.

3.3b Test results

In Figures 13 and 14 are plotted the data from which temperature coefficients were determined, for the green and red phosphorescent standards respectively. All values indicated have been corrected for offset as described earlier, hence the data represent the behavior of visual phosphorescence only. It is quickly apparent that the green phosphorescence drops rather rapidly with temperature increase, while the red phosphorescence increases at a lower rate.

In more detail, Figures 13 and 14 show phosphormeter readings after the correction for offset has been applied, for high, medium and low level standards. Each plotted point is the mean between two wafers from two sources, commercial and NBS. Additionally the plots show the relative output of the NBS calibrator when scaled to an empirically-determined fit with the phosphormeter data. This scaling permits preliminary conversion of the calibrator output in terms of PMU. At each of the three levels a single straight line has been constructed, chosen to represent estimated system performance, with allowance for measurement uncertainty. In general the data at each temperature agreed well between the phosphormeter and the NBS calibrator. Where the two instruments disagree, more weight was given to the indications from the NBS instrument, since the fit to a straight line was usually better. The slope of the drawn straight lines was used to determine values of the temperature coefficient in the formula given above. The derived values α are listed in Table 3 below:

Table 3

Temperature coefficients of phosphorescent standards

<u>Color and level of standard</u>	<u>Temperature coefficients, (per °F)</u>	<u>Temperature coefficients, (per °F)</u>
Green, high	-0.0019	-0.0011
" med.	- .0017	- .0009
" low	- .0021	- .0012
Red, high	+0.00038	+0.00021
" Med.	+ .00034	+ .00019
" low	+ .00034	+ .00019

From the values of temperature coefficient in the table it can be seen that each color of standard might well be represented by an average coefficient regardless of level. Thus we can say that the phosphorescent emission of green standards at all levels decreases by approximately 1.9% for each 10°F rise in temperature. The emission of red standards containing red phosphor increases by .35% for the same temperature rise. The precision of the coefficient determination is of the order of 10% according to these data. It should be emphasized that we are considering the behavior of true visual phosphorescent emission only; all contributions whether minor or major from the blank ceramic wafer have been subtracted.

The correlation of observed luminescent activity as a function of temperature was also checked against the manufacturer-supplied data listed in Appendix A of the Work Statement. When these data are converted to equivalent temperature coefficient, the resultant is a value of $-.0012$, applicable to both green and red. This of course is at variance with the adopted $-.0019$ and $+.0035$ from Table 3, where the coefficient for red phosphors is even slightly positive rather than negative. The explanation appears to lie in the behavior of the offset due to the intrinsic phosphorescence of the blank ceramic wafer itself. When the raw data from phosphormeter readings are taken, without correction for the offset, coefficients of $-.0017$ and $-.0007$ are found. The manufacturer's coefficients correlate better with those data, because

the overriding effects of the ceramic wafer provide agreement in the direction of change.

The offset itself appears to display a temperature coefficient of $-.0042$. This value is obtained from phosphormeter data when the instrument is calibrated with the red phosphorescent standard supplied with it. Because some proportion of the phosphormeter response is contributed by intrinsic phosphorescence, it is to be expected that the temperature behavior of the composite phosphor standard will reflect this proportion. It is particularly evident in the case of red phosphorescent standards. Thus it is not surprising that the observed small positive coefficient representing the true visual phosphorescence is masked when the offset generates about one-third of the phosphormeter's response.

To summarize the results of the temperature coefficient tests on phosphorescent standards, the measurements show for visual phosphorescence a negative coefficient of 0.0019 per $^{\circ}\text{F}$ for green phosphor standards, and a positive coefficient of 0.00035 per $^{\circ}\text{F}$ for red standards. Both coefficients can be considered as constant for low, medium and high levels of phosphorescent activity, and applicable to the temperature range from 32° to 140°F .

3.4 Immersion test

Six green and six red phosphorescent standards that had been subjected previously to aging, high temperature and temperature coefficient tests were given the immersion test. This latter test is designed to show the effectiveness of the sealing technique rather than the susceptibility of the wafer to moisture.

The standards were first measured before the test on Phosphormeter 4A8 calibrated with the standards supplied with the instrument. To conduct the immersion test, the standards were placed face down on the bottom of a laboratory sink at the end of the day. The sink was filled with water at 50°C to a level 8 inches above the standard. The next morning the standards were removed and dried. The windows were cleaned, and the standards were examined for water penetration. No penetration was observed. The green standard in holder No. 24 showed a dark spot in the upper left-hand corner of the wafer, but this had been noted

previously. It was due to silicone adhesive that ran under the corner when the wafer was sealed in the holder.

The standards were then remeasured on the phosphormeter. No significant difference in phosphorescence was observed after immersion. The measurement data obtained before and after immersion are tabulated below. The first holder in each pair contains a wafer of commercial manufacture, the second holder a wafer made at NBS.

Table 4

Immersion Test Data

<u>Green Phosphor Standards</u>			<u>Red Phosphor Standards</u>		
<u>Holder No.</u>	<u>Phosphormeter Reading</u>		<u>Holder No.</u>	<u>Phosphormeter Reading</u>	
	<u>Before</u>	<u>After</u>		<u>Before</u>	<u>After</u>
15	24.0	24.0	5	23.4	23.1
24	23.2	23.0	4	22.6	22.2
16	48.6	48.3	6	47.0	46.8
28	48.3	48.6	21	43.1	42.8
22	95.2	95.4	14	103.0	102.5
19	97.4	97.6	13	103.8	102.3

3.5 Shock test

An abbreviated shock test was performed on one standard. It was dropped several times from a height of approximately 18 inches (45 cm) onto an asphalt tile over concrete floor. No visible damage was sustained, nor was there any measurable change in PMU value as indicated on the phosphormeter.

4.0 Other characteristics

4.1 Effect of setback

The term setback refers to the displacement of the irradiated, emitting surface of the luminescent material as moved away from its "normal" position. Setback is a problem because the NBS calibrator is substantially independent of the displacement, while the phosphormeter and the facer-canceler are quite dependent upon it. The latter two, it should be mentioned, are understood to be

similar in geometry, hence should behave alike regarding setback.

The two conditions where setback is a particular concern are 1) variation among the phosphor standards of the thickness of the shoulder against which the quartz windows are mounted, and 2) definition of the PMU-efficacy relationship at the time of conversion computation. In regard to the former, which is the variation among standards, the problem is considerably aggravated by the method of specifying tolerance contained in the original mechanical drawing, wherein the shoulder thickness must be indirectly derived. This leads to possible summation of three or more individual tolerances. In the machining of the sample holders in the NBS shops using the supplied numerical control tape, it appears that an appreciable range of tolerance sums was encountered. Specifically, the distance from the front plane to the outer quartz surface ranged from 0.029 to 0.054 inch (0.74 to 1.4 mm). On the phosphormeter such a displacement range causes a 4.5 percent change in indicated PMU value. At the nominal 22-Pmu level, the resultant potential correction is approximately ± 0.5 PMU.

Trial application of corrections, based upon the individual measured shoulder thickness, appeared to reduce by a factor of about one-half the unexplained differences in the correlation between PMU values indicated by the phosphormeter and the NBS instrument. Thus eventually it may be possible to apply corrections for setback, and to this end, setback measurements have been recorded for all standards. For the present however, the correction step was omitted, primarily because this imprecision is masked by the greater uncertainty regarding intrinsic phosphorescence. Details of the latter are covered in Section 4.5 - Intrinsic phosphorescence.

The second area of concern involving the setback dependence of the phosphormeter arises because the stamps and test cards are located in a plane which is much closer to the irradiating and sensing elements, compared to that of the active luminescent wafer in the phosphor standards. Experiments have shown that this displacement causes a test card which gives a reading of 15 PMU at the wafer plane to increase to over 21 PMU at the normal stamp plane, the front face of the phosphormeter. The decision which this imposes is whether NBS-Phosphormeter conversion should be based upon phosphor standards or upon stamps and test cards. Agreement on phosphor standards was chosen as more

consistent with the intended service of the NBS calibrator, where stamps and test cards are only of secondary interest. The consequence of this choice is of course that the phosphormeter will display about 40 per cent greater readings on stamps than will the NBS instrument. Test cards may show up to as much as this, depending upon their prevailing setback.

The inconsistency regarding the measurement of stamps and test cards may be eliminated with the adoption of a single plane for positioning during measurement. This would require that a spacer plate of approximately 0.10 inch (2.5mm) be placed over the phosphormeter face when measuring stamps. Appropriate modification would be necessary for windowed test cards. With this technique it should be possible to obtain inter-instrument agreement on all the luminescent materials of interest.

4.2 Effect of surface finish

Experiments were made to determine the influence of surface grinding on phosphorescence; specifically (1) the effect of surface roughness on the magnitude of the phosphorescence, and (2) the effect of grinding technique (circular or linear grinding motion) on the magnitude and the anisotropy (directional effects) of the phosphorescence. Three green and three red phosphor ceramic samples, each with different amounts of phosphor additive, and hence phosphorescent intensity, were used. A zero phosphor sample was also prepared. Samples were ground by hand using abrasive paper placed on flat plate glass, and considerable care was taken to prevent contamination between different samples. After grinding, the debris remaining on the samples was brushed away with a camel hair brush, then blown with pressurized dry tank nitrogen. Samples were mounted for measurement in a special holder with an open 1 cm square aperture.

4.2a Surface roughness

For the surface roughness experiments, the samples were all circularly ground with 59 μ m grit (240 grade aluminum oxide) and the phosphorescence was measured with both the phosphormeter and the NBS meter. Four measurements of phosphorescence were made on each sample, corresponding to 90° intervals of rotation through the central axis normal to the ground surface. The procedure was repeated next with 23 μ m - and finally 8 μ m grit. Determinations of surface

roughness using a stylus instrument were made of the various samples, but were inconclusive as to the finish actually secured.

The results of the surface roughness experiments are shown in Figure 15, plots of the percentage of the initial value (after grinding with 59 μ m grit) vs. the grit size of the abrasive, for green phosphorescent wafers. Taking the phosphorescent activity with the coarsest grind as the reference, the activity of green phosphors appeared to increase by a few percent for medium grit (23 μ m), then decrease by 4 to 16 percent for the finest grit (8 μ m). Because the larger percentage effects were observed for the higher levels of phosphorescence, the PMU range due to surface finish could be as much as 15 PMU.

Red phosphors displayed the same general behavior, but on a larger scale, as can be seen in Figure 16. The overall range of finish-influenced effect was as much as 30 to 40 percent, with an absolute change as large as 20 PMU. Similarly to the performance of the green phosphors, the greater part of the observed change appeared to occur between the 23 and 8 μ m grit.

A comparison of the measured effects with regard to the phosphormeter and the NBS instrument showed no significant difference. Although in the latter the usual correction for intrinsic phosphorescent activity was applied so as to yield solely the visual phosphorescent activity the results are in approximate agreement, as is evident in figures 16 and 17. This suggests that effects due to surface roughness apply to the intrinsic phosphorescence of the ceramic base as well as the phosphorescence due to the introduction of luminescent material.

4.2b Anisotropy

For the anisotropy experiments, red phosphor samples were used; the samples were ground first with a specific grit size using circular motion and the phosphorescence measured, again at 90° intervals of sample rotation, using the NBS instrument. Then the sample was ground using a linear motion against abrasive of the same specific grit size and phosphorescence measurements were made as before.

This last step was taken to exaggerate any possible orientation effects for ease of measurement.

Figure 18 shows plots of the percentage change of NBS-PMU from the average value of the circularly ground sample vs. sample orientation; samples ground with three different abrasive grit sizes are shown. The orientation of the sample relative to the grinding direction and instrument set-up is depicted in the circular inset. It may be noted that in all cases, the circularly ground sample has a higher value of PMU than the linearly ground sample. In general, the circularly ground samples are quite isotropic; with a single exception the noted change with orientation was less than one percent. As expected, some anisotropy was found for the linearly ground wafers, amounting to about two percent. In view of the deliberate effort to maximize the effect, such a change is small. The anomaly shown by the $8\mu\text{m}$ sample at 270° is believed due to inhomogeneity of the phosphor at the surface.

It may be noted that in all cases the circularly ground sample has a higher value of PMU than when the same sample was linearly ground. An explanation for this is lacking.

4.2c Summary of effect of surface finish

From the results above, it would appear that anisotropy is not a problem and that merely nominal attempts at random circular grinding should be quite adequate.

A considerable problem does appear to exist, however, regarding surface roughness. Phosphorescent activity can be seriously affected by the grit size used in finishing. While grinding with the $8\mu\text{m}$ grit always reduced the PMU value compared to that for $23\mu\text{m}$ repeating the experiment would frequently produce different values. Thus, reproducibility of absolute readings was found to be rather poor. It is our conclusion from these measurements that uniform surface preparation, such as the use of the $23\mu\text{m}$ grit, is preferable to attempts at "trimming" using variable grit size.

The samples per se are exceedingly complex from a materials point of view, consisting largely of

sintered ceramic with a small percentage of phosphor embedded, and probably inhomogenously distributed. Thus, grinding not only affects surface roughness, but may also affect surface concentration of the phosphor. Other complexities may also exist. Consequently, the results of these experiments cannot be well explained, and a great deal of systematic experimentation would probably be required for a definitive model.

4.3 Spectral distribution of luminescent emission

In this section the known information regarding the spectral emittance of the luminescent materials has been assembled. The significant characteristics are discussed, along with the limitations on available data. As will be seen, there are problem areas where more data would be desirable.

Four luminescent materials are involved:

- 1) green phosphorescence
- 2) red "
- 3) red fluorescence
- 4) yellow "

Ideally it would be desirable to know the spectral emittance of these materials under the various conditions of use, in the facer canceller, the Model 4A phosphormeter and the NBS calibrator. The term "conditions of use" here refers to the manner in which the phosphors are excited and measured. These are different in the three systems of implementation, as is covered more fully later in Section 4.4 - Rise and decay times.

The apparent presence of several different time factors in the measured function of luminescent decay suggests that several components are present in the phosphors. Each component can conceivably be expected to possess individual spectral characteristics. The contribution of these components would be superimposed under any given conditions of excitation and measurement according to the proportionality of the relative efficiency excitation and measurement. One example would be when the measurement delay is so great that the phosphorescence from a rapid-response component has decayed virtually completely. Then this portion of the spectral emittance

would not be evident in the measured characteristic. Another example might be a phosphor with a component of very long time of rise and decay which would not be stimulated appreciably by a short pulse of ultraviolet irradiation, yet a quicker-response component might be fully excited. This would lead to displaying the spectral contribution primarily of the latter. But the same material, when excited for a length of time, could then reveal the contribution from its slower-response component. It seems logical to expect that the resultant spectral characteristics would be dissimilar. Unfortunately the resources of the project did not permit pursuit of the subject.

The data of Section 4.4 below, wherein it appears that three distinct time constant values are required to match the measured decay function, cast doubt that one common spectral characteristic can be derived for any one phosphor. The alternative, that of determining the characteristic for each implementation (facer canceler, phosphormeter, NBS calibrator is difficult and costly. In particular, for the facer canceler it would be necessary to simulate the excitation build-up as a typical stamp-bearing envelope approached the sensing head. For the NBS calibrator it might be possible to interpose a variable filter such as an interference wedge between the phosphor sample and photomultiplier tube. Because it would require considerable fabrication however, this approach has not been attempted. Thus within the scope of this report, we have not found it feasible to develop a quantitative model of the spectral emittances of the four phosphors with which phosphor standards are involved. We have instead assembled and reproduced data from earlier investigators, some from the manufacturers of luminescent materials and some from prior measurement at the NBS. By and large these are believed to represent data on fluorescent rather than phosphorescent emission, since the derived characteristics is not as critically specific to the conditions of excitation and measurement. These data are listed in Table 5 below.

Table 5

Summarized Spectral Characteristics of Luminescent Materials
Relative spectral emittance for total area equal 1.00

Wavelength, nm	Green Phosphorescent Source (1)	Red Phosphorescent Source (2)	Yellow Fluorescent Source (3)	Red Fluorescent Source (4)
450			--	
55			--	
60			--	
65			--	
70			0.0152	
475	--			
80	0.0021		.0396	
85			.0701	
90	.0087		.0854	
95			.0030	
500	.0371	--	--	
05			--	
10	.1064	--	--	
15			--	
20	.1911	0.0028	--	
525			--	
30	.2095	.0072	--	
35			--	
40	.1661	.0137	--	
45			--	
550	.1123	.0241	--	
55			--	
60	.0701	.0359	.0061	
65			.0366	
70	.0426	.0488	.2134	
575			.3018	0.0071
80	.0244	.0656	.1006	.0141
85			.0213	.0177
90	.0169	.0828	.0091	.0318
95			.0061	.0318
600	.0127	.0965	.0061	.0282
05			.0061	.0141
10		.1026	.0030	.3357
15				.1131
20		.1000		.0283

625			--	.0530
30	--	.0295	--	.0495
35			--	.0247
40	--	.0790	.0015	.0071
45				.0071
650	--	.0665	.0018	.0106
55			.0013	.0071
60	--	.0490	.0010	.0071
65			.0005	.0071
70	--	.0401	.0001	--
675			--	--
80	--	.0307	--	--
85			--	.0035
90	--	.0236	--	.0071
95				.0071
700	--	.0169	--	.0071
05			--	.0283
10	--	.0113	--	.0212
15			--	.0035
20	--	.0072	--	--
725				
30	--	.0031		
35				
40				
45				

Sources

- (1) "Development of phosphormeter standards, measurement techniques, and specification of solar cell characteristics" NBS Report 10 596, Table 2a
- (2) Same Table 2b
- (3) Manufacturer's data sheet (plot, transcribed) as reproduced in "Development and testing of ceramic wafers used in secondary standards for the improved Model 4 Phosphormeter, Addendum I to Work Group II", Contract RE 7-70, 22 February 1971, Attachment VII
- (4) Same Attachment VIII

4.4 Rise and decay times

The nature of phosphorescent materials is to display a storage characteristic, in that when an irradiating ultraviolet source is cut off, the visible or other luminescent emission does not cease immediately. The materials used in phosphor standards show this characteristic, requiring from 10 to 100 milliseconds for the afterglow to decay to one per cent of the initial emission.

The decay characteristic as a function of time after source extinction has been measured for typical green and red phosphor standards, and is shown in Figure 18. The values were measured by varying the elapsed time between the end of the exciting ultraviolet radiation and the sampling time, using the Sample Delay provision in the instrument. The response shown in Figure 18 is plotted on a semi-logarithmic graph, wherein an exponential decay characteristic would be represented by a straight line. If a simple straight-line representation were possible, the sloping function would be completely described by the time for the luminescent emission to die away to $1/e$ or 37% of its value at zero time. Using the customary technique of specifying the time to this $1/e$ value, the green phosphor would be considered as having a time constant of 3.2 milliseconds. For the red phosphor the time constant is 22 milliseconds.

It is evident from Figure 18 that such single-value representations of the decay characteristics of green and red phosphors produce only a very rough approximation to the measured function. A much better match can be found if it is assumed that there are as many as three components. Solving by best fit for the three time constants and their relative proportions yields a composite curve which matches very closely the measured decay functions. Table 6 below lists these components.

Table 6

Components of Phosphorescent Decay Characteristics

<u>Standard</u>	Time Constant No. 1		Time Constant No. 2		Time Constant No. 3	
	<u>T₀</u>	Relative Amplitude	<u>T₀</u>	Relative Amplitude	<u>T₀</u>	Relative Amplitude
Green phos.	1.4 ms	0.40	3.3 ms	0.32	9.3 ms	0.28
Red phos.	3.0 ms	0.16	17 ms	0.44	48 ms	0.40

The sum of these components matches the observed data to better than approximately one percent of the initial value.

The significance of the multiple time constants is that any measured properties of the phosphorescent materials will depend rather strongly on how they are measured. Both the apparent phosphorescent activity and the spectral distribution can be affected. For an understanding of this, it is necessary to examine the build-up as well as the decay characteristics.

It is to be expected that phosphorescent materials acquire energy during excitation with the same general characteristic at which energy is emitted after cessation of excitation. For example a phosphor with a long time constant requires prolonged excitation in order to develop maximum phosphorescent activity. The data on relative amplitudes of the various components in Table 6 above apply to the duty cycle in the NBS calibrator, which is 10 milliseconds on, 90 milliseconds off. If the lamp-on time were increased, the relative amplitude would increase for the component having the longest time constant. Thus the shape of the composite decay characteristic would be altered, leading to a change in the percentage decay during the sample delay period. This of course would result in a different scaling factor of apparent phosphorescent activity, even though the sample time remained unchanged.

Furthermore there is at least a possibility that the components responsible for the several time constants have different spectral emittance characteristics. Their sum, which is the overall spectral distribution, might therefore be altered by a change in excitation conditions. Somewhat the same effect could be introduced in the selection of the time delay between cessation of excitation

and the measurement sampling time. When this delay is made long enough to allow full decay of the shorter time constant, any spectral contributions from these components would thereby be eliminated.

It is known that the excitation and measurement duty cycles are different in the three systems of interest, which are the facer-canceler, the phosphormeter and the NBS calibrator. Excitation conditions in the first two are similar (7.5 ms on, 24.5 ms off) except for the rising buildup as the stamp approaches the irradiating uv lamp in the facer-canceler. This buildup function is not duplicated in either of the other systems. Measurement conditions however (0.5 ms delay) are similar in the facer-canceler and the NBS instrument. Here the phosphormeter differs from the others, since the sample period begins immediately after lamp extinction.

Thus all the systems involved have differences in excitation and measurement conditions, and in view of the observed composite of several time constants, can be expected to show differences in response. These differences will chiefly be evident in scaling factors, where small variations in sample delay are likely to have more effect in the phosphormeter, since response is large to the short time constant section of the decay characteristic.

4.5 Intrinsic phosphorescence

The ceramic base material in the present design of phosphor standards displays a strong phosphorescence of its own. This can seriously interfere with the calibration process unless measures are taken to either 1) standardize and calibrate this intrinsic phosphorescence, or 2) eliminate the effect and calibrate only the phosphorescence resulting from the added luminescent material. The latter course is the one employed in the NBS calibrator. However a certain amount of information has been collected about this essentially-unwanted phenomenon of intrinsic phosphorescence, even though a detailed investigation was considered beyond the scope of the project. Such data as we have learned are presented here for completeness.

Zero-phosphor standards were made in the normal process but without the inclusion of luminescent material. Measurements on these specimens on the phosphormeter and the NBS calibrator were then made to establish the general degree of response to intrinsic phosphorescence. In the

phosphormeter, the response varied from low in the green range (1 PMU) to moderate in the red phosphorescent mode (8 PMU). There was also a variability with regard to specific phosphormeters and zero-phosphor samples. In the NBS calibrator there was a small response amounting to approximately 0.2 PMU.

Response to intrinsic phosphorescence in the facer-canceler was not measured, since there would be no normal occasion for the device to look at phosphor standards. The inference from other conditions, such as the timing of the sample period (0.5 ms), suggest that the facer-canceler response would be somewhat less than that of the phosphormeter.

In order to determine at least qualitatively the reasons for the observed response in the phosphormeter to intrinsic phosphorescence, the following information has been developed.

The spectral distribution of the emitted intrinsic phosphorescence appears to lie in the region of 700 to 800 nanometres. Supporting evidence for this conclusion comes from experiments with long-wave pass/exclusion filters inserted into the NBS calibrator, and from off-line experiments with a monochromator, the latter not fully documented. When the infrared region above 650 nanometres is excluded by optical filters, the observed response to intrinsic phosphorescence is greatly reduced. A report from the original manufacturer of the phosphormeter and standards indicated that the infrared emission may equal or exceed that in the visible region. Presumably the heat-absorbing filter incorporated in phosphormeters and facer cancelers is to suppress the response in this near infrared region as much as possible.

The time constant of intrinsic phosphorescence is in the order of 1.0 millisecond. This value was derived by emphasizing the response to the near infrared in the NBS instrument through the use of filters. Test specimens have included those from zero to high values of phosphor content.

The variability of intrinsic phosphorescence is appreciable, judging by readings ranging from 7.6 to 8.7 PMU on a series of eight zero-phosphor standards, as measured on one phosphormeter. This variability on zero-phosphor specimens suggests that there can also be variability in the contributions of the ceramic base in the normal phosphor standards. It is possible that further work could develop a method for direct measurement of intrinsic phosphorescence on the normal standards. Correlation so far has been poor between phosphormeter readings and attempts to isolate intrinsic phosphorescence in the NBS instrument.

It should be apparent from the foregoing discussion that intrinsic phosphorescence in the ceramic is a serious problem which interferes with accurate evaluation of phosphor standards. In our view, response to this factor should be eliminated, either through improved selections of materials for the standards, or through minimizing phosphormeter response. For the latter there are the dual possibilities of excluding the near infrared spectral region or lengthening the sample delay.

In the NBS calibrator the equivalent magnitude of response to intrinsic phosphorescence is approximately 0.2 PMU. This amount, although small, must be removed. Two methods were tried, 1) subtraction of the measured response to zero phosphor standards and 2) increased sample delay to allow complete decay. The results were equivalent, with operational convenience favoring the adoption of the subtractive technique. The criterion for agreement was equal ratios between low, medium and high-level standards.

In the absence of techniques for measuring the intrinsic phosphorescence on assembled phosphor standards, the approximations of one PMU (green) and 8 PMU (red) have been adopted. The application of these corrections is covered later in Section 5 - Calibration of standards.

5.0 Calibration of standards

In this section the process is described by which the present level of luminescent activity as it exists in the Bureau of Engraving and Printing and in the Postal Service, was related to output indications from the NBS instrument. Specifically the goal was to determine the multiplying constants so as to convert

to current PMU values from the efficacy figures derived from the NBS instrument. Efficacy is the name given to the instrument's output as described in the companion report "Technical manual for phosphor standards calibrator". Efficacy is an indicator of luminescent efficiency which is in many ways analogous to reflectance but which takes into account the wavelength shift due to luminescence. It is equivalent to the ratio of emitted visible luminescent power divided by the ultraviolet power which would be reflected from a perfectly diffusing surface under the same conditions of uv irradiation. As it is accomplished in the NBS instrument, efficacy is substantially independent of detailed characteristics in the system.

5.1 Procedure, phosphorescent standards

In order to establish the conversion coefficient it was first necessary to acquire a standard, or preferably a group of standards, of known value(s). This was done by collecting a number of the new phosphor standards (3 red and 3 green) plus two prior reference standards, all in the vicinity of 22 PMU. These were measured on 5 phosphormeters in the Washington area, with normal calibration based upon the reference standards for the individual phosphormeters. An intercomparison of plotted measured values yielded the group average, which could in turn be represented by any member standard provided a correction was applied to compensate for that standard's departure from the group average. On this basis the two reference standards for the 4A8 phosphormeter were selected, and assigned the values of 23.16 and 23.76 PMU for the standards 258 (green) and 458 (red) respectively.

The cited PMU values include the effects of surface reflectance and intrinsic phosphorescence to which the phosphormeter is known to respond. When the correction for this undesired response was applied, so as to indicate the visible phosphorescence (NBS-PMU) only, the two final values became 22.16 and 15.76.

The efficacy of these two conversion standards was then measured in the NBS instrument approximately 15 times over a period of two weeks, establishing mean efficacy figures of 0.002096 and 0.001616. The probable uncertainties in these measurements (standard deviation) were 0.5 and 0.8 per cent for green and red respectively.

The conversion of efficacy to NBS-PMU was established on the basis of the above data. To obtain NBS-

PMU for green phosphorescent standards, for example, it is necessary to multiply the measured efficacy by 10583. Similarly the conversion constant for red standards is 9771. With the completion of the one-time conversion process, it was then possible to evaluate in terms of NBS-PMU any phosphorescent standard whose efficacy was known.

Each of the newly fabricated phosphor standards was measured for efficacy at least three times over a two-week interval. The resultant efficacy figures were converted to NBS-PMU values, using the two conversion coefficients for green and red standards as mentioned above. Mean NBS-PMU values were found for each standard, rounded off to the nearest 0.1 unit, and assigned to the individual standards. These are the calibrated levels of phosphorescent activity for the new standards.

As described in detail in the Technical Manual, the NBS-PMU values must be corrected by the addition of a constant to take into account the response in the phosphormeter to surface reflectance and intrinsic phosphorescence. Thus the working USPS ratings of the new green phosphorescent standards has 1.0 PMU added to the NBS-derived level, in order to determine the meter indication to which the phosphormeter must be set. Red standards require correction by 8.0 PMU for the same purpose. These final working values were then marked on the labels attached to the standards, using the labelling technique mentioned in Section 2.3 - Mechanical modifications.

5.2 Procedure, fluorescent standards

Fluorescent standards are instrumented in the NBS calibrator so as to provide measurement of the emitted luminescent output (efficacy) in two spectral ranges, namely the red and yellow regions of the spectrum. The same general arrangement is employed in the phosphormeter. The two responses are combined by separately measuring red and yellow channel efficacies, converting these to PMU with appropriate constants, then subtracting the yellow-channel PMU from the red. The purpose of the overall conversion process was to establish the two scaling factors, for the red and yellow channels respectively, so that efficacy readings from the NBS instrument could be converted to PMU values for the phosphormeter. Since it was necessary to determine two conversion constants, data from two measurement conditions were required. The most convenient approach was to take two standards, one high and one low,

and force agreement with two simultaneous equations of the form:

$$\text{PMU value} = K_1 (\text{red channel efficacy}) - K_2 (\text{yellow channel})$$

Data from two standards consisting of known or designated PMU, together with instrument response, then allowed solving for K_1 and K_2 .

The first step was to determine the PMU values to be assigned to the two standards used for the conversion. For this evaluation one group of six Red Fluorescent and another of six Background Fluorescent standards were assembled. The chosen standards were obtained principally from those at the Bureau of Engraving and Printing (Standards nos. 861, 862, 867, 868, 870, 661, 662, 667, 668, 670) plus the calibration for Phosphormeter 4A8 (no. 858 and 658). This group was assumed to be representative of fluorescent standards in operating use, and hence suitable for establishing the conversion scale factor. The marked values on each standard were taken as their reference values, in contrast to a round-robin program of measurement on phosphormeters used for the phosphorescent standards. Then the 12 standards were measured for red channel and yellow channel efficacy on the NBS instrument.

From comparison of the measured red channel efficacy with respect to marked PMU values, it was determined that standard no. 858 was representative of the group average within a small fraction of one PMU. Its marked value and indicated response were then entered into the equation above. The same procedure was followed for Background standard no. 658, yielding a second set of values. Solution of the equations produced the two conversion constants of $K_1 = 8506$ and $K_2 = 930$. These are the proportioning constants listed in the Technical Manual for the instrument, under Section 2.2c - Conversion to PMU values.

It should be mentioned that the derived constants are critically dependent upon the spectral characteristics of the red and yellow channel isolating filters, particularly as regards cross-channel pickup. It may be necessary to re-examine the derivation of the conversion constants in the event that the filters are changed.

Thus the steps described so far were to select a group of standards whose overall activity level was chosen for perpetuation, to select two representative samples from

this group and to use them for the determination of conversion constants. The remaining step as a check was to convert all the other standards in the group on the basis of these constants, comparing the resultant and marked values. Agreement was found to be within approximately 0.5 PMU in all cases, with a standard deviation of 0.3 PMU.

The conversion constants of 8064 (red) and 822 (yellow) were applied to the figures of efficacy as provided by the NBS calibrator instrument when measuring the new standards. The resultant assigned values are given in the following section.

The method of derivation of efficacy is covered in detail in the Technical Manual under Sections 2.1b - Definition of efficacy, and 2.2 - Theory of operation, detailed.

5.3 Assigned measured values of phosphor standards

5.3a Phosphorescent standards

Application of the conversion constants derived as in Section 5.1 resulted in assignment of PMU values to the new standards as listed below. For reference, readings on the Model 4A8 phosphormeter are also given.

Table 7

Assigned values of new phosphorescent standards

<u>Standard</u>	<u>Value assigned by NBS Calibrator</u>	<u>Reading on 4A8 Phosphormeter</u>
Green phosphorescent		
G20	23.4	24.0
21	23.3	23.8
22	23.1	23.2
23	21.8	23.0
24	23.4	23.4
25	23.2	23.2
26	23.8	23.8
27	23.7	23.3
28	23.6	23.5

G40	48.8	47.9
41	49.0	47.6
42	48.5	46.1
43	48.7	48.0
44	46.0	44.7
45	46.3	46.0
46	45.4	44.2
47	45.8	45.6
48	46.6	46.3
49	43.0	41.9
G80	85.6	88.4
81	90.3	93.9
82	89.2	90.1
83	94.6	97.0
84	89.7	89.5
85	89.0	87.9
86	88.8	86.0
87	87.1	84.7
88	90.2	89.1
89	87.0	87.1

Red phosphorescent

R20	22.0	21.7
21	22.6	23.3
22	23.2	23.4
23	23.8	22.9
24	24.5	24.2
25	25.4	23.6
26	24.3	22.7
27	25.5	23.3
28	24.8	23.9
R40	51.4	50+
41	46.1	46.4
42	49.7	48.1
43	42.3	42.6
44	42.2	40.9
45	44.0	41.9

46	42.6	40.9
47	42.4	40.4
R80	89.8	89.5
81	99.4	98.1
82	97.8	94.3
83	100.9	98.6
84	91.6	88.8
85	92.1	88.3
86	90.8	87.9
87	90.3	85.9

5.3b Fluorescent standards

Application of the conversion constants mentioned in Section 5.2 to the new standards fabricated from commercially-procured wafers resulted in the PMU values listed below. For reference, readings on the 4A8 phosphormeter are also given.

Table 8

Assigned values of new fluorescent standards

<u>Standard</u>	<u>Value assigned by NBS Calibrator</u>	<u>Reading on 4A8 Phosphormeter</u>
Background fluorescent		
B1	2.4	2.5
B2	2.4	2.5
B3	2.5	2.5
Red fluorescent		
F21	22.2	23.2
F22	21.1	22.5
F23	21.6	23.0
Reference standards		
658	1.0	1.2
858	22.5	22.5 (set)

6.0 Conclusions and recommendations

This section contains comments and recommendations which have resulted during the progress of the work. Minor suggestions for improvements in the fabrication procedure were made earlier in Section 2.4 - Notes on the fabrication procedure. The emphasis in this last section of the report is on inconsistencies in measurements found between the three major elements of the overall system: the facer canceler, the phosphormeter and the NBS calibrator. The desirability of bringing all of these closer to similarity on critical performance items is obvious. Lastly the need is pointed out for improvements in fluorescnet standards, in both fabrication and calibration.

Our study has shown at least four areas of concern relating to inter-instrument measurements on luminescent materials. These are, in decreasing order of significance:

- 1) Displacement of the measurement plane (setback)
As presently conducted with the phosphormeter the active surface is much closer to the uv lamp for stamps than it is for phosphor standards. This results in a 40% increase in apparent luminescent activity for stamps and test cards.
- 2) Inclusion of intrinsic phosphorescence in response to red standards.

This factor accounts for about 30% of the red phosphorescent indication for 22 PMU standards. It also introduces complications when measuring high-level phosphor standards.

- 3) Response in the phosphormeter to surface reflectance.

Because of the visible components of emission from the uv lamp in the phosphormeter, plus a possible hang-on characteristic in recovery from signal overload, there appears to be a 5 to 10 percent response to reflective materials such as barium sulfite. As in (2) above, this complicates extrapolation to high values of luminescence.

- 4) The different duty cycles of excitation and times prevailing among the instruments produce

arbitrary scaling factors. However it has not been proved that this interferes with scale extrapolation.

The above are the four problem areas where we believe that remedial action should be taken. Specific recommendations on each item are given in the sections which follow.

The effect of displacement of the plane of measurement in the phosphormeter means that use of the device will over-rate stamps and test cards by approximately 40 percent, as compared to measurement on a displacement-independent system. The exact degree of over-rating will depend upon local conditions, even such apparently trivial ones as rotation of the uv lamp, which is the prescribed approach for initial mid-range adjustment. We believe that the proper solution is to make all measurements with stamps in the same plane as the wafer faces in the phosphor standards. Then there will be a good chance of agreement between instruments on comparative evaluations of stamps, test cards and phosphor standards. This agreement cannot now exist.

One possible implementation would be to add a spacer mask to the phosphormeter when measuring stamps, which is the technique used in the NBS calibrator. Such a mask for stamps should be 0.10 inch (2.5 mm) in thickness to match the average setback in phosphor standards. In the event that other configurations of luminescent materials are to be calibrated, compensating changes should be made in the mask thickness.

The question naturally arises as to whether PMU evaluations should be based upon present levels of phosphor standards or of stamps, with the distinction possibly accounting for as much as a 40 percent change in overall scale. We recommend retention of the present scale of conversion, which is based upon phosphor standards, as using the most stable, reproducible elements in the system for conversion determination. Adoption of this approach is also consistent with the recommendation of a single plane for measurement.

Response to intrinsic phosphorescence should be eliminated if at all possible, since it is the major source of uncertainty on red phosphorescent standards. It should be possible to reduce the effect considerably by employing a low pass interference filter to suppress the near infrared above approximately 650 nanometres. Some benefit should also be obtained by delaying the time of signal sampling to 0.5 millisecond, in view of the 1-ms time constant for intrinsic phosphorescence.

It should be possible to reduce the response to surface reflectance by either 1) delaying the time of signal sampling, or 2) adding a filter to pass only the 254-nm line from the pulsed uv lamp.

Because it appears that several of the items have in common certain potential benefits from delaying the time of signal sampling, we are recommending that signal sampling be changed to approximately 0.5 ms, matching the delay in both the facer canceler and the NBS instrument.

In regard to the desirability of improvements in fluorescent standards, the problems chiefly originate in spectral mismatches. The present two-channel approach used in the facer canceler and the phosphormeter and hence in the NBS calibrator, greatly complicates the task of standardization. The spectral characteristics of the required red and yellow isolating filters have critical influence in the magnitude of output indications from all of the devices. Operationally the problem is most noticeable in the use of the phosphormeter, which must deal with both fluorescent standards and indicia-imprinted envelopes or test cards, where the fluorescent inks may exhibit spectral characteristics differing from those of the standards. Under these conditions it is not assured that standards which have been fabricated and calibrated by the present process are adequate for control of the activity levels of fluorescent inks.

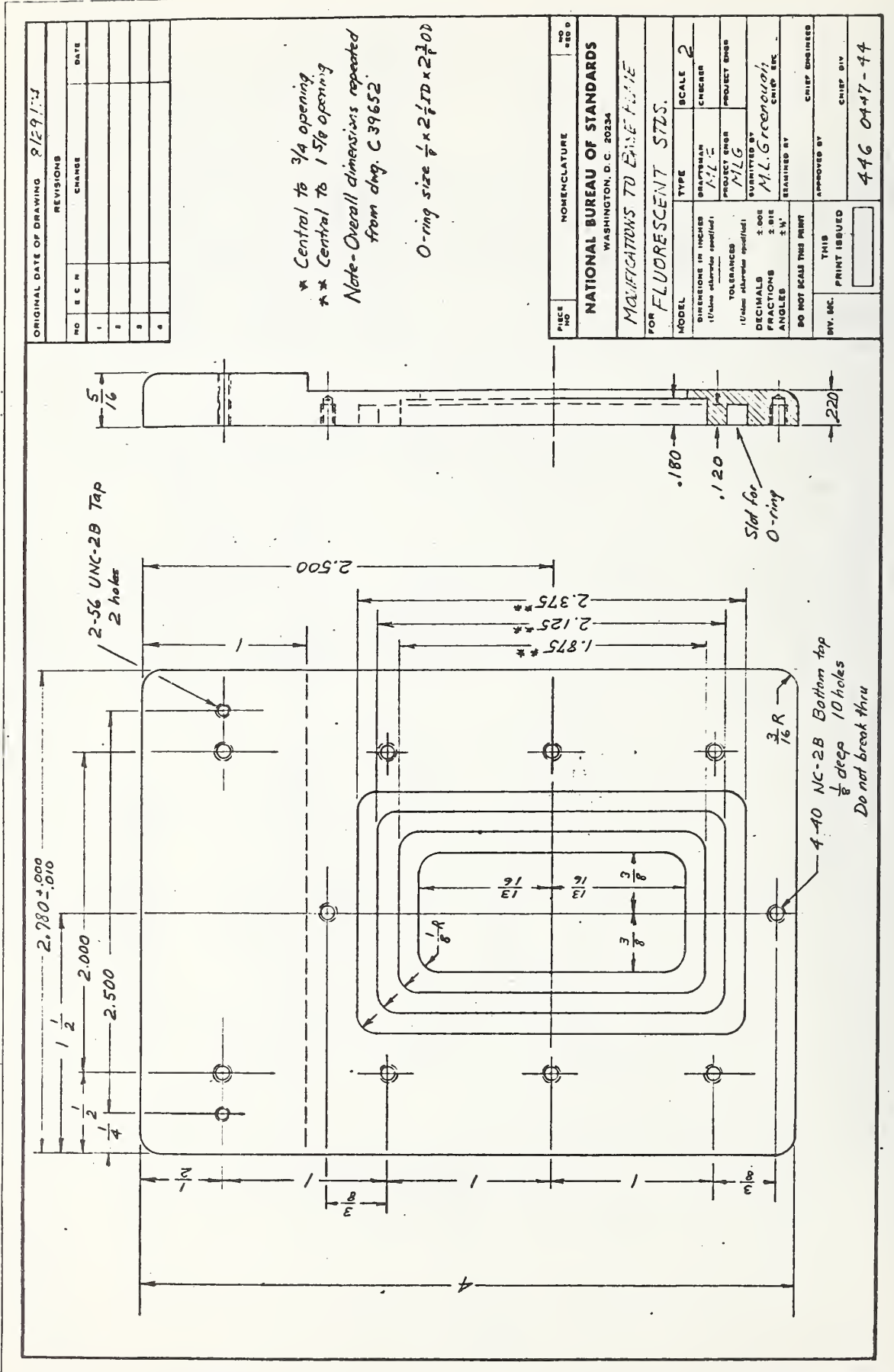
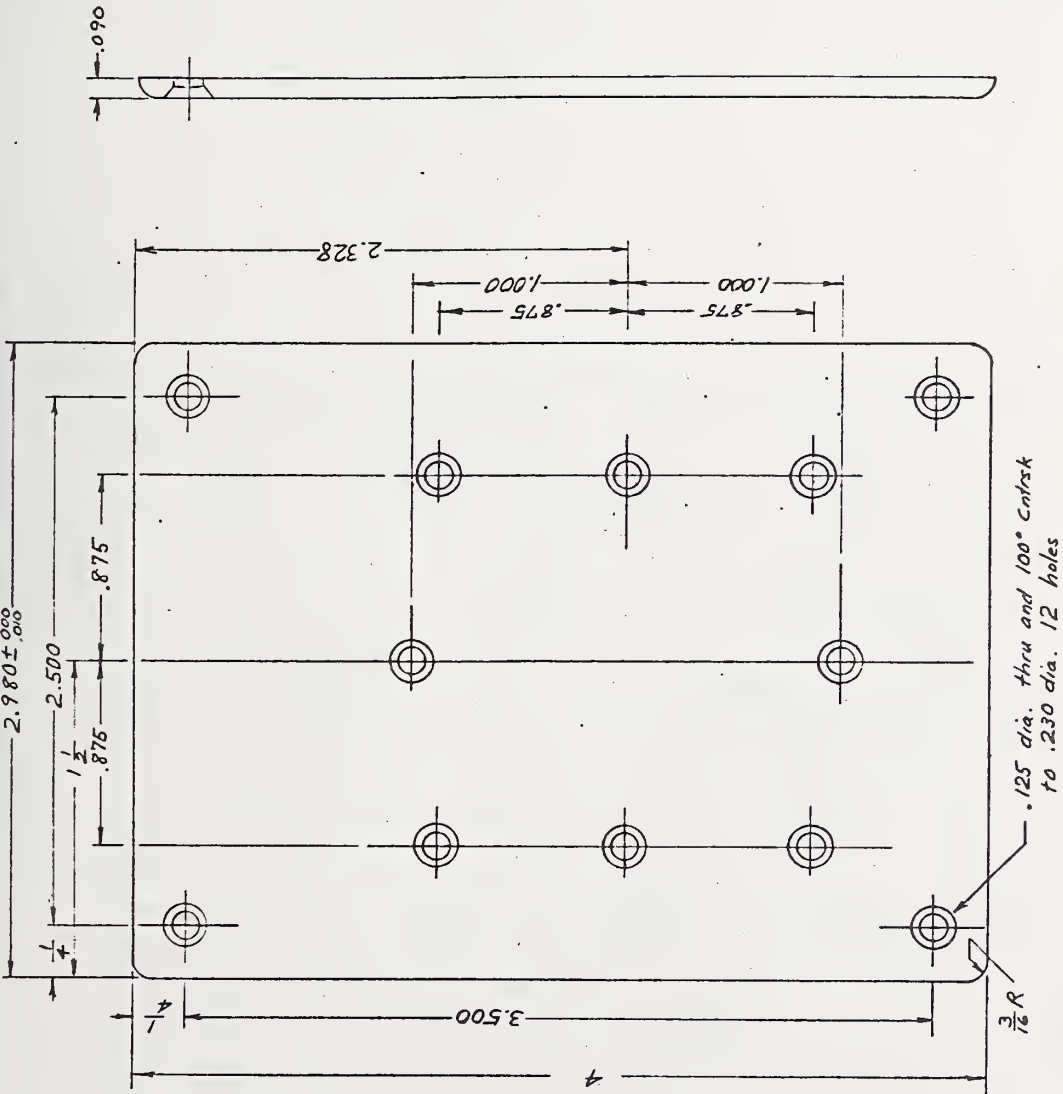


FIGURE 2. MODIFICATIONS TO BASE PLATE, FLUORESCENT STANDARDS

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REVISIONS		
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1	CHANGE	
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Note - Overall dimensions repeated from dwg C 39653



PIECE NO.	NOMENCLATURE	NO. OF PAGES
	NATIONAL BUREAU OF STANDARDS	
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MODIFICATIONS TO EARLY STANDARDS FOR PHOSPHORESCENT STD.		
MODEL	TYPE	SCALE
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	PROJECT ENGR	PROJECT ENGR
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	APPROVED BY	CHIEF ENGINEER
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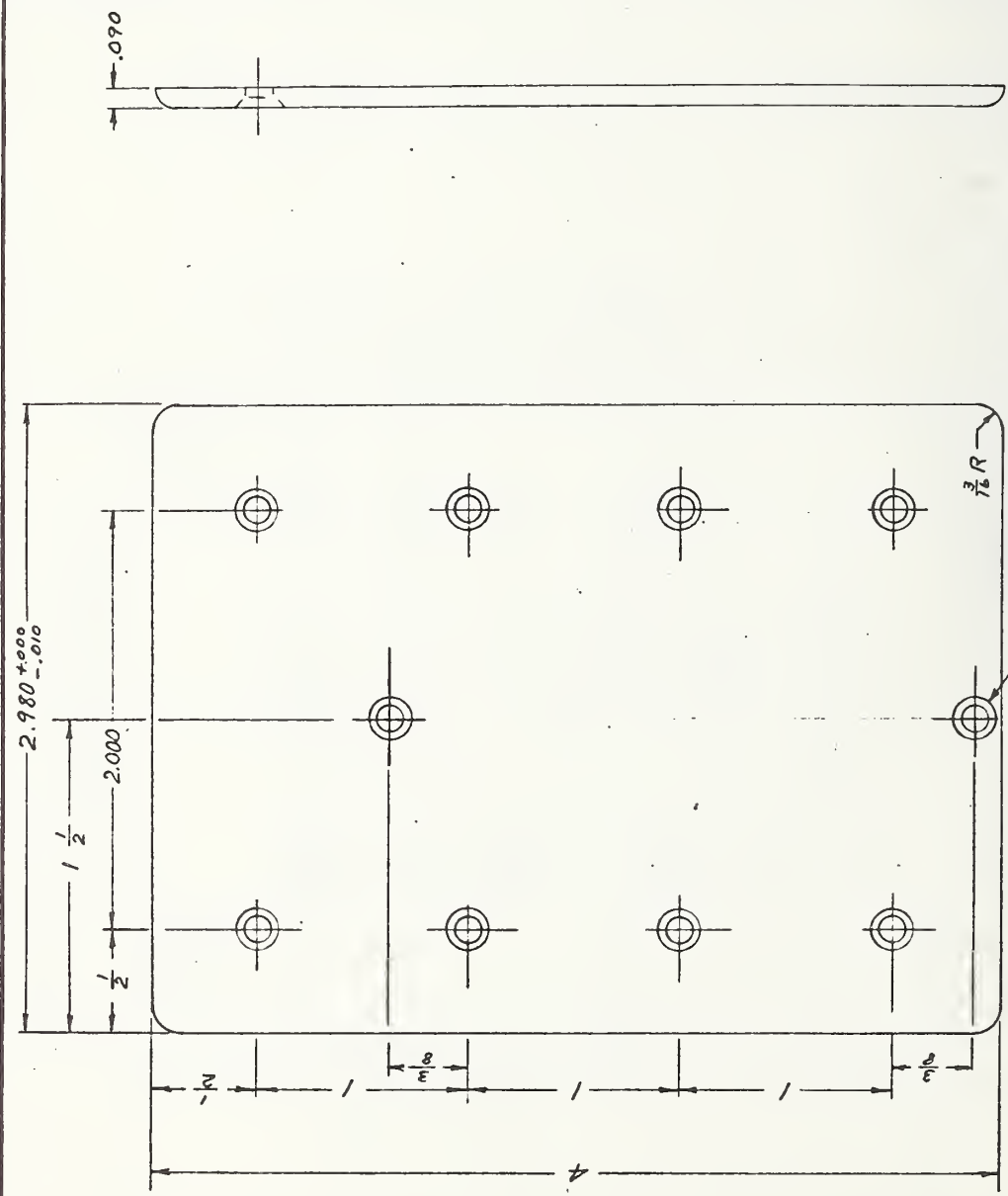
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FIGURE 3: MODIFICATIONS TO BACK PLATE, PHOSPHORESCENT STANDARDS

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.125 dia thru and 100° Cntersk
to .230 dia. 10 holes

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FOR FLUORESCENT SIZES.			
MODEL	TYPE	SCALE	2
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(1/16th increments smallest)	MLG		
TOLERANCES	PROJECT ENG	PROJECT ENGR	
(1/16th increments smallest)	MLG		
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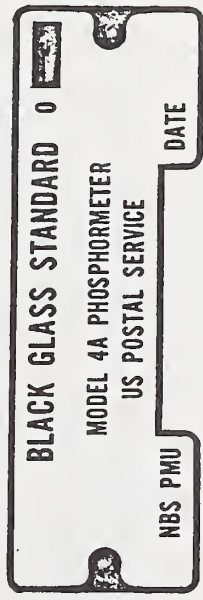
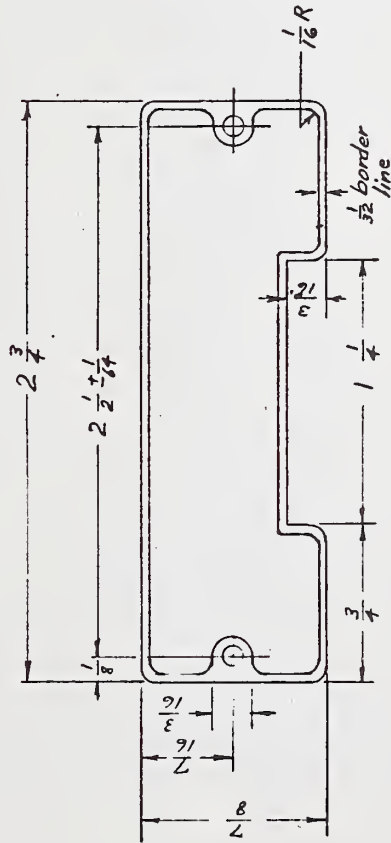
FIGURE 4. MODIFICATIONS TO BACK PLATE, FLUORESCENT STANDARDS

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Mat'l $\frac{1}{32}$ Photo etched aluminum
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FIGURE 5. REPLACEMENT FOR USPS
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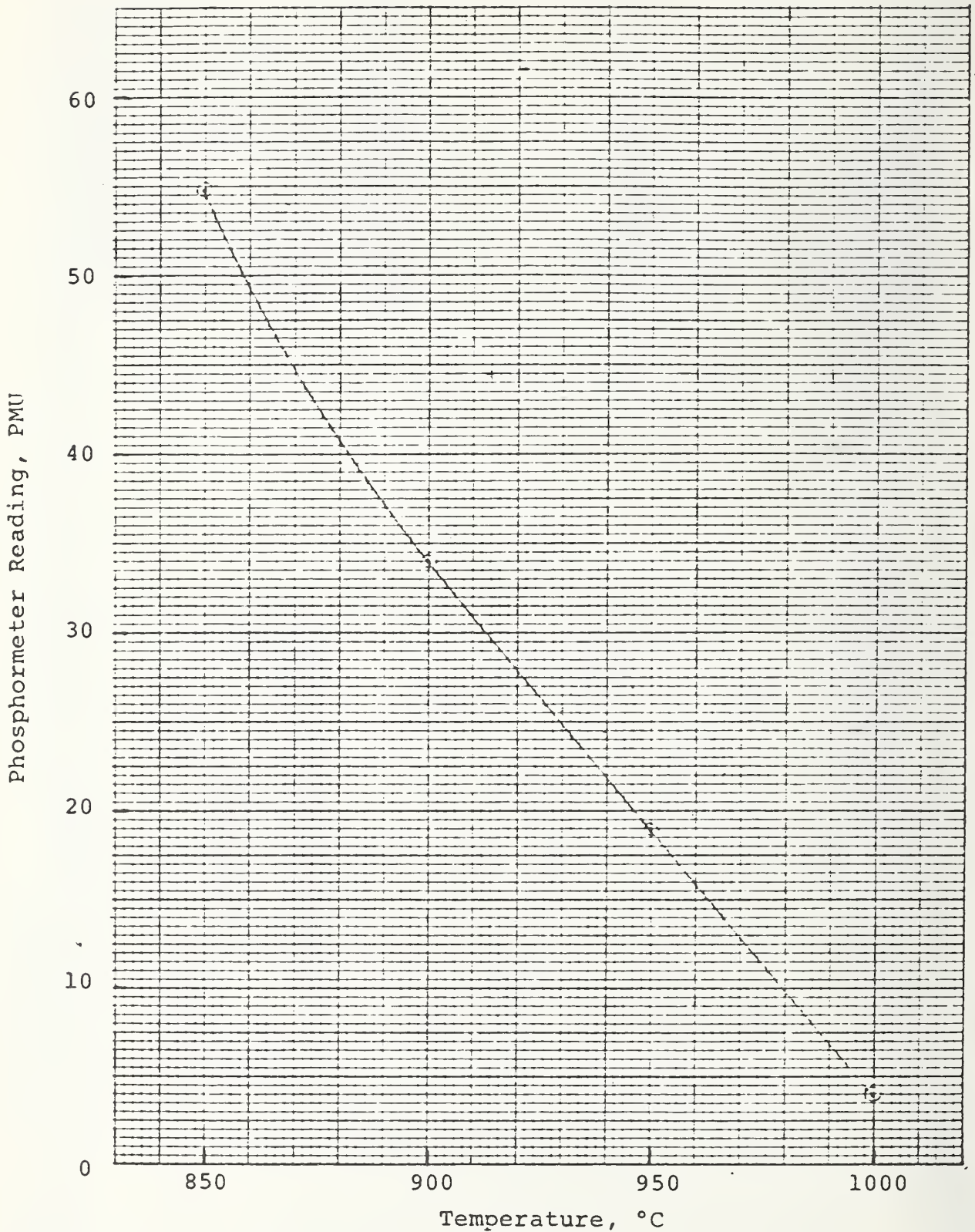


Figure 6. Plot of phosphormeter readings as a function of firing temperature for green ceramic wafers containing 4 w/o phosphor. At 920°C gradient is $-0.3 \text{ PMU}/^\circ\text{C}$.

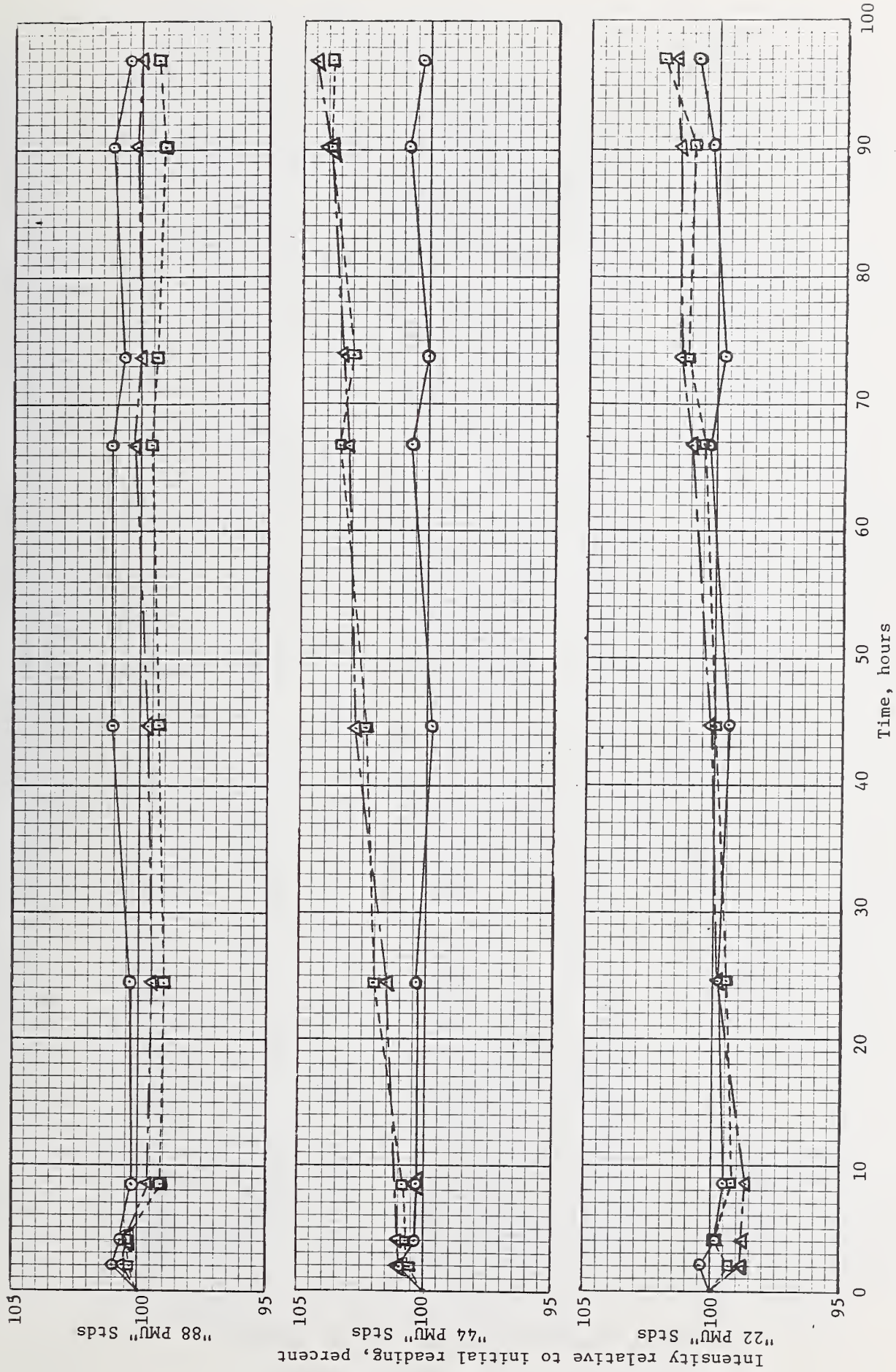


Figure 7. Aging effect of green phosphorescent standards with radiation from low-pressure mercury arc.
 ○ = Unaged control standard, COM wafer. ◻ = Aged standard, COM wafer. △ = Aged standard, NBS wafer. NBS Calibrator

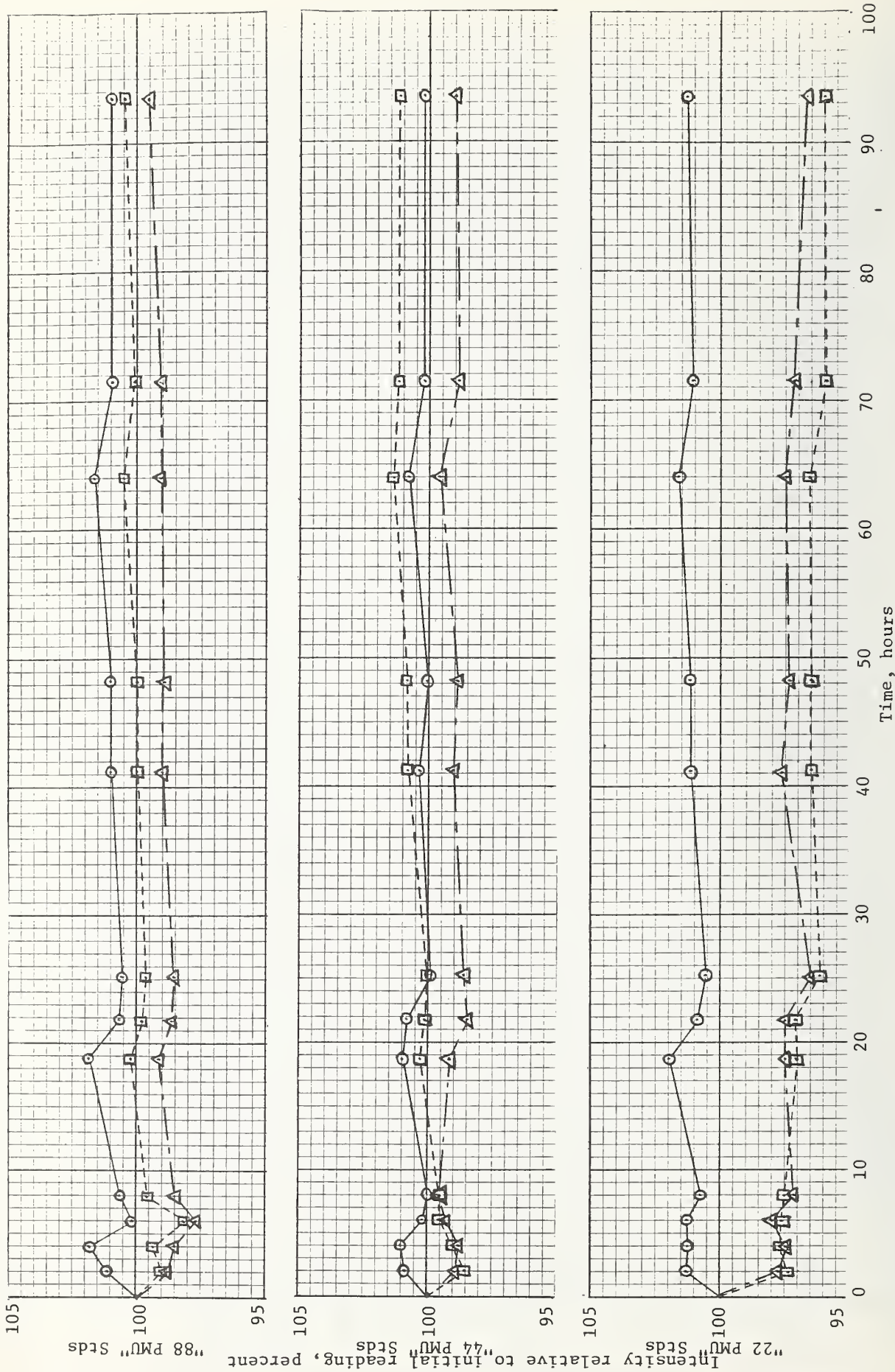


Figure 8. Aging effect of red phosphorescent standards with radiation from low-pressure mercury arc.

○ = Unaged control standard, COM wafer. □ = Aged standard, COM wafer. △ = Aged standard, NBS wafer. NBS Calibrator

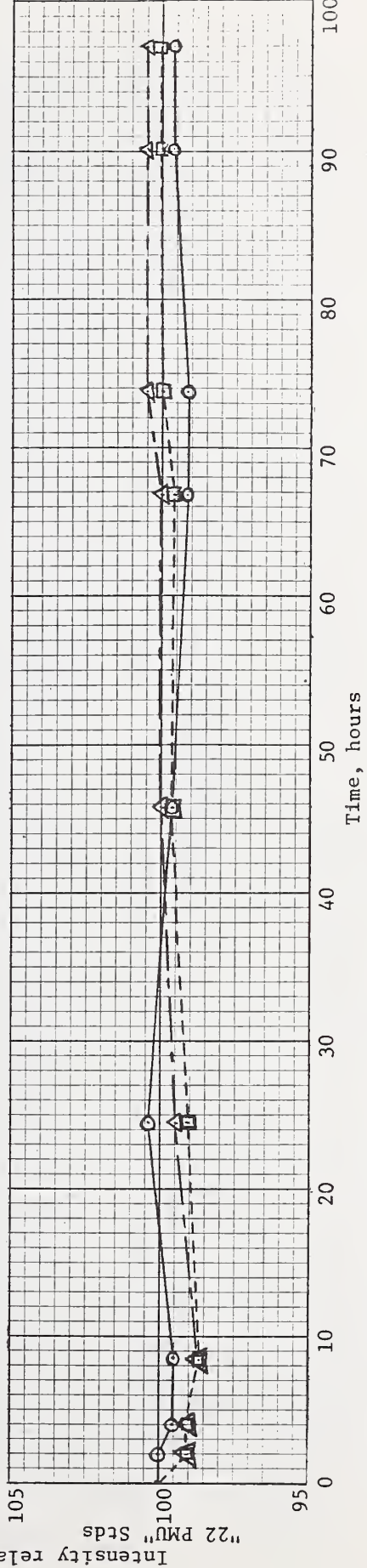
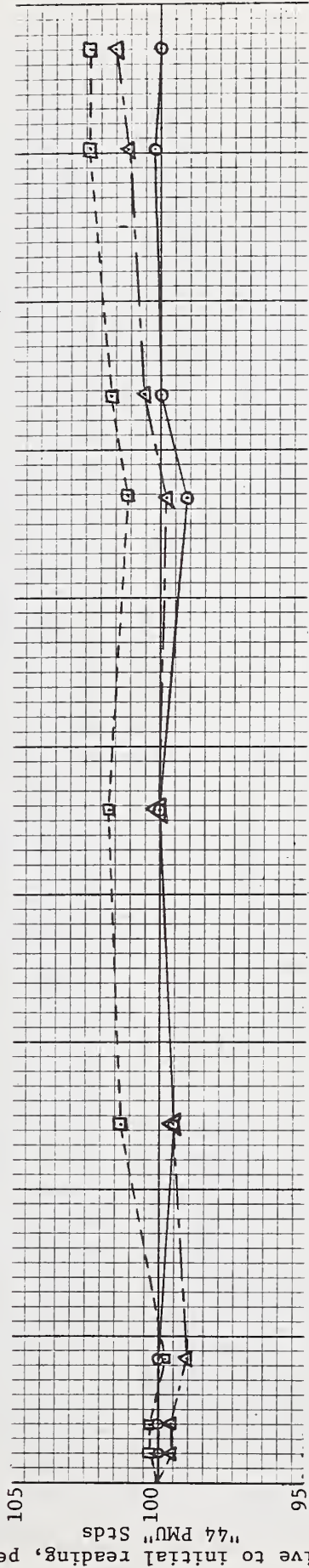
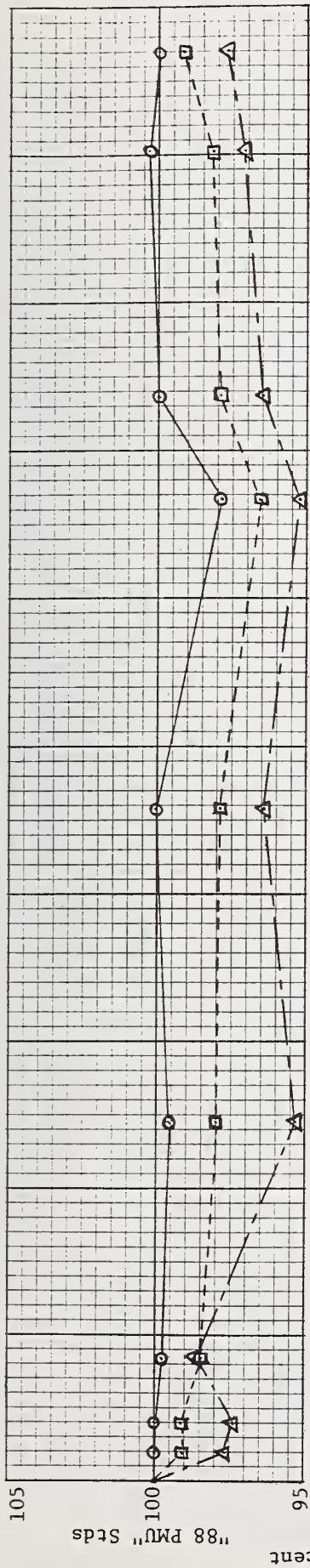


Figure 9. Phosphormeter measurements, aging of green phosphorescent standards, low-pressure mercury arc. ○ = Unaged control standard, COM wafer. ◻ = Aged standard, COM wafer. △ = Aged standard, NBS wafer.

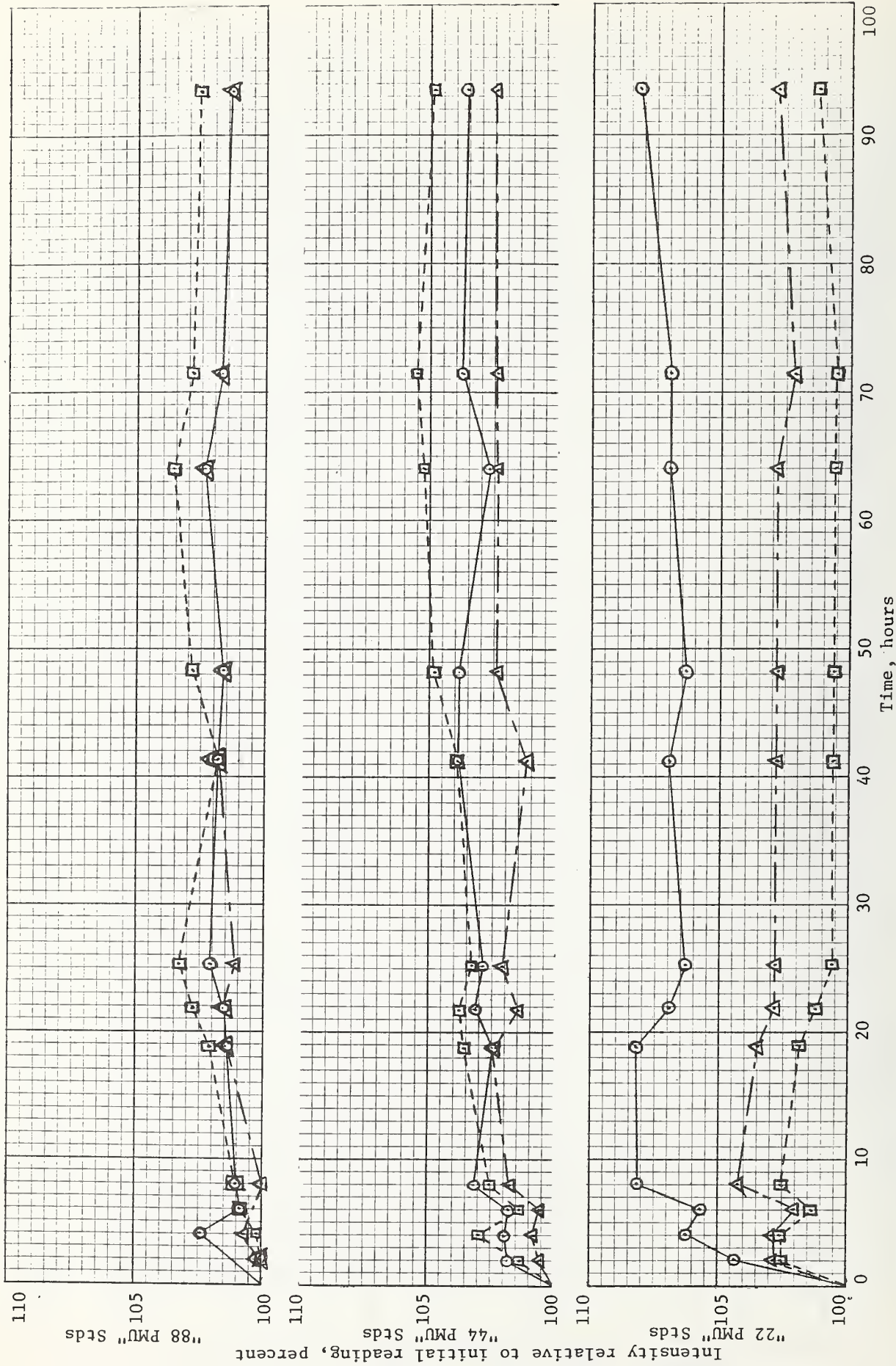


Figure 10. Phosphormeter measurements, aging of red phosphorescent standards, low-pressure mercury arc. \circ = Unaged control standard, COM wafer. \square = Aged standard, COM wafer. \triangle = Aged standard, NBS wafer.

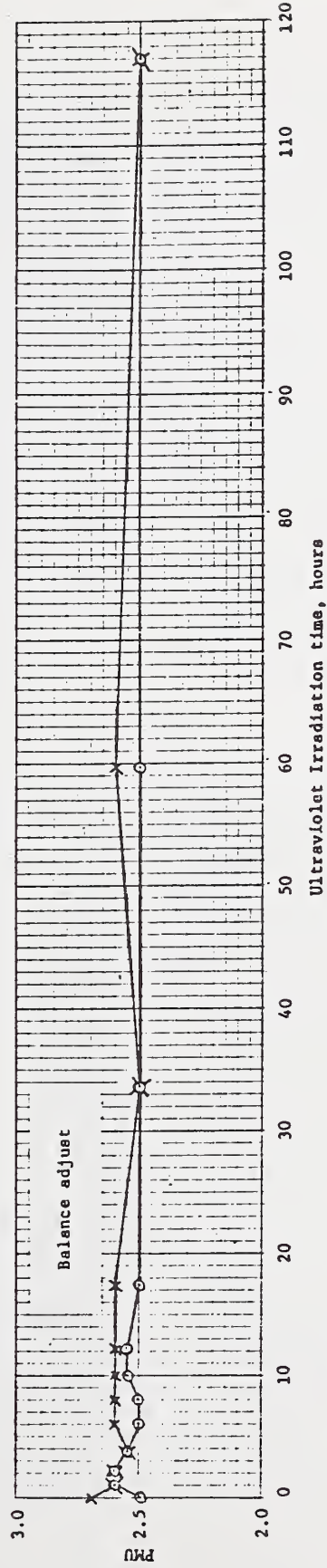
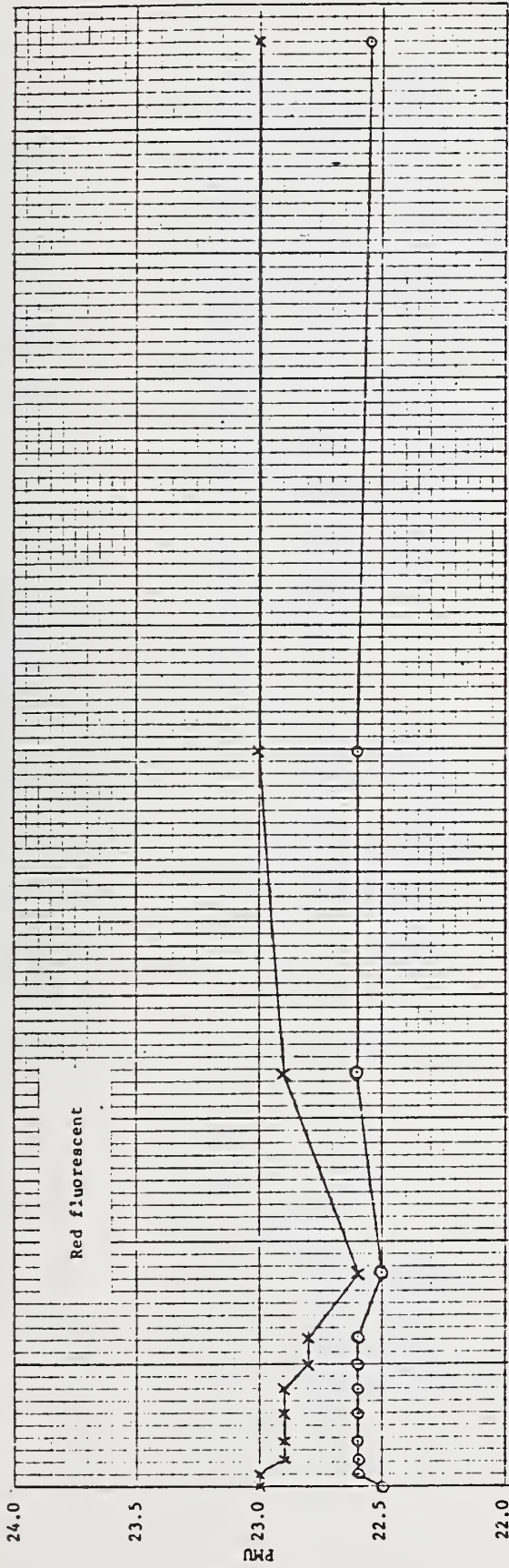


Figure 11. Phosphormeter measurements of aging effect of fluorescent standards.
 O = Unaged control standard. X = Aged standard.

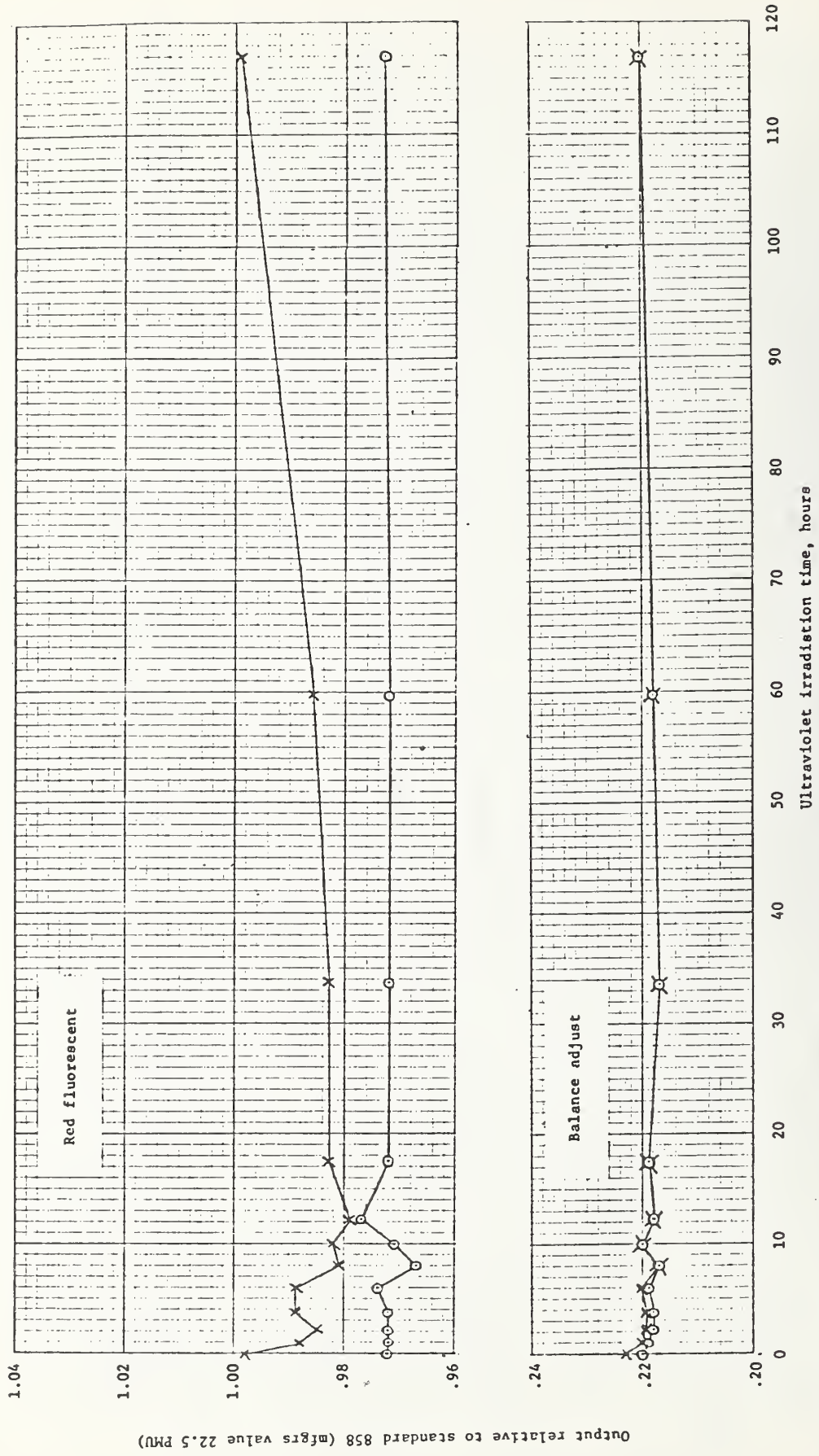


Figure 12. NBS calibrator measurements of aging effect of fluorescent standards.

⊙ = Unaged control standard. X = Aged standard.

Output relative to standard 858 (mfg's value 22.5 PMU)

Ultraviolet irradiation time, hours

OUTPUT -- Phosphormeter, PMU, corrected for intrinsic phosphorescent
 -- NBS Calibrator, equivalent PMU derived from best fit

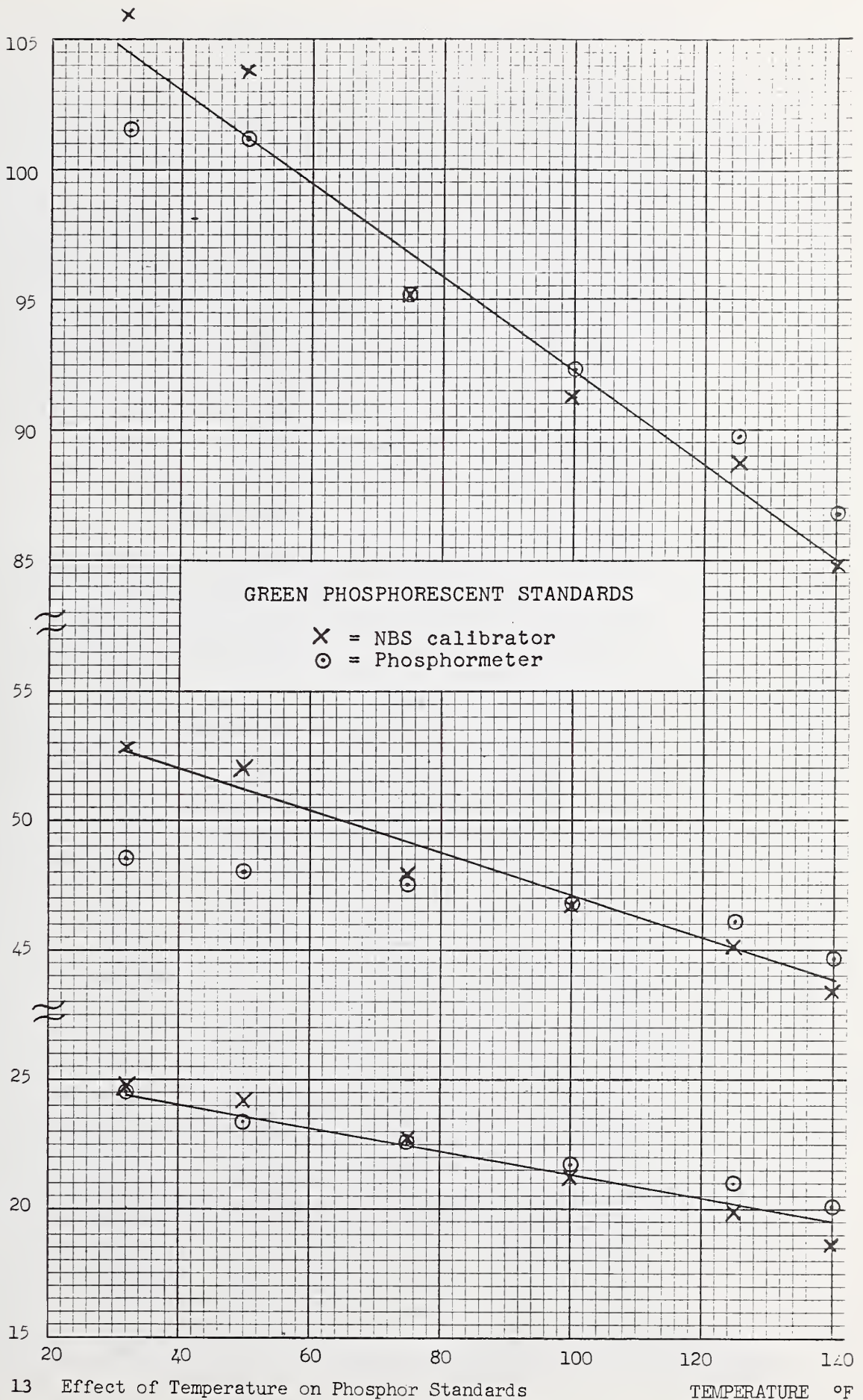


FIGURE 13 Effect of Temperature on Phosphor Standards

TEMPERATURE °F

OUTPUT -- Phosphormeter, PMU, corrected for intrinsic phosphorescent

-- NBS Calibrator, equivalent PMU derived from best fit

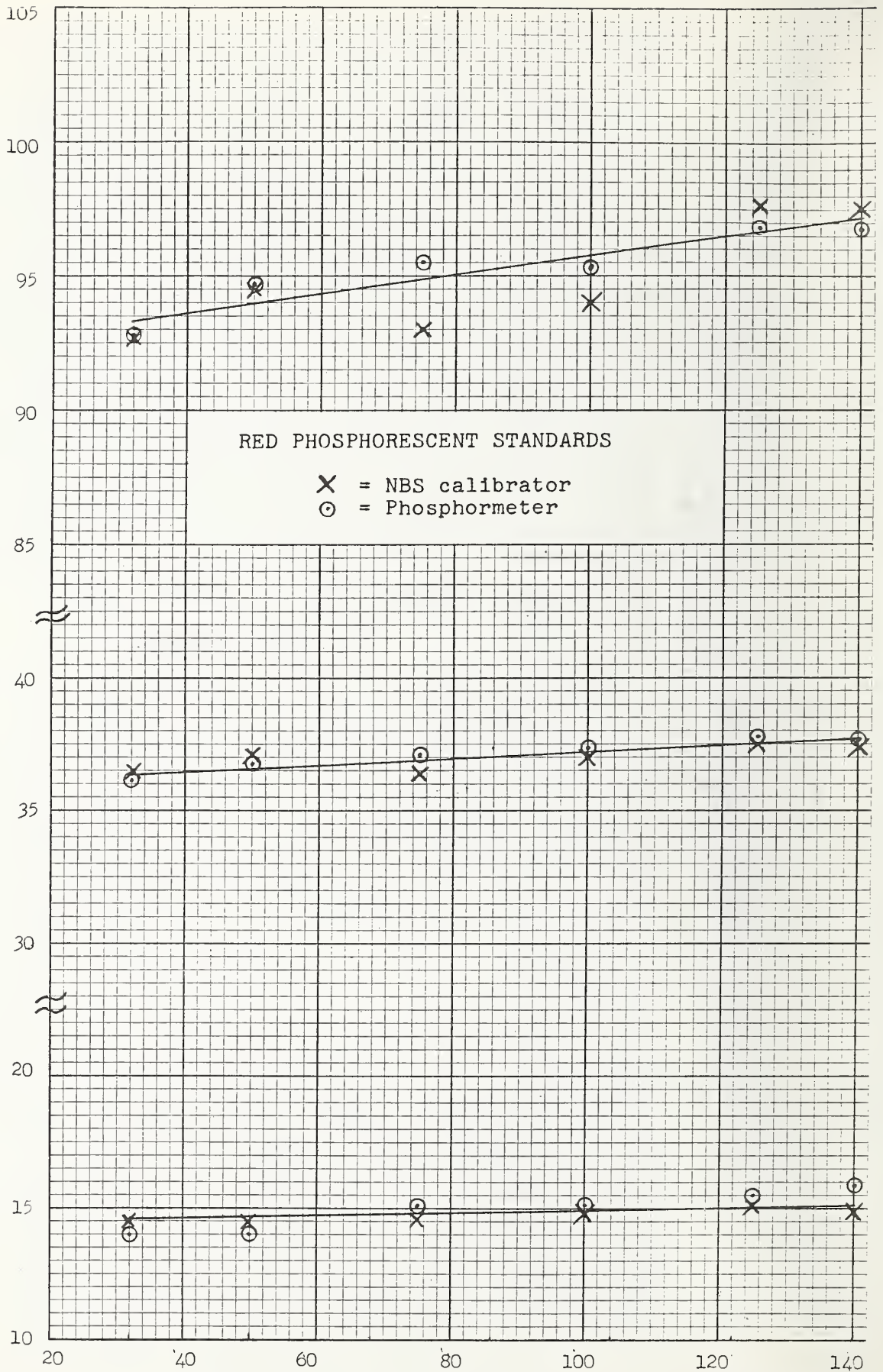


FIGURE 14 Effect of Temperature on Phosphor Standards

TEMPERATURE °F

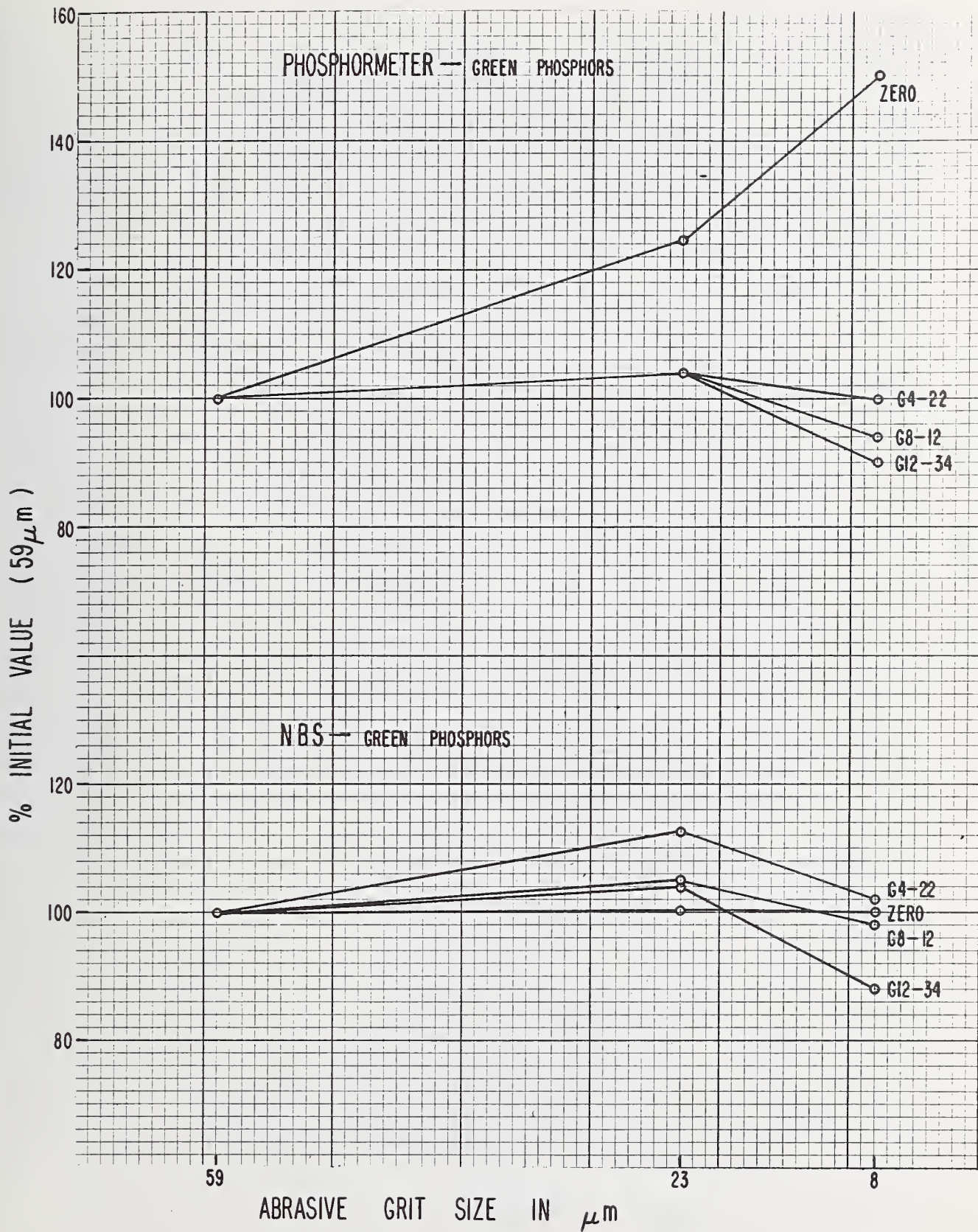


FIGURE 15 EFFECT OF SURFACE FINISH UPON PHOSPHORESCENT ACTIVITY, GREEN

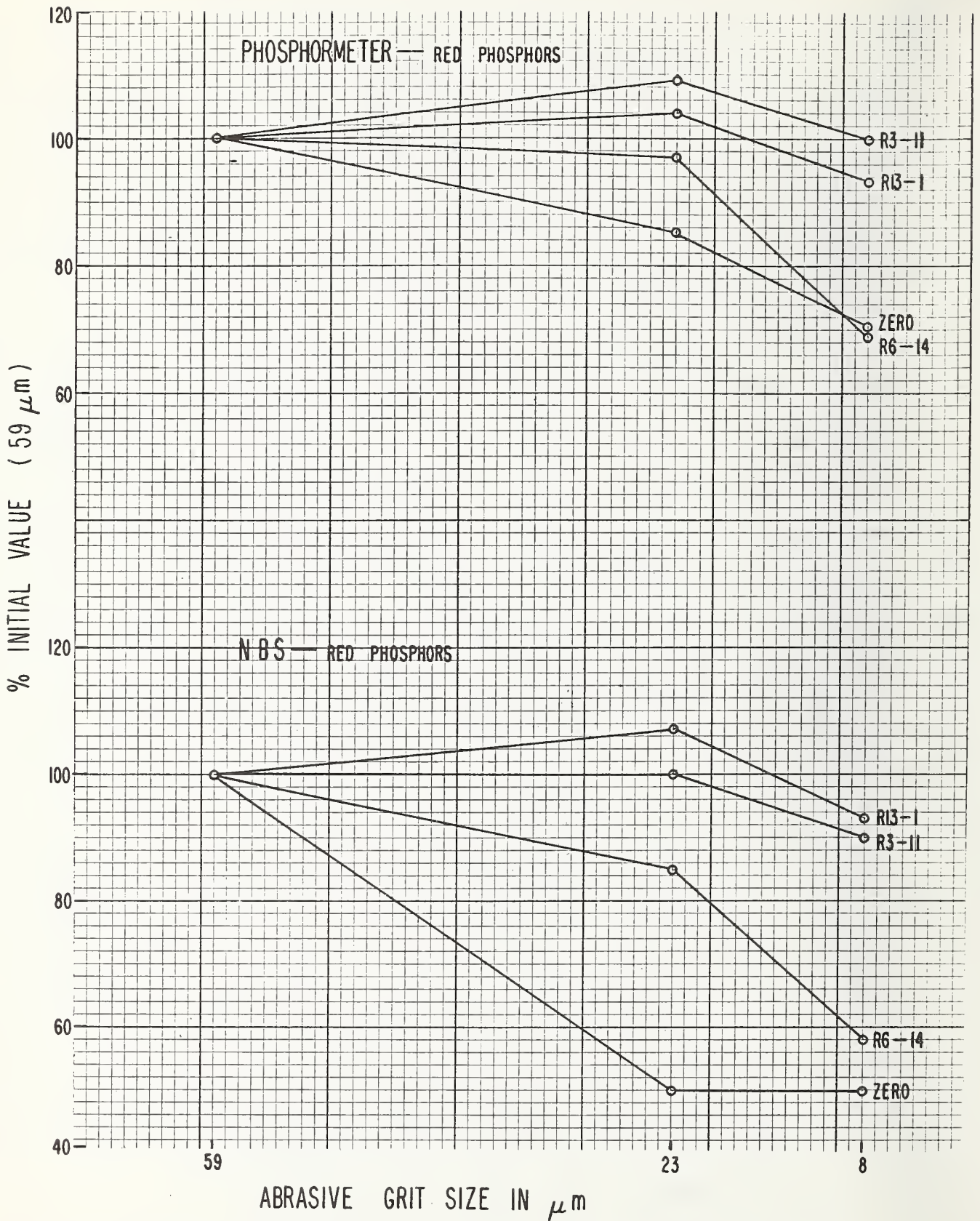


FIGURE 16 EFFECT OF SURFACE FINISH UPON PHOSPHORESCENT ACTIVITY, RED

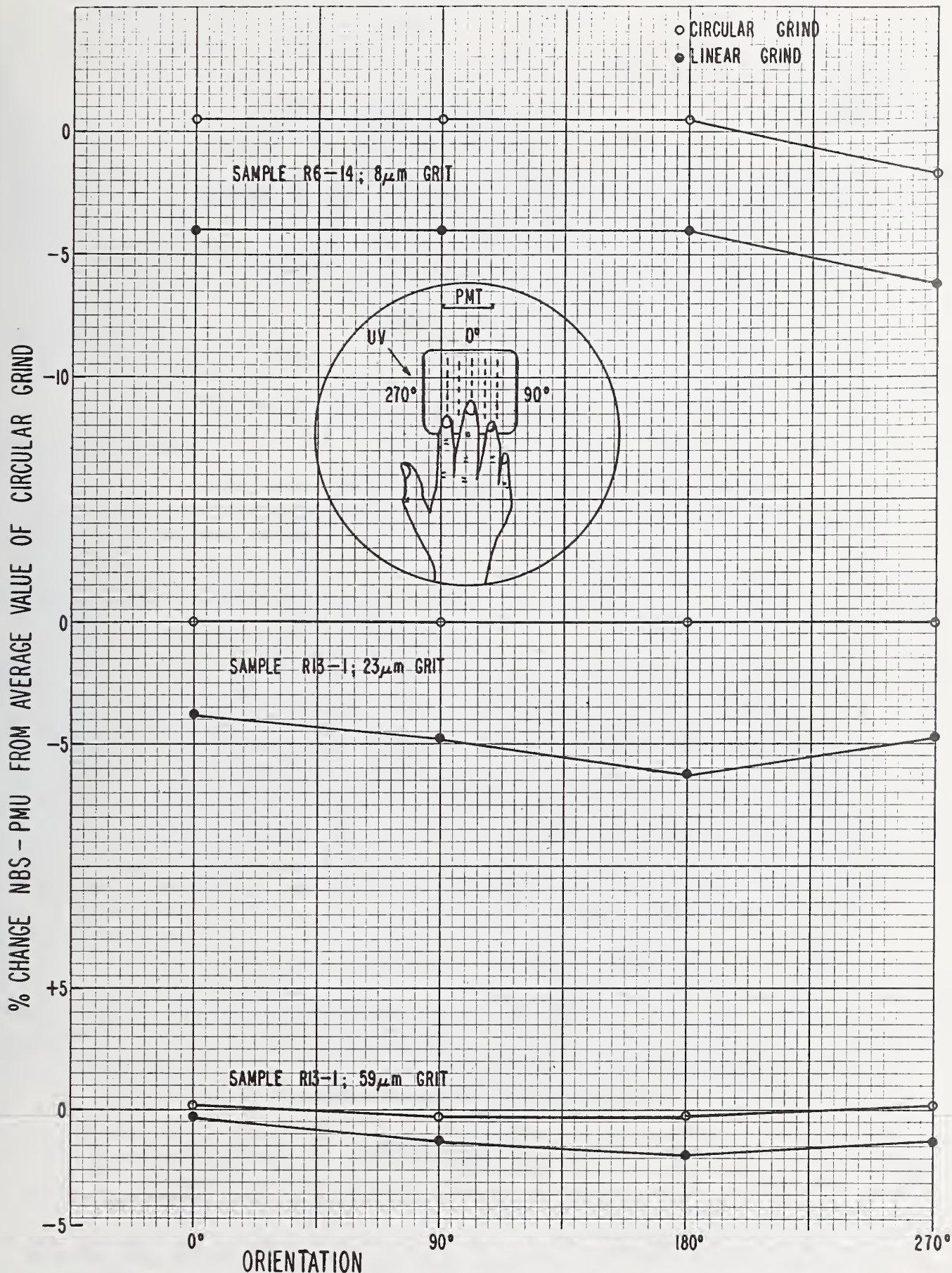


FIGURE 17 RELATION BETWEEN ORIENTATION OF SURFACE GRINDING AND MEASURED PHOSPHORESCENT ACTIVITY

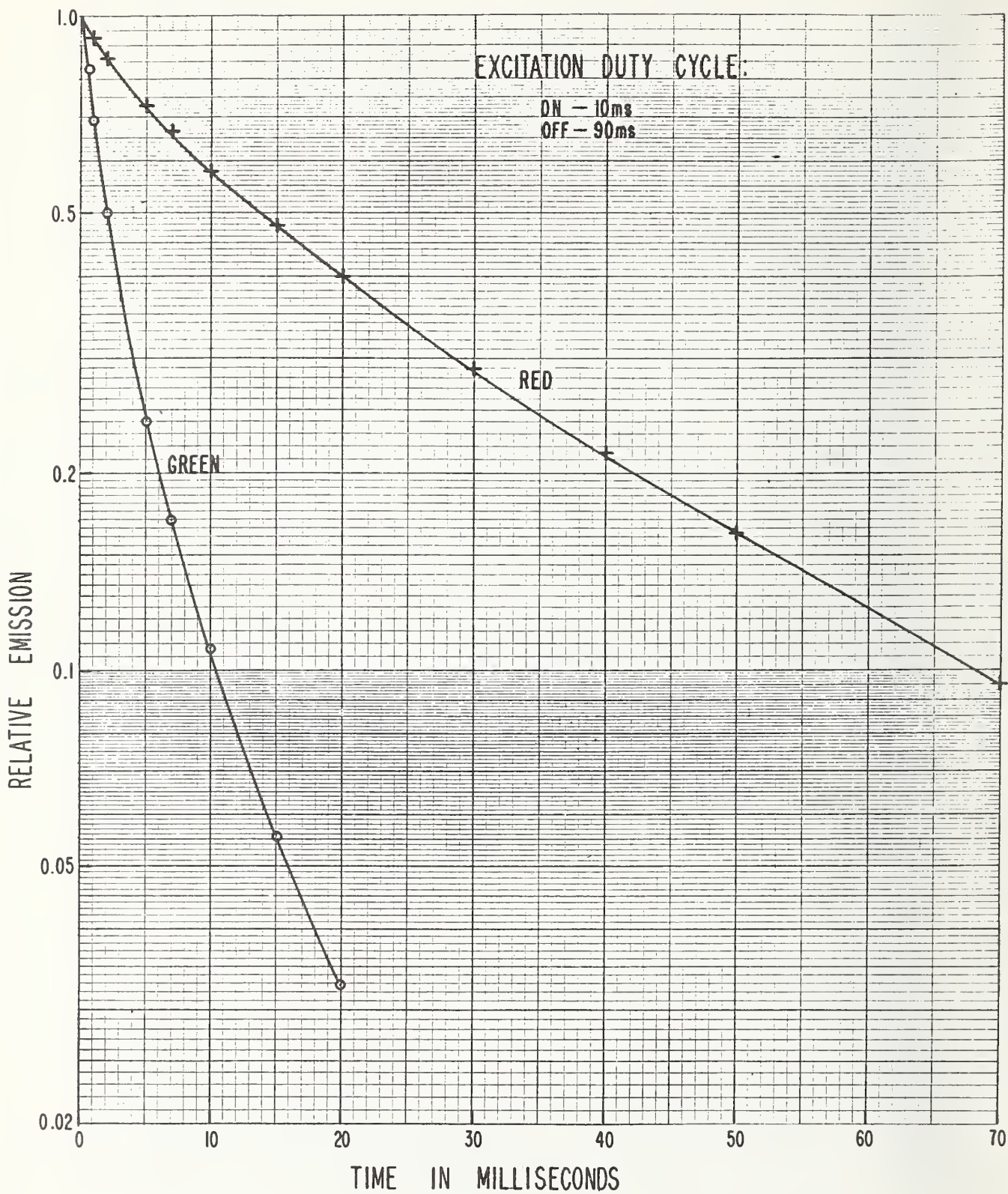


FIGURE 18. DECAY CHAR. OF GREEN & RED PHOSPHOR STANDARDS IN NBS CALIBRATOR

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 74-553	2. Gov't Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE Preparation and Calibration of Phosphor Standards		5. Publication Date October 1974	6. Performing Organization Code
7. AUTHOR(S) M. L. Greenough, H. K. Hammond III	8. Performing Organ. Report No. NBSIR 74-553	9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234	
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) U.S. Postal Service Planning and New Development Dept. 11711 Parklawn Drive Rockville, Md. 20852		10. Project/Task/Work Unit No.	11. Contract/Grant No. 13. Type of Report & Period Covered Final report 7/72-9/74 14. Sponsoring Agency Code
15. SUPPLEMENTARY NOTES A draft of this report has been reviewed and approved by the sponsor			
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)			
<p>This project involved two activities, 1) the fabrication and calibration of phosphor standards for use in the Postal Service Model 4A8 Phosphormeter and 2) the construction of an instrument to perform the calibration function. Both of these relate to the standardization of the phosphorescent and fluorescent activity of the luminescent coatings applied to postage stamps by the Bureau of Engraving and Printing. The purpose of the luminescent coatings is to facilitate detecting the orientation of envelopes in facer-canceler machines during mail processing.</p>			
<p>Work on the project entailed the fabrication of approximately 60 phosphor standards, which are hand-sized aluminum blocks into which stamp-sized wafers of luminescent materials are mounted. Fabrication was carried out following the specific procedures supplied by the Postal Service, with however, authority to verify or alter the process as necessary. On the other major project effort, an instrument was designed and constructed following in general the basic design of an earlier breadboard device developed under a prior project. Quantitatively in the system, evaluations are ultimately referred to calibrations at NBS of the relative irradiance of a lamp in the ultraviolet and visible regions of the spectrum.</p>			
<p>This report, one of two covering the project activities, describes the preparation of luminescent wafers, their assembly into phosphor standards and the test procedures on completed standards. It includes a tabulation of the calibrated values of the new standards.</p>			
17. KEY WORDS (six to twelve entries; alphabetical order, capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Fluorescence measurement; Instrumentation, luminescence measuring; Luminescence measurement; Phosphorescence measurement			
18. AVAILABILITY <input checked="" type="checkbox"/> Unlimited <input type="checkbox"/> For Official Distribution. Do Not Release to NTIS <input type="checkbox"/> Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13 <input type="checkbox"/> Order From National Technical Information Service (NTIS) Springfield, Virginia 22151	19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED 20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	21. NO. OF PAGES 72 22. Price	

