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RESEARCH AND DEVELOPMENT OF A SINGLE GUN COLOR CRT

PHASE I - FINAL REPORT

by Thomas E. Sisneros, Paul A. Faeth, and Joseph A. Davis

Prepared by
ITT INDUSTRIAL LABORATORIES
Fort Wayne, Ind.
for Electronics Research Center

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ITT Industrial Laboratories
Fort Wayne, Indiana

ABSTRACT

The feasibility of producing cathode-ray tubes which have a current density-dependent color variation at constant accelerating voltage has been demonstrated. The screens for these tubes were prepared by combining superlinear phosphors with linear or sublinear phosphors. The preparation of phosphors having a superlinear intensity versus current density behavior was studied. Phosphors having superlinear behavior in the current density range normally used for CRT operation were prepared by partially poisoning (ZnCd)S:Ag with a few ppm of Ni. A number of experimental screens and tubes were prepared utilizing various combinations of experimental phosphors. Color shifts from reddish-orange to yellow and from yellowish-green to yellow to orange have been obtained.

INTRODUCTION

Since the human eye is much more sensitive to differences in hue than it is to brightness differences, it is desirable to incorporate color capability in cathode-ray tubes used for information display. Many studies have been made in which the advantages of color coding have been established for rapid identification and evaluation of alphanumeric and other types of data (Ref. 1-9).

Most of the recent work in the area of color cathode-ray tubes has been oriented toward the development and improvement of full-color systems for entertainment purposes. Very little attention has been given to the development of cathode-ray tubes having high resolution or limited color range for use in simplified color display systems.

Color cathode-ray tubes may be divided into two general classes: those having patterned screens and those with non-patterned screens. The patterned screens are those in which the phosphors are deposited in some type of pattern so that a phosphor emitting in one color can be excited independently of the phosphors which emit in other colors. This class of color cathode-ray tubes includes the well-known shadow-mask tube which is used for color television (Ref. 10). The phosphor screen in this tube consists of the primary color phosphors (blue, green, red) deposited in a triad dot pattern. A shadow mask having one hole for each phosphor dot triad is placed between the phosphor screen and the electron guns. The tube employs three guns and each electron beam is focused such that it excites only the dots of one phosphor. The desired spectral colors are obtained by varying the emission from each of the three primary colors.

Another type of patterned tubes employs screens in which the three phosphors are deposited as stripes. Included in this type are the Lawrence tube, the Sunstein tube, the Apple tube and the Goodman tube (Ref 11-12). These tubes are all single-gun cathode-ray tubes while the chromatron, which is actually a variation of the Lawrence tube, employs three guns. The Lawrence tube and chromatron use a beam-switching grid near the phosphor screen to deflect the electron beam to the desired phosphor. The other three tubes employ various types of beam indexing methods to excite the three phosphors to the desired intensity.

Another example of a cathode-ray tube having the phosphor in a stripe pattern is the Gabor tube (Ref 13). This is a three-gun flat tube in which the beam must be deflected through 180 degrees followed by a 20 degrees deflection to the screen. A storage tube has been described in which the screen consists of a red phosphor dot surrounded by a ring of green phosphor (Ref 11). Flood beam electrons pass through holes in the storage grid in a small spot area when the grid is operated near cut-off potential thus producing a red image. As the grid potential becomes more positive, a larger area is excited and the green phosphor ring emits also, producing a yellow luminescence. Other variations of patterned screen color cathode-ray tubes have been

described but are of less importance and will not be described here.

Color cathode-ray tubes of the patterned screen type have several drawbacks for use in display systems. One drawback is the complexity of the electronic circuitry required to operate these tubes as compared with monochrome tubes. A major drawback is the limited resolution imposed by the phosphor screen pattern. Operation of these tubes using random scan as required by many display applications also presents problems not encountered when using normal TV raster scan.

The best known of the non-patterned screen color cathode-ray tubes is the penetration type of tube (Ref 14-15). In these cathode-ray tubes the phosphors are deposited in individual layers which are separated by non-luminescent buffer layers. The color variation is achieved by varying the accelerating voltage so that different phosphor layers are excited. Thus, at low voltage ($\simeq$ 6 kv) the layer closest to the electron gun is excited; then as the voltage is increased the electrons penetrate through the buffer layer and excite the second phosphor layer. A third layer can then be excited by increasing the voltage further. In general, voltage increments of 4-6 kv are required to switch from one phosphor layer to the next. A variation of the layered screen in which layered phosphor particles are used is described in the patent by Kell (Ref. 16). Two-color cathode-ray tubes and storage tubes (Ref. 11-17) utilizing penetration screens have been described and are commercially available.

The major drawback of the penetration type of tube is the necessity of switching the accelerating voltage. One approach is to use a separate electron gun for each layer and operate the guns at different voltages. The more common approach is to use one gun and switch the high voltage whenever it is desired to change colors. Both of these methods create deflection and focusing problems especially if high frequency switching is desired. Thus, optimum operation of these tubes requires rather complicated circuitry.

A color cathode-ray tube for radar display has been reported recently in which a long-decay photoluminescent phosphor is used along with cathodoluminescent phosphors to differentiate between moving and stationary targets (Ref. 18). The screen consists of a layer of a long-decay green-emitting photoluminescent phosphor (such as P-2), an electron-beam-barrier layer (such as evaporated silica) which is transparent to UV and visible radiation, and a layer of mixed red-emitting and UV-emitting cathodoluminescent phosphors (such as P-22R and P-16). A screen such as this shows fixed objects as white while moving objects appear in shades of red with a green tail.

Because of the problems associated with the various types of color cathode-ray tubes, the approach to a single-gun, non-patterned screen cathode-ray tube chosen for this study is one in which the color variation is current density-dependent at constant accelerating voltage. This effect can be obtained by using a mixture of phosphors in which there is a large difference in the rate of change of emission intensity as a function of excitation current density. This type of approach has many advantages over the

various types of tubes already described. Since a single-layer, non-patterned screen is used, the screen application is simple and similar to that used for monochrome mixed-phosphor screens such as those using P-4 phosphor. The operation of the tube is also relatively simple since only the current density must be varied and the capability for doing this is available in all systems by what is normally the brightness control. This type of screen is adaptable to practically all types of cathode-ray tube structures and these tubes could be used in most existing types of display systems. This approach is discussed in greater detail in the following sections.

There are many additional references in the literature to color cathode-ray tubes; the references listed in this report can serve as sources for many other references. A brief survey of color cathode-ray tube developments is included in the paper by Davis (Ref 19).

TECHNICAL DISCUSSION

The approach chosen for this program was that of combining a phosphor having superlinear intensity versus current density behavior with a phosphor having linear or sublinear behavior and a different emission color. This combination will produce a phosphor screen giving a color shift which is dependent on current density. This effect is illustrated in Figure 1 where curve A represents a superlinear phosphor and curve B represents a sublinear phosphor. Thus, at low current densities the emission color will be that of B and as the current density is increased, A will contribute more and the color will shift toward that of A. For example, if A is green and B is red, the color shift will be from red to orange to yellow to yellow-green. If A is red and B is green, the color shift will be from green to yellow-green to yellow to orange. Similarly, other color combinations will give other color shifts. However, it is preferable to choose two emission colors which do not give white when mixed together. As can be seen from the Kelly chart (Ref. 20) shown in Figure 2, the white region is quite large and combinations passing through it would give color shifts consisting mostly of pastel and off-white colors. This would result in poorer color discrimination than combinations which result in a range of relatively saturated colors. Thus, combinations such as blue-green, red-green and red-blue should be best. Of these the red-green combination was chosen for initial study because this region contains several readily distinguishable colors (red, orange, yellow, green) which are quite suitable for display applications.

The major advantage of this approach to a color cathode-ray tube is its simplicity. A tube of this type is analogous to a monochrome tube having a screen which consists of a two-component phosphor blend such as P-4. Therefore, a screen of this type could be substituted for the phosphor screen in any type of monochrome cathode-ray tube to give a color cathode-ray tube which could be operated with essentially the same parameters as the monochrome tube. These tubes could be substituted for monochrome tubes in present display systems with little or no modification to the electronic circuitry required to operate the tube. The main requirement would be a means for changing the current density whenever a color shift is desired. These tubes could be used with any

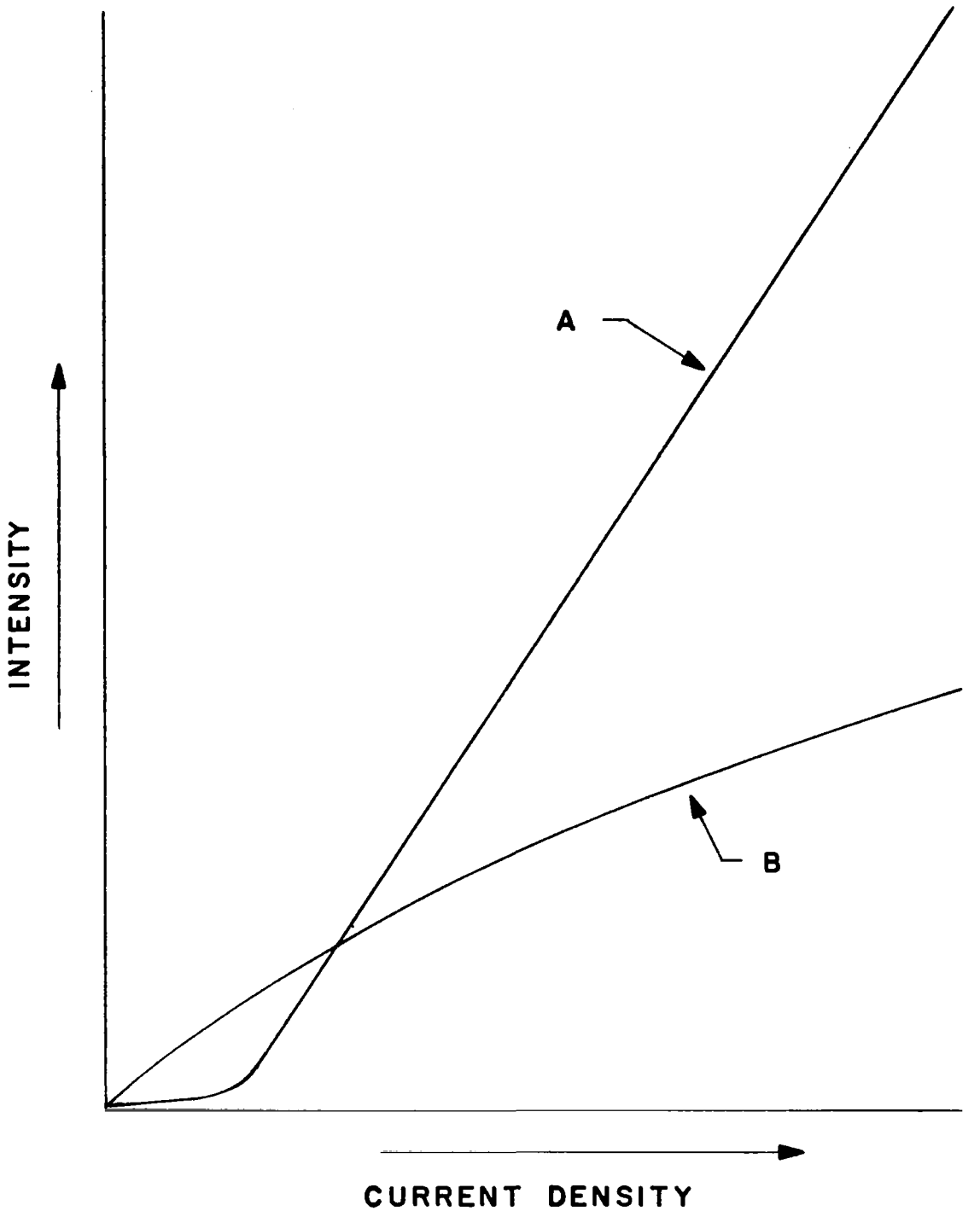

Figure 1 Emission Linearity of Phosphors
Curve A - Superlinear Phosphor,
Curve B - Sublinear Phosphor

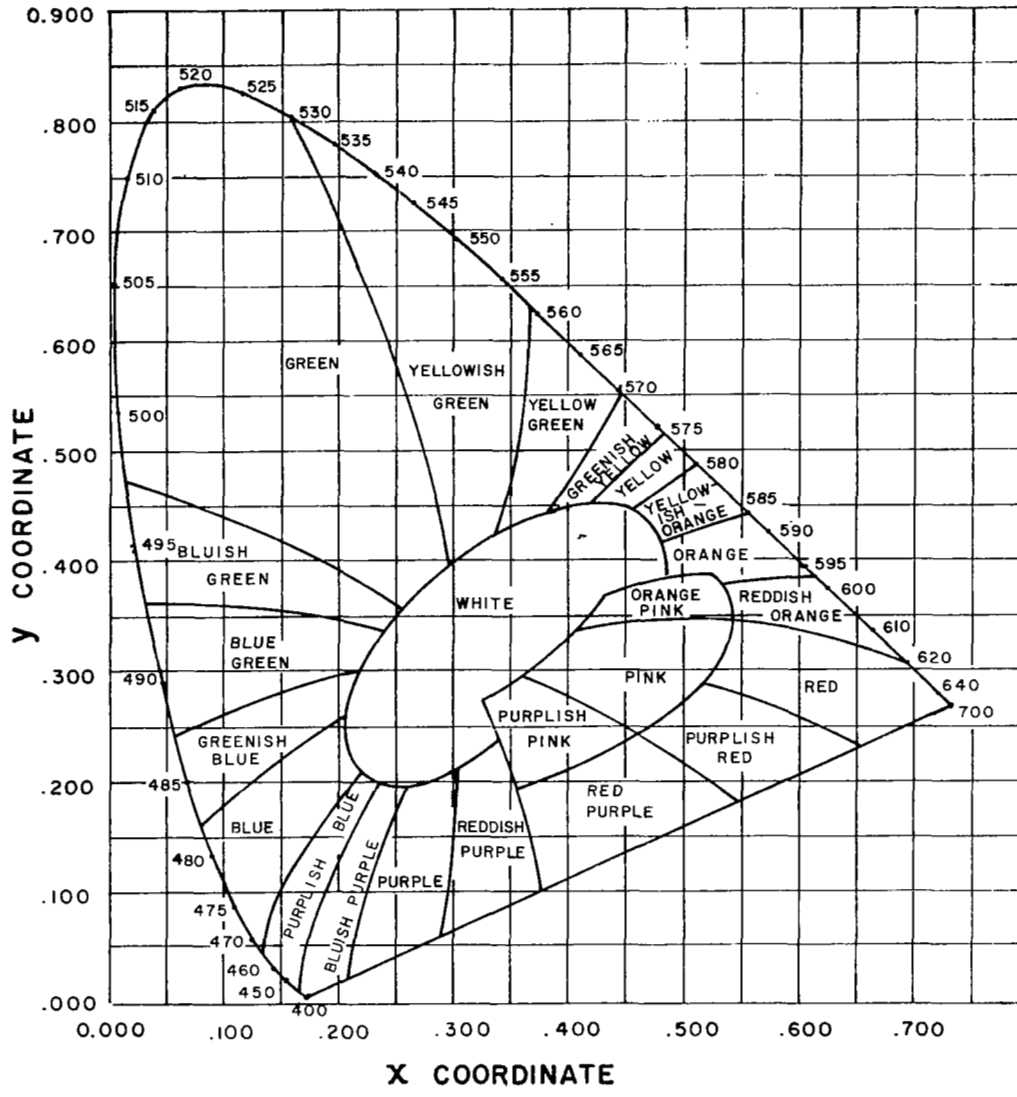

Figure 2 Kelley Chart of Color Designation For Lights

type of scanning systems used for monochrome cathode-ray tubes and would be capable of high resolution since a non-patterned screen structure is employed.

The two major disadvantages of this approach are limited color gamut and simultaneous variation of brightness with color shift. The reason for the limited color gamut is that at the higher current densities both phosphors are contributing to the color and the color of the pure superlinear phosphor cannot be reached. The color ranges from that of the sublinear phosphor to a color approaching that of the superlinear phosphor. Other types of color tubes, such as the penetration type, also have a reduced color gamut. In the penetration screen it is rather difficult to excite one layer with no excitation of the other layer and this causes some reduction in the achievable color gamut. The interdependence of brightness and color variation is a major drawback for many potential applications, but in many uses involving display of alphanumeric information this would be of less importance. The effect of the brightness variation can be reduced by using a sublinear green phosphor combined with a superlinear red or blue phosphor. In this way the color shift as the current density is increased is toward colors to which the eye is less sensitive; thus, the increased brightness is less apparent. It may also be possible to vary the brightness without greatly affecting the color by varying the writing rate. However, this may not be a completly satisfactory solution since changing the writing rate changes the excitation rate and could affect both color and brightness to a similar extent. Also, this complicates the circuitry and reduces the advantage of simplicity.

Superlinear Sulfide Phosphors

The success of this approach to single-gun color cathode-ray tubes depends on the preparation of suitable superlinear phosphors. These phosphors should have a relatively saturated emission color which should preferably be blue, green, or red as discussed earlier.

There are only limited references in the literature to superlinear phosphors. The most important earlier work appears to be that of Nail, Urbach, and Pearlman (Ref. 21). They studied the behavior of (ZnCd)S:Ag,Ni phosphors under UV excitation over a wide range of excitation intensities and showed that small amounts of Ni enhanced the superlinear behavior. No detailed descriptions of similar behavior under electron beam excitation are found. In the book by Leverenz (Ref. 22), measurements made by Lasof are reported in which an aluminized screen of (ZnCd)S:Ag was found to increase in efficiency as the excitation current density increased from about 0.005 to 5 $\mu a/cm^2$. A more recent paper by Francis and Stoudenheimer (Ref. 23) reports similar behavior for P-11 (ZnS:Ag) in image tubes as the excitation current density increased from about 3×10^{-7} to 3×10^{-5} $\mu a/cm^2$.

Some work on the preparation of superlinear sulfide phosphors was done at ITT Industrial Laboratories prior to the awarding of this contract. Initial efforts to prepare a superlinear blue-emitting phosphor by doping ZnS:Ag with 1 and 10 ppm of Ni resulted

in sublinear rather than superlinear behavior. The results are shown in Figure 3 compared to a commercial P-11 phosphor. Samples of green-emitting (ZnCd)S:Ag doped with Ni were prepared using a ZnS:CdS wt. ratio of 65:35. With this composition a slight superlinear behavior was observed as shown in Figure 4. Samples of (ZnCd)S:Ag doped with Fe and Co were also prepared but these did not exhibit superlinear behavior. Samples of red-emitting (CdZn)S:Ag (CdS:Zns wt. ratio of 86:14) doped with Ni were also prepared but no superlinear behavior was found.

A major portion of the work on this contract has been concerned with the preparation of superlinear sulfide phosphors. A large number of samples have been prepared and evaluated; these are listed in Appendix B. Experimental multi-color screens prepared with some of these superlinear phosphors are discussed in a later section.

The preparation of these phosphors followed the same general procedure in most cases. A modified procedure will be discussed in the next section. Starting materials in all cases were luminescence grade ZnS, (ZnCd)S, and CdS. The ZnS (Z-19) and (ZnCd)S (unactivated Z-286A which is 1:1 ZnS:CdS by wt.) were obtained from RCA, while the CdS (S-20) was from Sylvania. The desired ZnS:CdS ratio was obtained by mixing ZnS with the required amount of (ZnCd)S or CdS. The mixture was slurried in deionized water and the required amount of $AgNO_3$ solution (1mg Ag/mℓ) was added slowly while stirring the slurry. In most cases a silver concentration of 0.005 percent by wt. (50ppm) was used. The required amount of $NiSO_4$ solution (0.1 mg Ni/mℓ) was then added slowly while stirring the slurry; in most of the later samples a small amount of Na_2S solution was added before the $NiSO_4$ solution. The purpose of this was to provide S^{-2} ion to insure precipitation of all the Ni^{+2} since NiS is more soluble than ZnS or CdS. A suitable flux (such as NaCl) was added last. The slurry was then oven-dried with occasional stirring. After drying the unfired phosphor was again mixed thoroughly, placed in quartz beakers and fired for 1-2 hours at temperatures ranging from 600 degrees to 1000 degrees C. After firing the samples were examined under UV excitation and any surface oxide and dead spots were removed. The phosphor was then washed with deionized water until all the halide was removed. The resulting phosphors were then ready for evaluation as described in Appendix A.

Work on sulfide phosphors during the initial phase of the contract was concentrated on optimizing the preparation of green-emitting superlinear phosphors. The effect of Ni content was evaluated, and it was found that 5-10 ppm gave the best results. Below 5 ppm there was only a slight superlinear effect, while above 10 ppm the emission intensity was quite low.

Attempts to prepare superlinear red-emitting phosphors by poisoning (CdZn)S:Ag (using Cd:Zn ratios of about 8:2) with Ni, Fe, Co or Pd were unsuccessful. The poisons reduced the emission intensity but did not produce superlinear behavior. By using lower Cd:Zn ratios it was possible to prepare superlinear phosphors having reddish-orange emission. In general it was found that the maximum superlinear behavior in the (ZnCd)S:Ag, Ni system occurs near a Zn:Cd ratio of 1:1 and drops off on both sides of this.

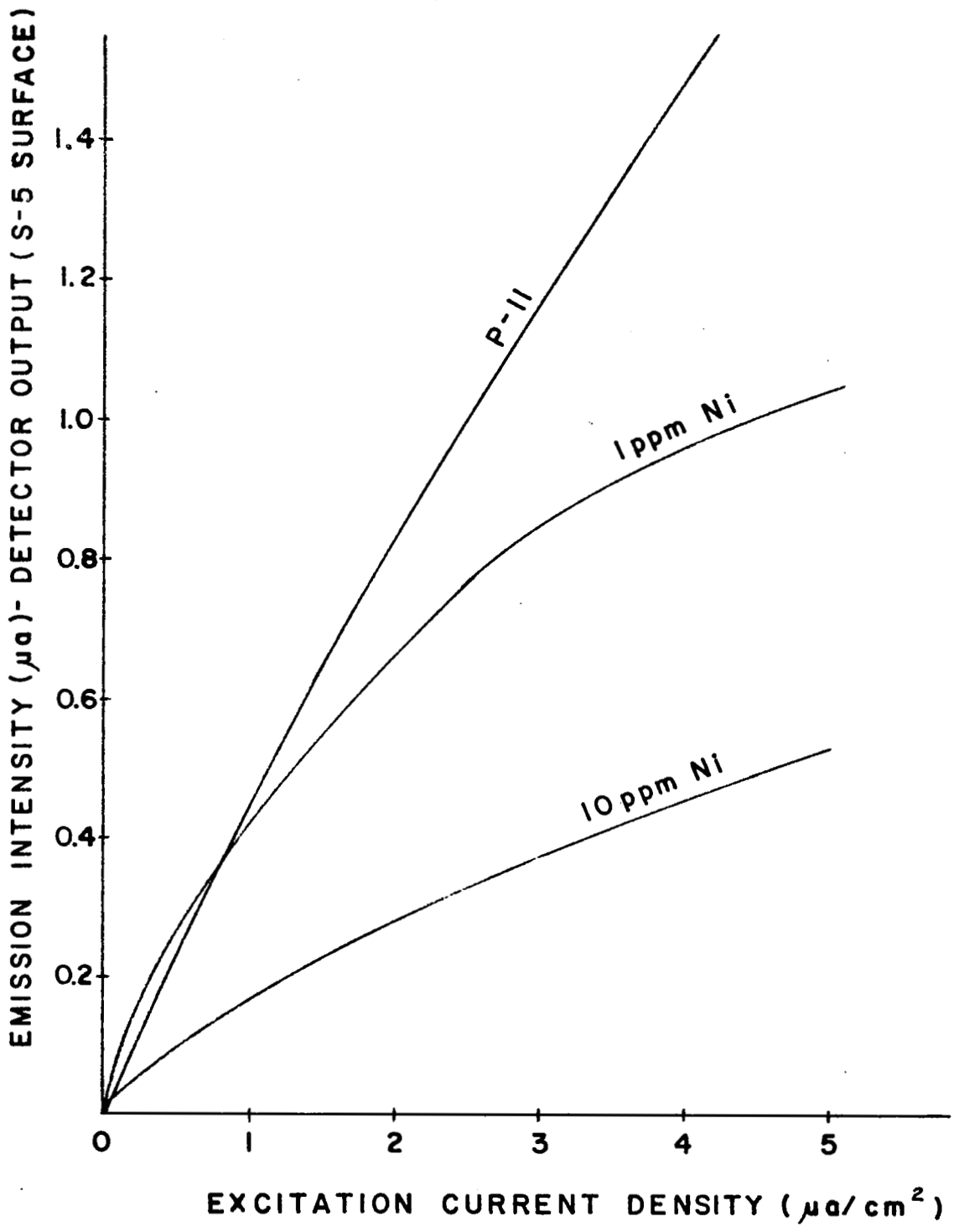

Figure 3 Effect of Ni on Emission Linearity of ZnS:Ag

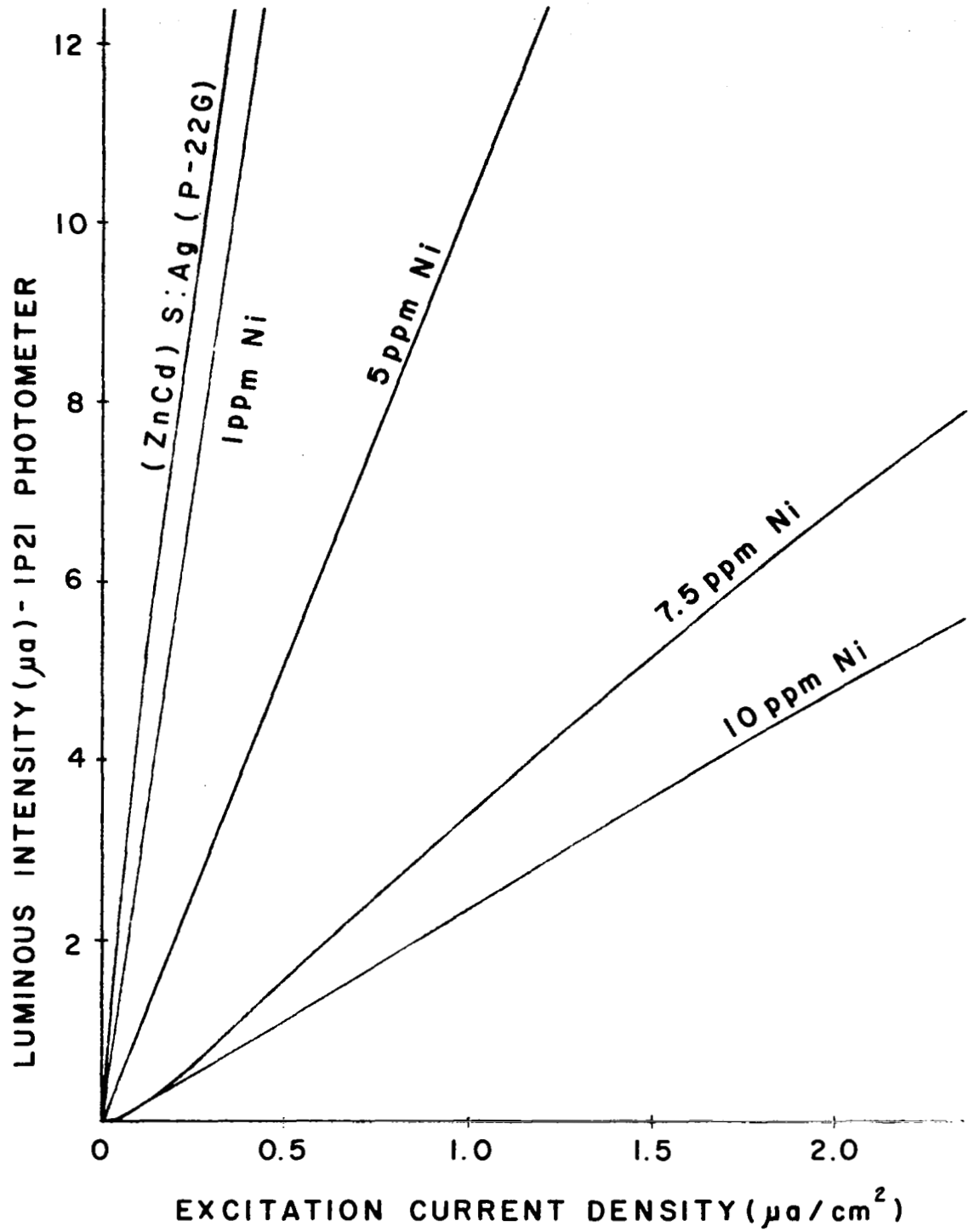

Figure 4 Effect of Ni on Emission Linearity of Green-Emitting (ZnCd)S:Ag

This is illustrated in Figures 5 and 6 where intensity versus current density curves are shown for several (ZnCd)S;Ag, Ni phosphors. The Zn:Cd ratio and peak emission wavelength are shown for each phosphor. All the samples were prepared with 50 ppm Ag and 7.5 ppm Ni. The reason for the dependence of superlinearity on Zn:Cd ratio is not as yet understood.

There are still problems with the reproducibility of superlinear sulfide phosphors. It has not always been possible to prepare a duplicate sample and obtain the same intensity versus current density behavior. In some cases it is believed that the mixing of the unfired material had not been as thorough and this is quite critical. However, in many cases there were no apparent reasons for the differences; apparently there are some variables in the preparation which are not being controlled closely enough.

Separate Incorporation of Poison and Activator

One of the preparation parameters which was evaluated was the sequence of addition used for the Ag and Ni. Some samples were prepared in which the sequence described in the previous section was reversed, i.e., the $NiSO_4$ solution was added to the sulfide slurry before adding the $AgNO_3$ solution. This variation had little or no effect on the intensity versus current density behavior. However, addition of the Ni and pre-firing before addition of the Ag appears to improve the superlinear behavior. This is illustrated in Figure 7 where the behavior of two sets of phosphors is shown. The two phosphors in each set have the same composition except that in one case the Ag and Ni were added together and the sample was then fired; while in the second case the Ni was added first and the sample was fired, then the Ag was added and the sample was re-fired. Because of the problems with reproducibility of results and the limited number of similar samples prepared with the two procedures, it has not been definitely established that improvement is due to the Ni and Ag incorporation sequence. An additional effect obtained with this preparation procedure is that the emission band is shifted to higher wavelengths.

The reasons for these effects when the Ni is incorporated first are not completely understood as yet. However, it is apparent that the relative diffusion of the poison and activator and the subsequent positioning in the host crystal are important. To demonstrate at least qualitatively that the diffusion and positioning of the activator and coactivator relative to each other is important, a series of experiments were performed to indicate changes in luminescent output with firing procedure. The curves of Figure 8A demonstrate the expected effects of successive poisoning of (ZnCd)S:Ag with Ni (curves a through e). Curves f through i in Figure 8B demonstrate luminescent recovery obtained by refiring sample (e). Recovery of luminescence might be expected if the poison ions diffuse away from the activator ions thus allowing more of the Ag to function again as luminescent centers.

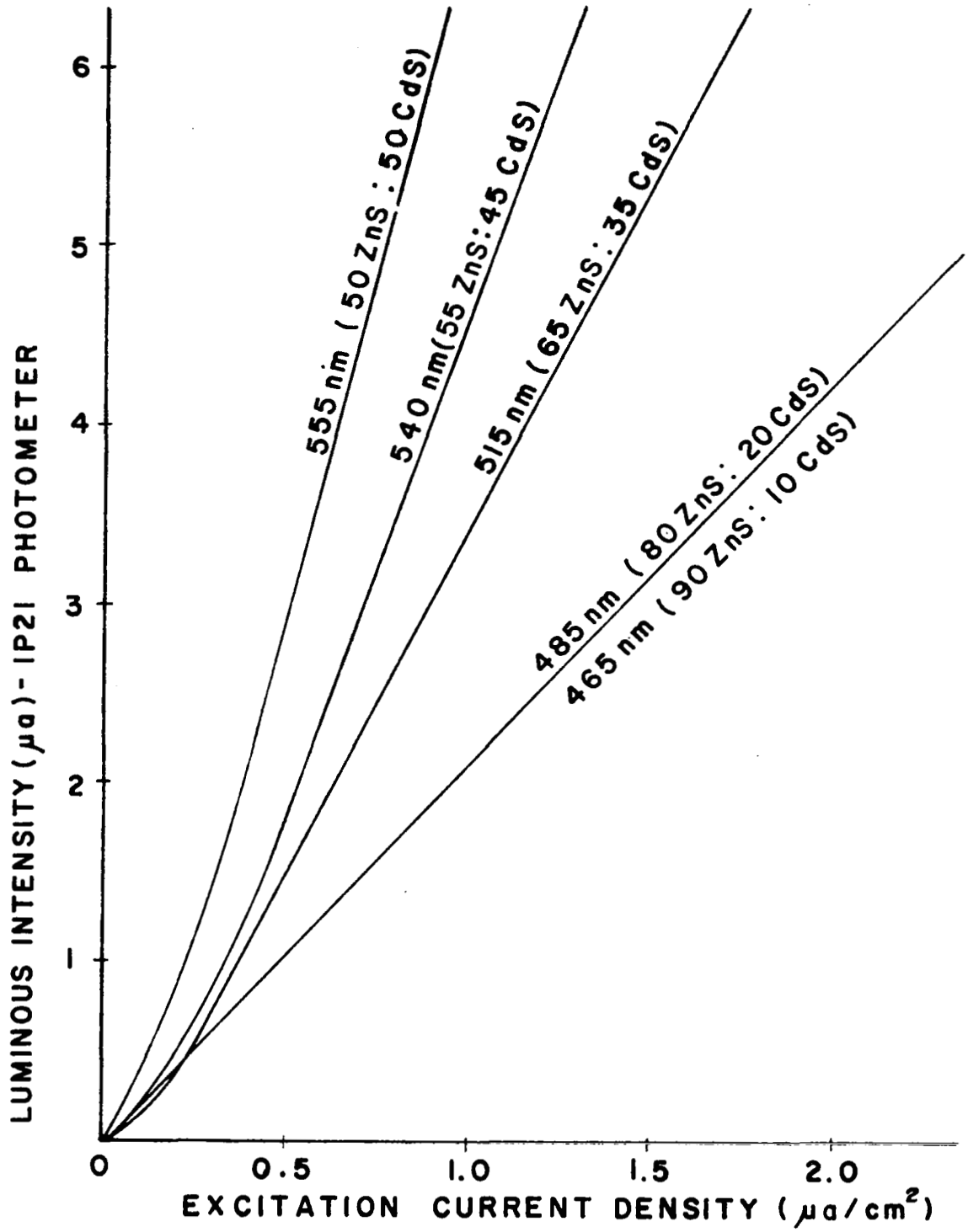

Figure 5 Effect of Zn:Cd Ratio on Emission Linearity of (ZnCd)S:Ag, Ni

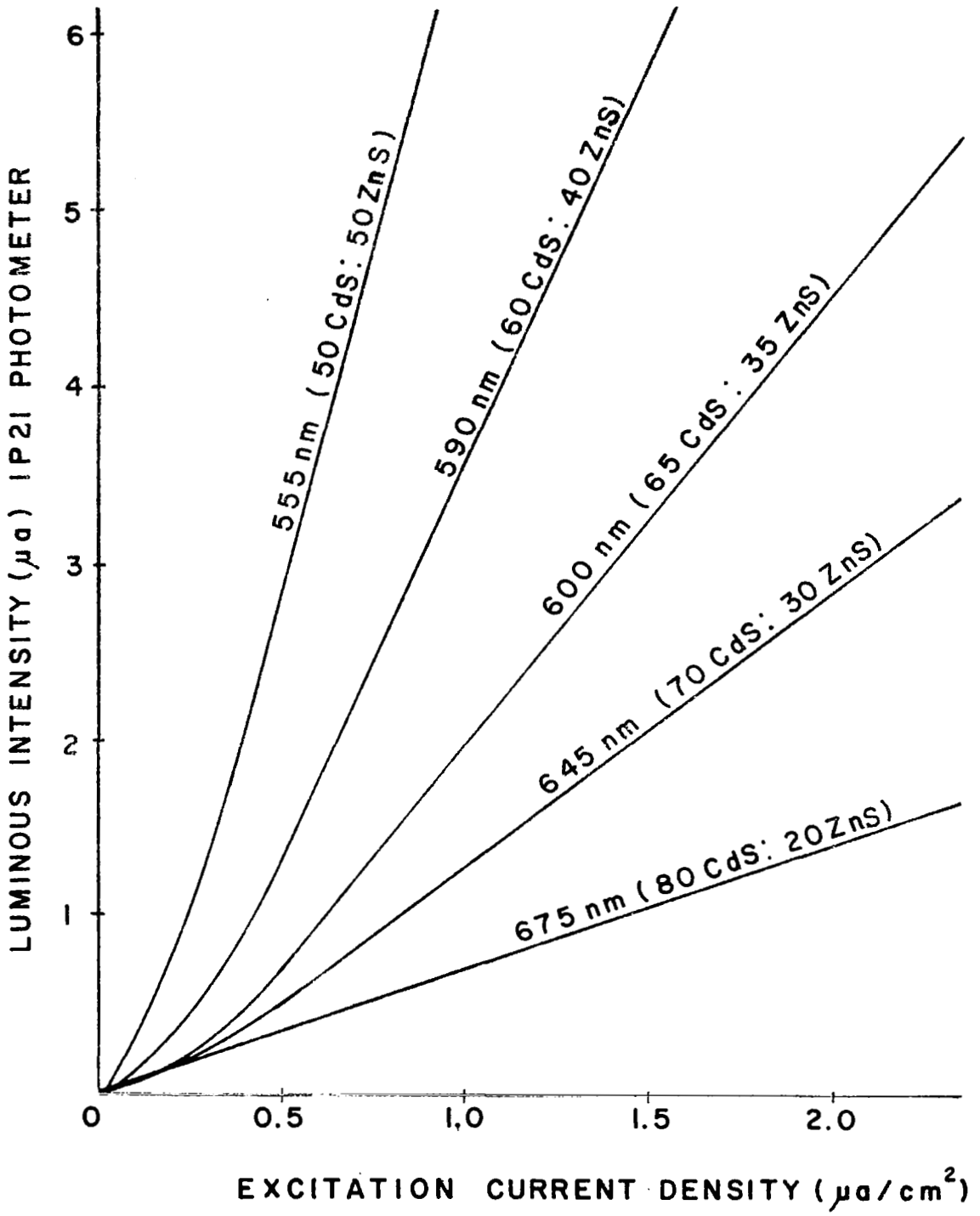

Figure 6 Effect of Cd: Zn Ratio on Emission Linearity of (CdZn)S: Ag, Ni

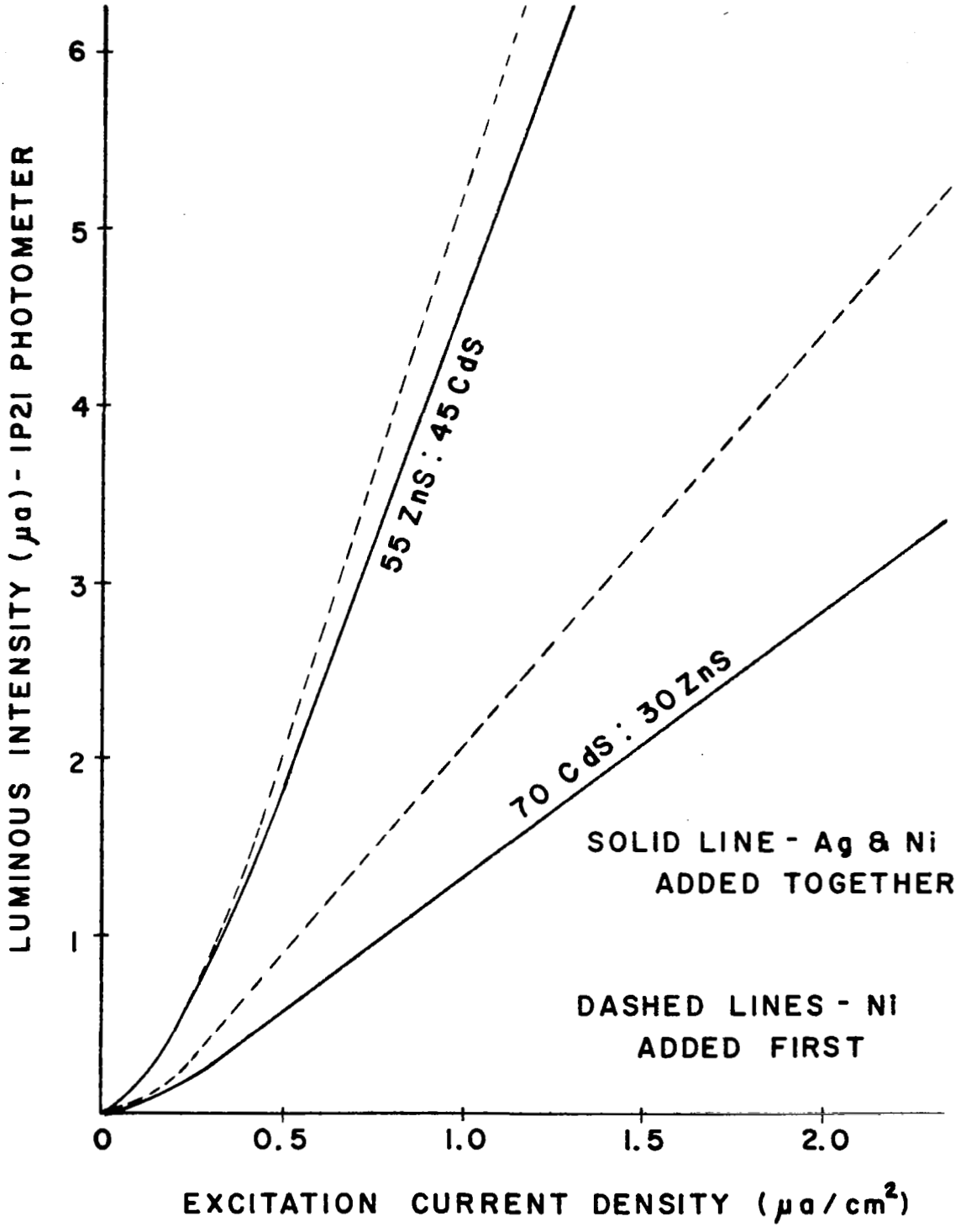

Figure 7 Effect of Sequence of Incorporation of Ni and Ag on Emission Linearity

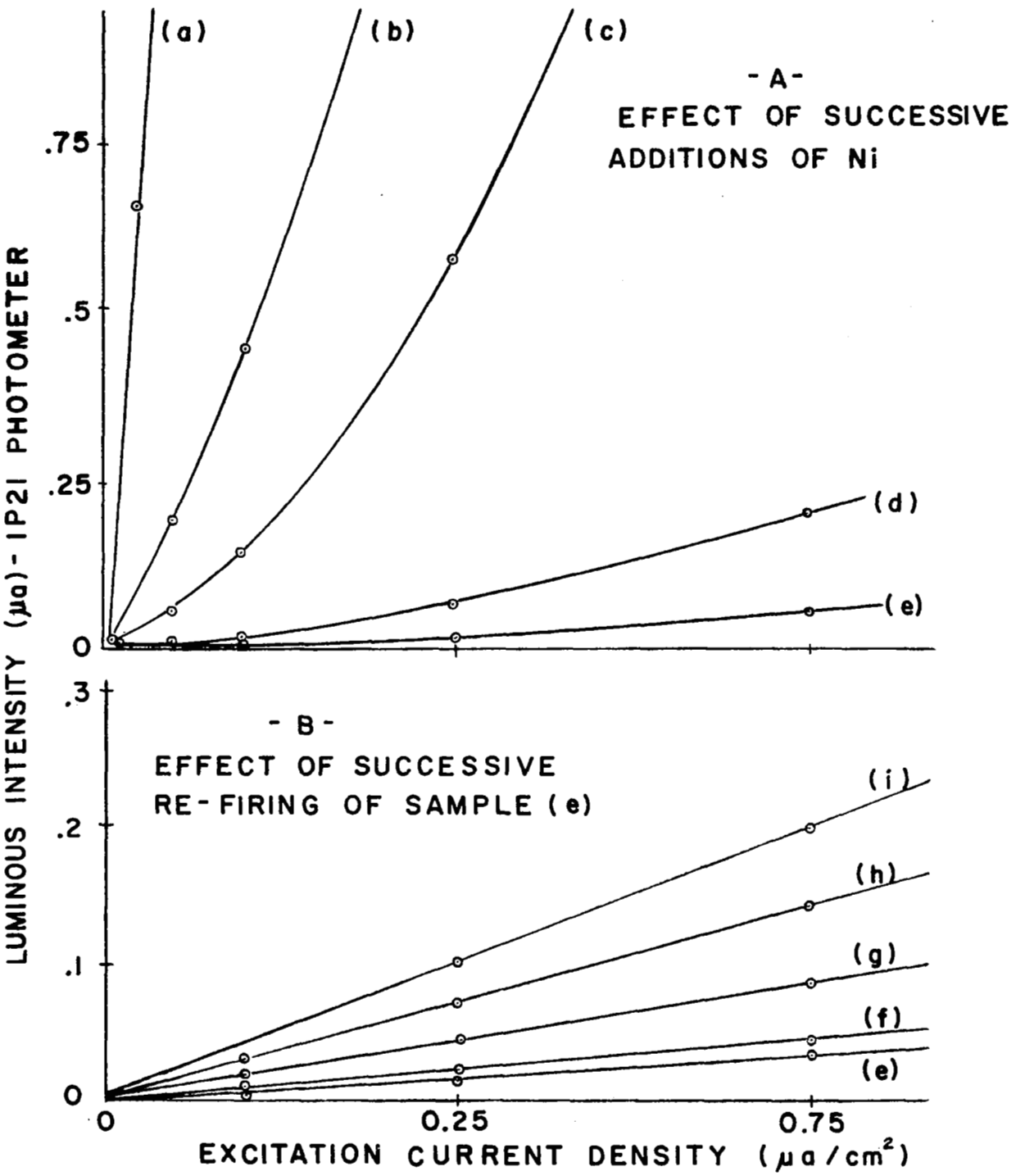

Figure 8 Poisoning and Recovery of Luminescence of (ZnCd)S:Ag

Other Phosphors

In addition to (ZnCd)S:Ag, Ni a number of other phosphors have been evaluated for possible superlinear behavior. One such material was ZnS:Cu, Ni. One sample of this phosphor exhibited a color shift from green to blue green as current density increased from 0.005 to 5 $\mu a/cm^2$. This shift is shown in Figure 9. As can be seen this is due to an increase in the intensity of the blue band. ZnS:Cu phosphors normally exhibit an increase in the relative intensity of this band as the current density is increased; however, the increase is not normally as pronounced as obtained with this sample of ZnS:Cu, Ni. Work with the Cu-activated sulfides has been very limited to date; however, more extensive studies are planned.

Some other interesting effects were noted with some Tb^{+3} -activated silicates which had been prepared as part of a company-funded phosphor program. In some of these phosphors the relative intensities of the groups of lines due to the $^5D_3 \longrightarrow {}^7F$ (blue) and the $^5D_4 \longrightarrow {}^7F$ (green) transitions vary as the current density is changed, thus giving slight color shifts. These color shifts are relatively small but these observations indicate that it may be possible to find suitable hosts in which more pronounced color changes may be obtained.

Other phosphors were prepared with pairs of rare-earth ions, such as Tb-Eu, for which energy transfer under UV-excitation has been reported. However, none of these exhibited any evidence of color shift or superlinear behavior. Attempts to prepare a superlinear green phosphor from Zn_2SiO_4:Mn and a superlinear red phosphor from $Mg_2CdSi_3O_9$:Mn were unsuccessful.

Sublinear Phosphors

During the early phase of this program, the experimental screens which were prepared utilized linear phosphors in combination with superlinear phosphors. Since the color shift can be enhanced by using sublinear instead of linear phosphors, some effort was devoted to the preparation of phosphors having sublinear behavior.

A red-emitting phosphor having a slight sublinear behavior was obtained by doping a red (CdZn)S:Ag with 2 ppm of Ni. This sample had a high Cd content (86CdS:14ZnS wt. ratio) and the addition of Ni produced a sublinear rather than superlinear behavior. The intensity versus current density behavior compared to that of a sample with no Ni is shown in Figure 10. Use of this phosphor instead of a linear phosphor resulted in a larger color shift.

When a reddish-orange phosphor having a superlinear behavior was prepared, it became necessary to use with it a green-emitting phosphor having a lower brightness than commercial phosphors such as P-1 or P-22G. Since a phosphor with a fairly saturated color was desirable, some samples of Zn_2SiO_4:Mn were prepared with a much lower than normal Mn content. By using 10^{-2} or 10^{-3} mol% Mn, it was possible to

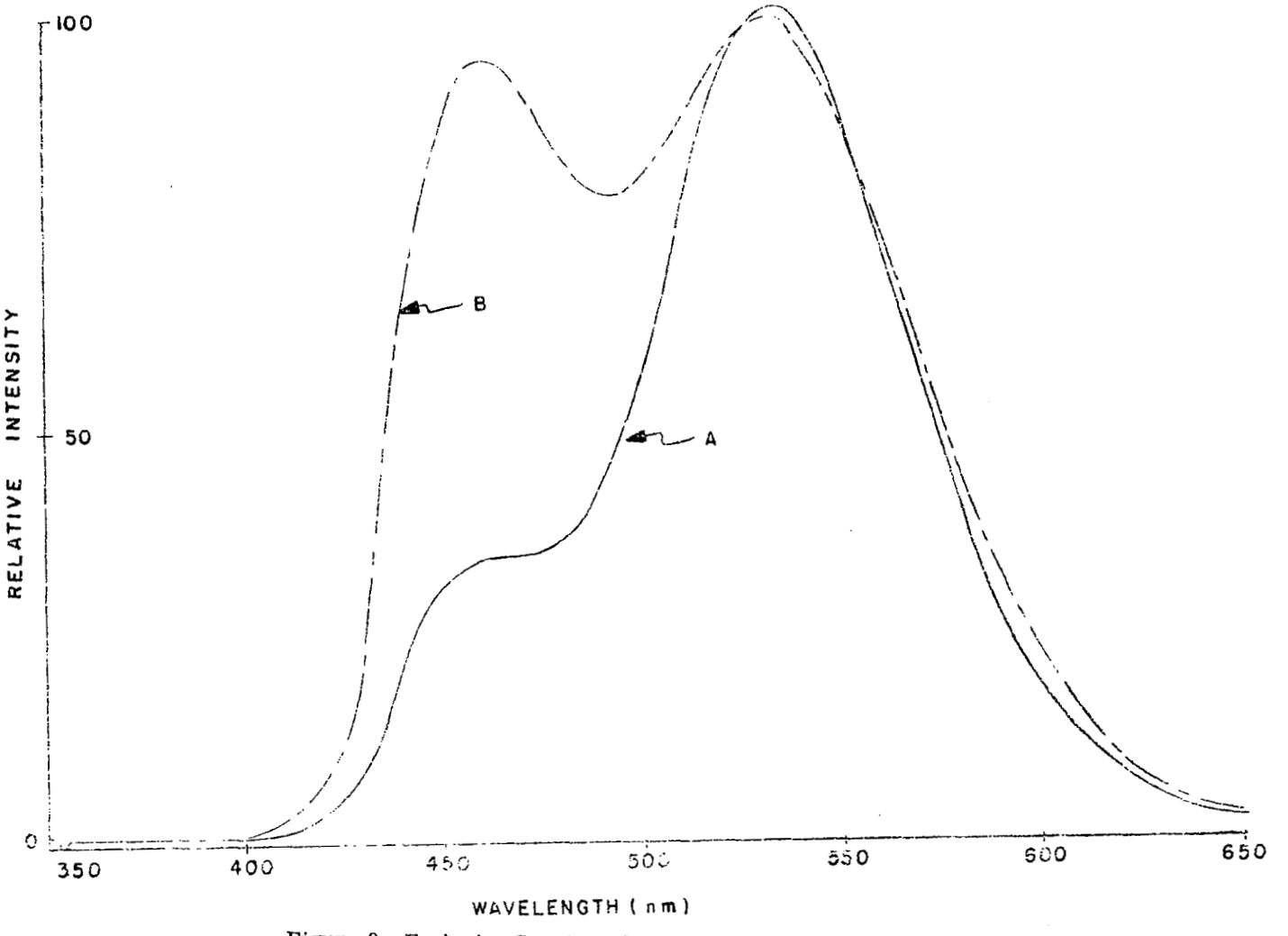

Figure 9 Emission Spectra of ZnS:Cu, Ni
Curve A - 0.005 $\mu a/cm^2$,
Curve B - 5 $\mu a/cm^2$; both at 10 kv.

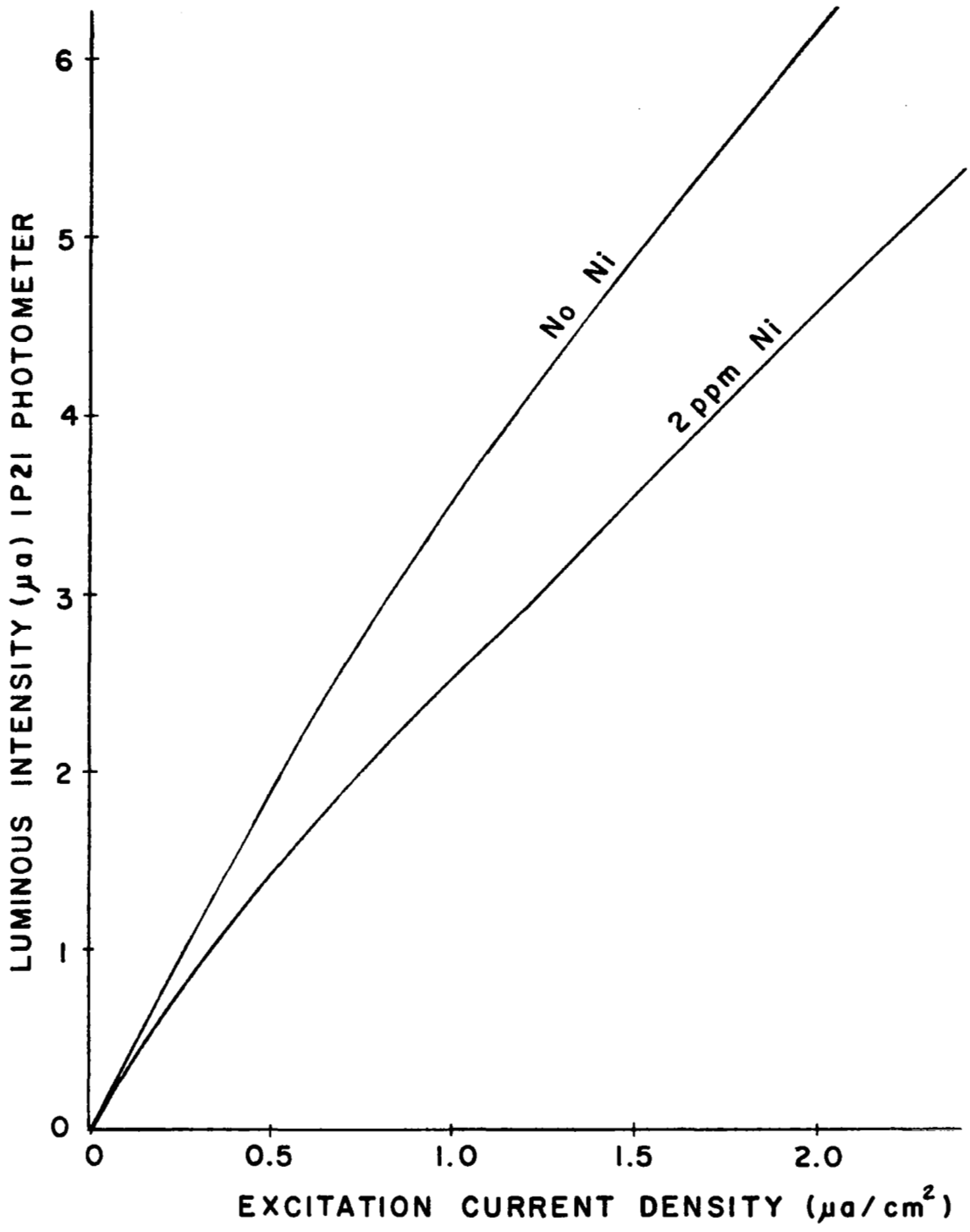

Figure 10 Effect of Ni on Emission Linearity of Red-Emitting (CdZn)S:Ag

prepare phosphors having lower brightness and also sublinear behavior. Intensity versus current density behavior for these two samples is shown in Figure 11. Combination of these phosphors with a reddish-orange superlinear sulfide resulted in screens with quite good color shift.

Experimental Multi-Color Screens

A large number of screens have been prepared with various experimental superlinear phosphors. A list of these screens is tabulated in Appendix C. These screens were visually evaluated in a demountable cathode-ray tube system and the more promising ones were picked for further evaluation. For most of these more promising screens, spectral distribution curves were plotted at several values of current density, and from these chromaticity coordinates were calculated. This data is also included in Appendix C.

The early screens were composed of red-emitting YVO_4:Eu combined with a superlinear green-emitting (ZnCd)S:Ag, Ni having a composition (ZnS:CdS wt. ratio of 65:35) similar to that of P-22G. This combination gave a color shift from reddish-orange to yellowish-white. Chromaticity coordinates were not calculated for any of these screens so that sample data cannot be given. In order to avoid the whitish color, later screens were prepared with superlinear green-emitting phosphors having a lower Zn:Cd ratio which shifts the color toward yellow. The changes in chromaticity for screens with two different green phosphors are shown in Figure 12. In each case the current density change is from 0.1 to 1 to 10 $\mu a/cm^2$. Screen No. 57 was prepared with a green phosphor having a ZnS:CdS wt. ratio of 60:40 while a phosphor having a ratio of 57.5:42.5 was used for screen No. 62. The chromaticity coordinates for the two green phosphors are indicated by x's. The shift of screen No. 62 away from the white region is quite evident.

The next change was to use a red-emitting sulfide phosphor combined with the superlinear green. This gave a wider color range because the sulfide phosphor has a slight sublinear behavior while the YVO_4:Eu has a linear behavior. Figure 13 shows the chromaticity shift for two screens composed of the same superlinear green phosphor (ZnS:CdS wt. ratio of 55:45) combined with YVO_4:Eu in one case (screen No. 88) and (CdZn)S:Ag, Pd in the other (screen No. 68). In this case, the current density change is from 0.01 to 0.1 to 1 to 10 $\mu a/cm^2$. As can be seen the sulfide red gives a greater color shift, especially in the 1 to 10 $\mu a/cm^2$ range. The change in the spectral energy distribution for screen No. 68 is shown in Figure 14.

Reddish-orange sulfide phosphors having superlinear behavior were synthesized and used to prepare experimental screens with various green emitting phosphors. It was found that most of the green phosphors were either too linear or too bright for best results. As discussed in the previous section, samples of Zn_2SiO_4:Mn having lower brightness and sublinear behavior were prepared by using a low Mn content. Use of this green phosphor gave experimental screens having good color shift as

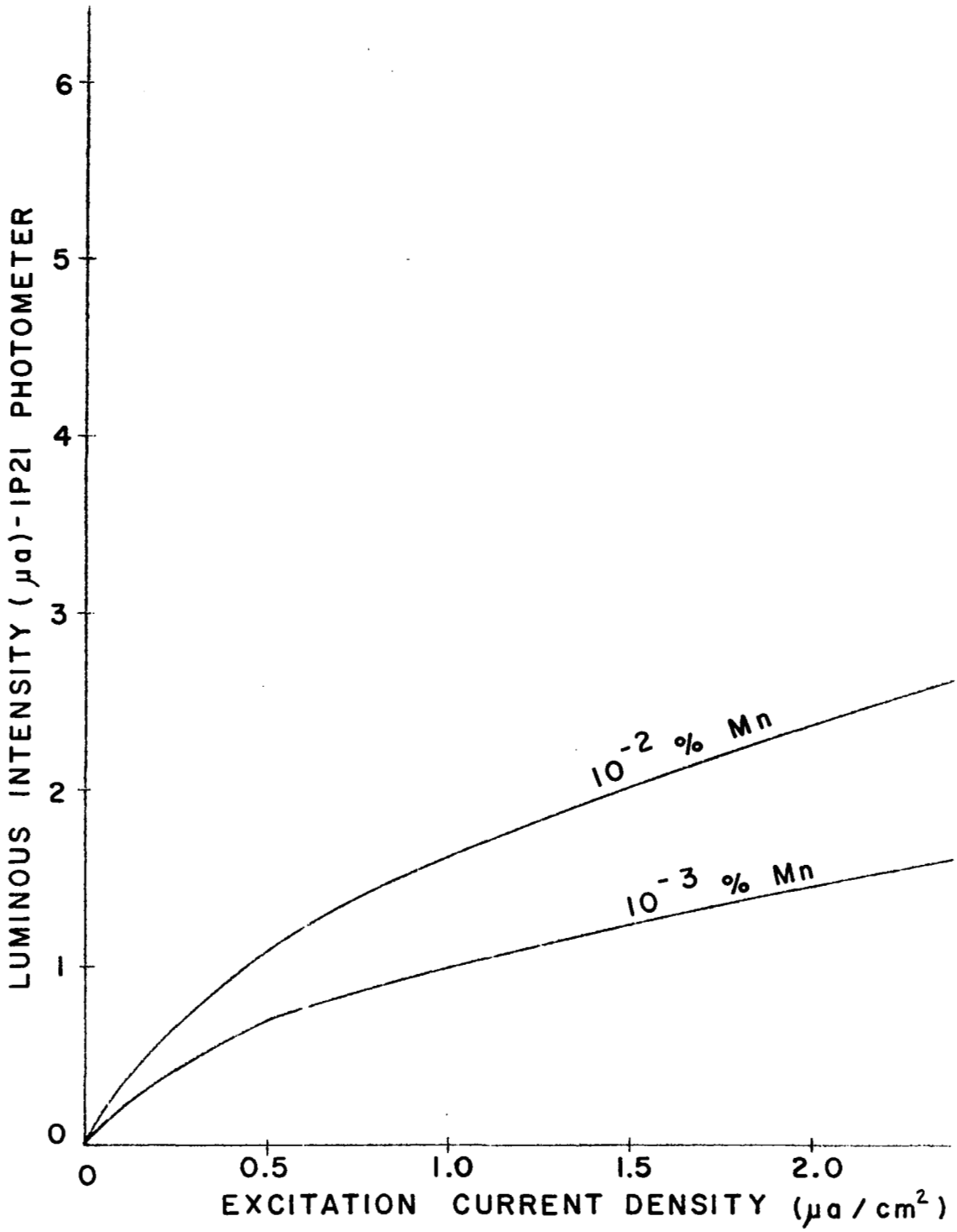

Figure 11 Emission Linearity of Zn_2SiO_4:Mn with Low Mn Content

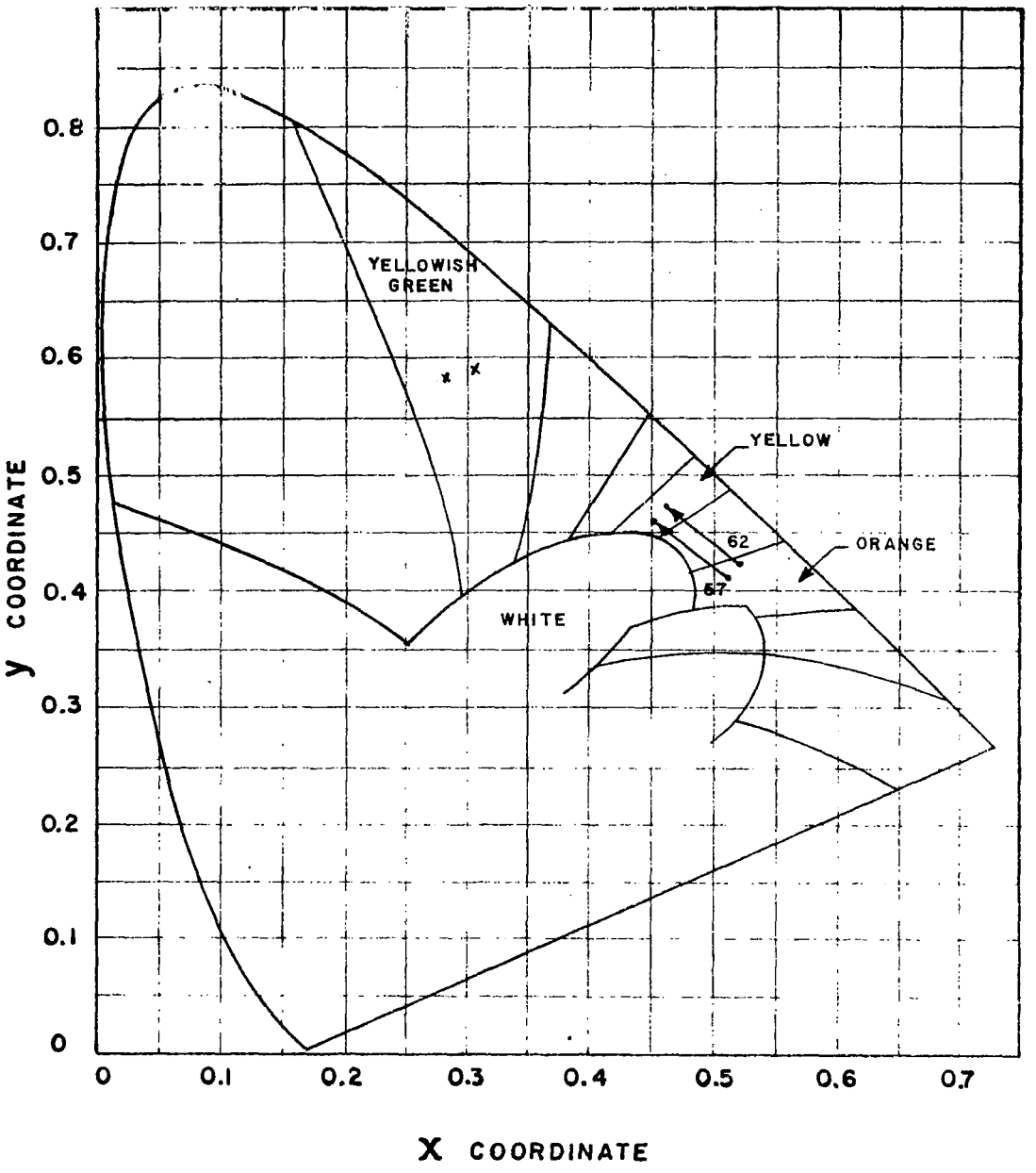

Figure 12 Effect of Green Phosphor Color on Screen Color. Chromaticities of green phosphors used are indicated by x's.

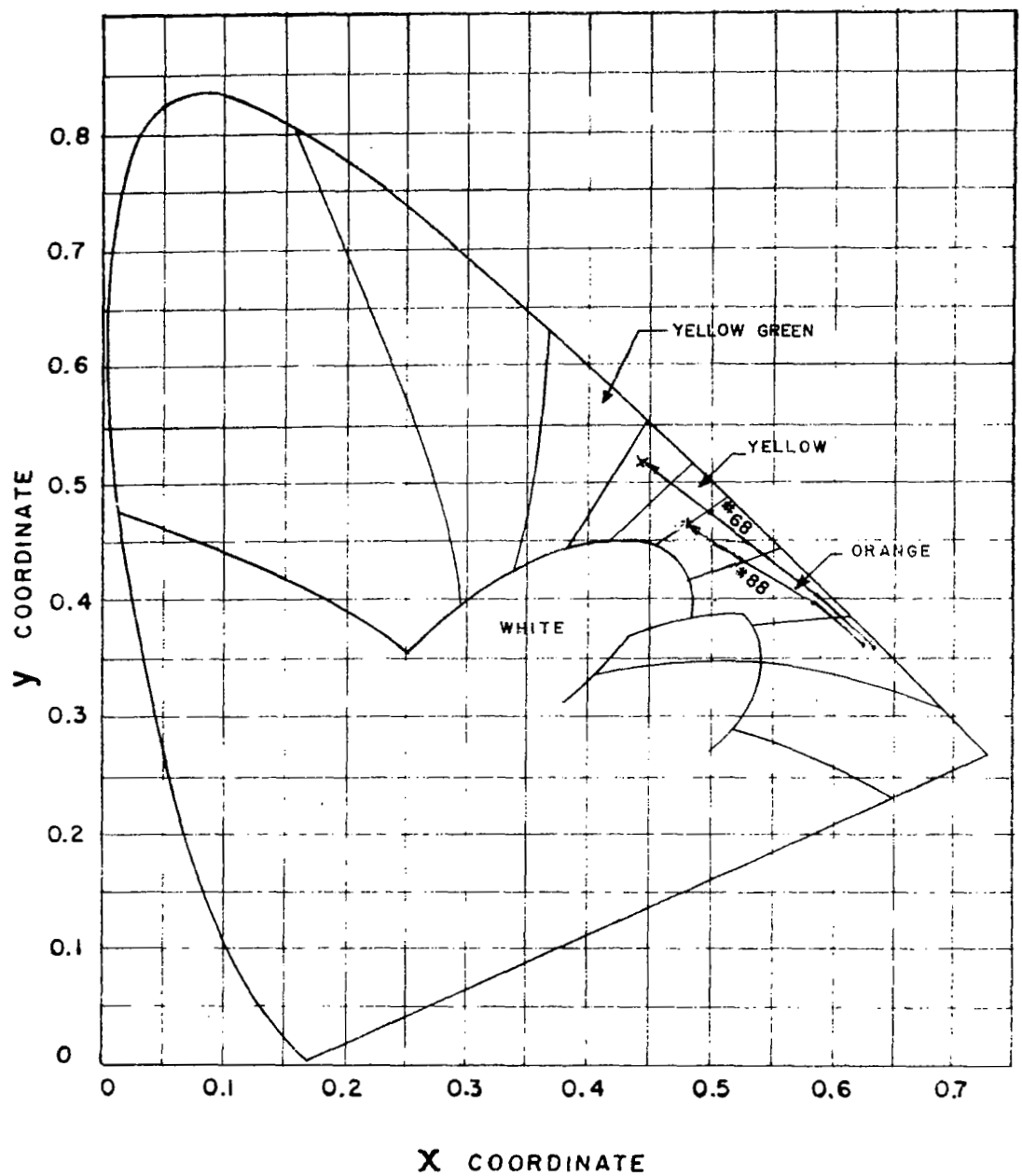

Figure 13 Effect of Red Phosphor on Color Shift. Screen No. 68 prepared with sublinear (CdZn)S:Ag, Pd; screen No. 88 prepared with linear YVO_4:Eu

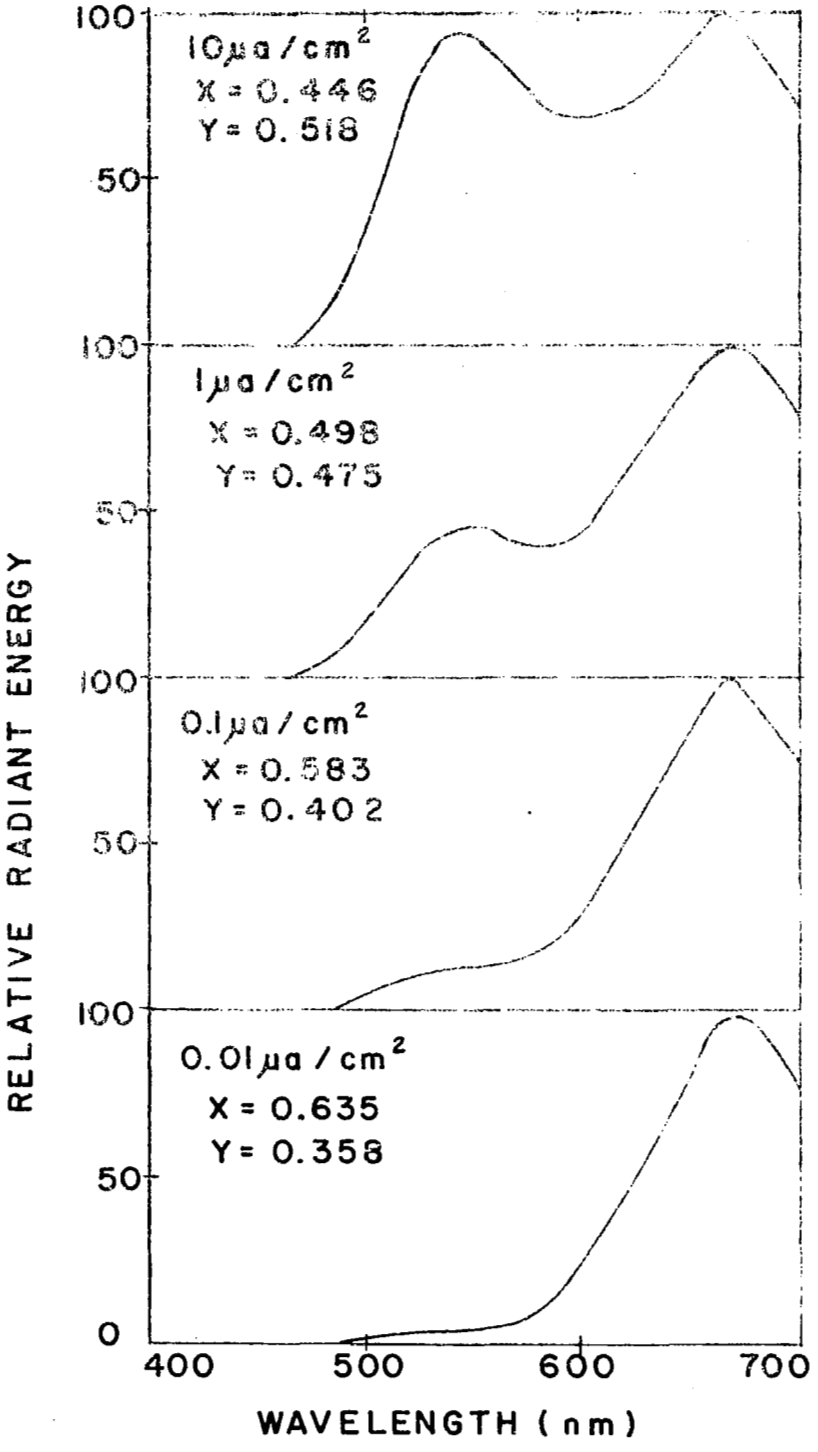

Figure 14 Spectral Energy Distribution for Red → Yellow Screens

shown in Figures 15 and 16. The chromaticity change is shown in Figure 15 and the change in spectral energy distribution is shown in Figure 16. It can be seen that this combination gives a more pronounced color shift; the major reason for this is that the sublinear behavior of the low-Mn silicate green is more pronounced than that of the sulfide red phosphors used with the superlinear green phosphors.

Experimental Cathode-Ray Tubes

Several experimental cathode-ray tubes have been fabricated using phosphor combinations which appeared promising on the basis of data from experimental screens evaluated in the demountable cathode-ray system. A list of these tubes and data obtained from them is tabulated in Appendix D.

Two types of tubes have been built: 5-inch round tubes using a two-piece construction and 8-inch rectangular tubes which are identical to 8NP4 black-and-white kinescopes except for the phosphor screen. The 5-inch tubes are simpler to build because the faceplate is separate and is Heliarc welded to the bulb after depositing the phosphor, filming and aluminizing. The processing of these was readily carried out by the ITTIL Tubes and Sensors department since the faceplates are identical to ones used for storage cathode-ray tubes. The 8-inch rectangular tubes presented more problems because they are not similar to any tubes currently processed at ITTIL. The major problem encountered was screen pull-off during filming or aluminizing. This was most likely caused by marginal adherence characteristics of these experimental phosphors. It would be impractical to determine the best coating and settling parameters for each phosphor in order to get optimum adherence characteristics. Because of these problems the 5-inch round two-piece bulb construction has been used for most of the experimental tubes.

We have observed a slight color change and a less pronounced color shift in going from experimental screens to tubes. This is most likely due to the effect of tube processing conditions on the phosphor. The effect of tube processing parameters on experimental superlinear and sublinear phosphors will have to be studied in more detail.

Figure 17 illustrates the progress that has been made with experimental tubes. The chromaticity shifts for three tubes are shown going from a superlinear green + YVO_4:Eu red combination (tube I-1), to an improved superlinear green + (CdZn)S:Ag red (tube 8-3), to a superlinear reddish-orange (CdZn)S:Ag, Ni + sublinear green Zn_2SiO_4:Mn (tube J-2). Tube 8-3 is an 8-inch rectangular tube while the other two are 5-inch round tubes. The improvement in color shift is readily apparent from this diagram.

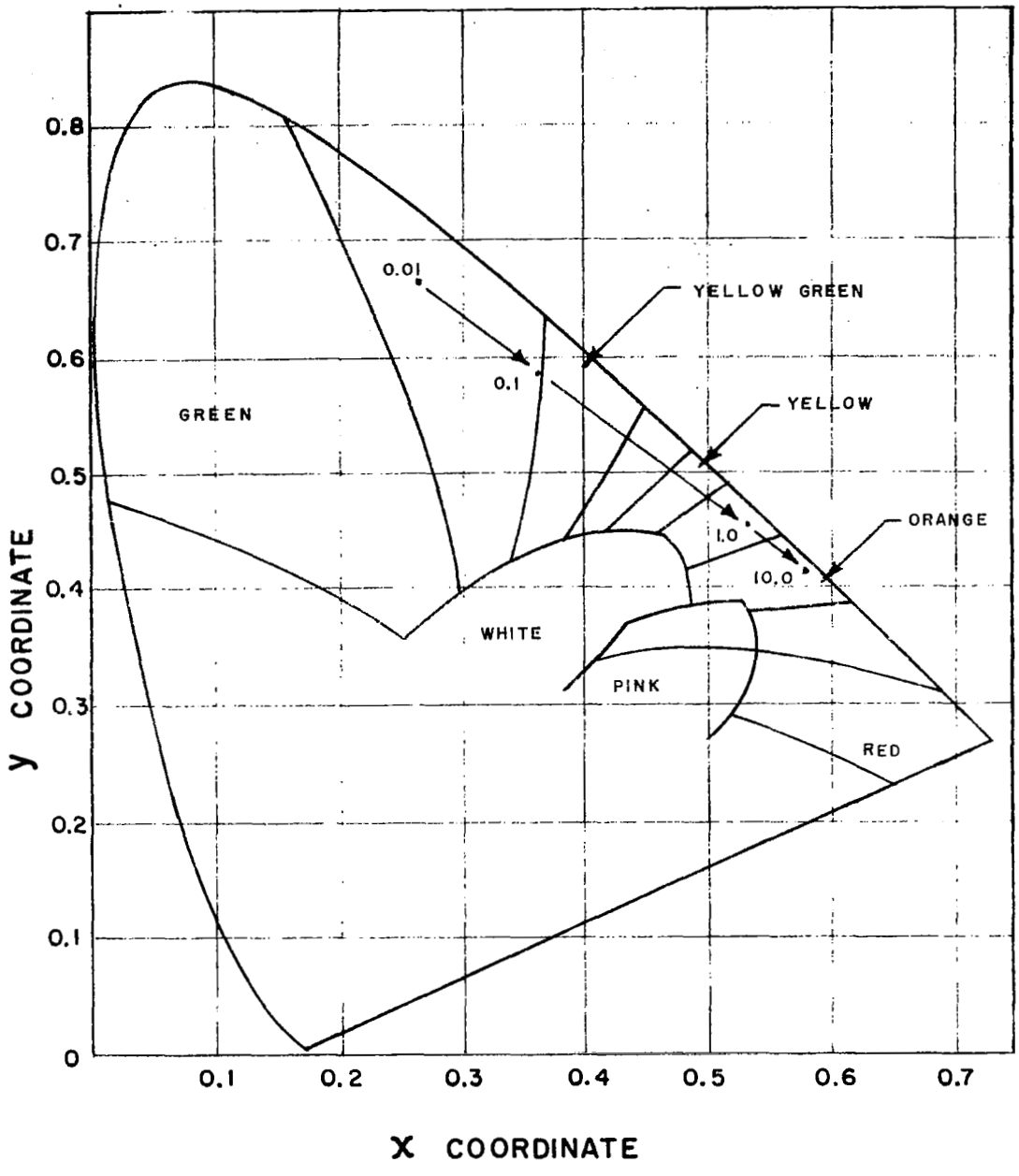

Figure 15 Color Shift for Green → Orange Screens

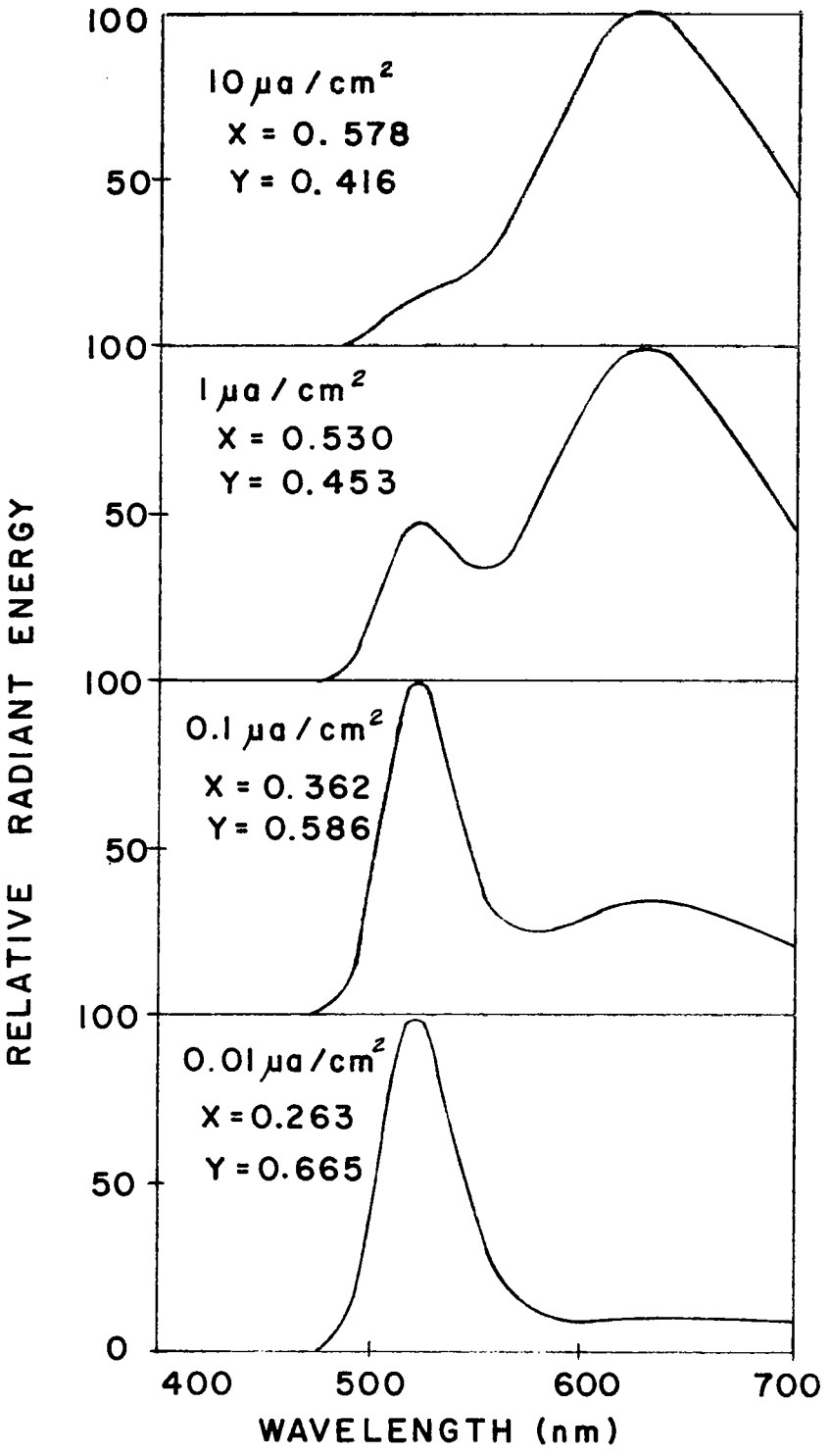

Figure 16 Spectral Energy Distribution For Green→Orange Screens

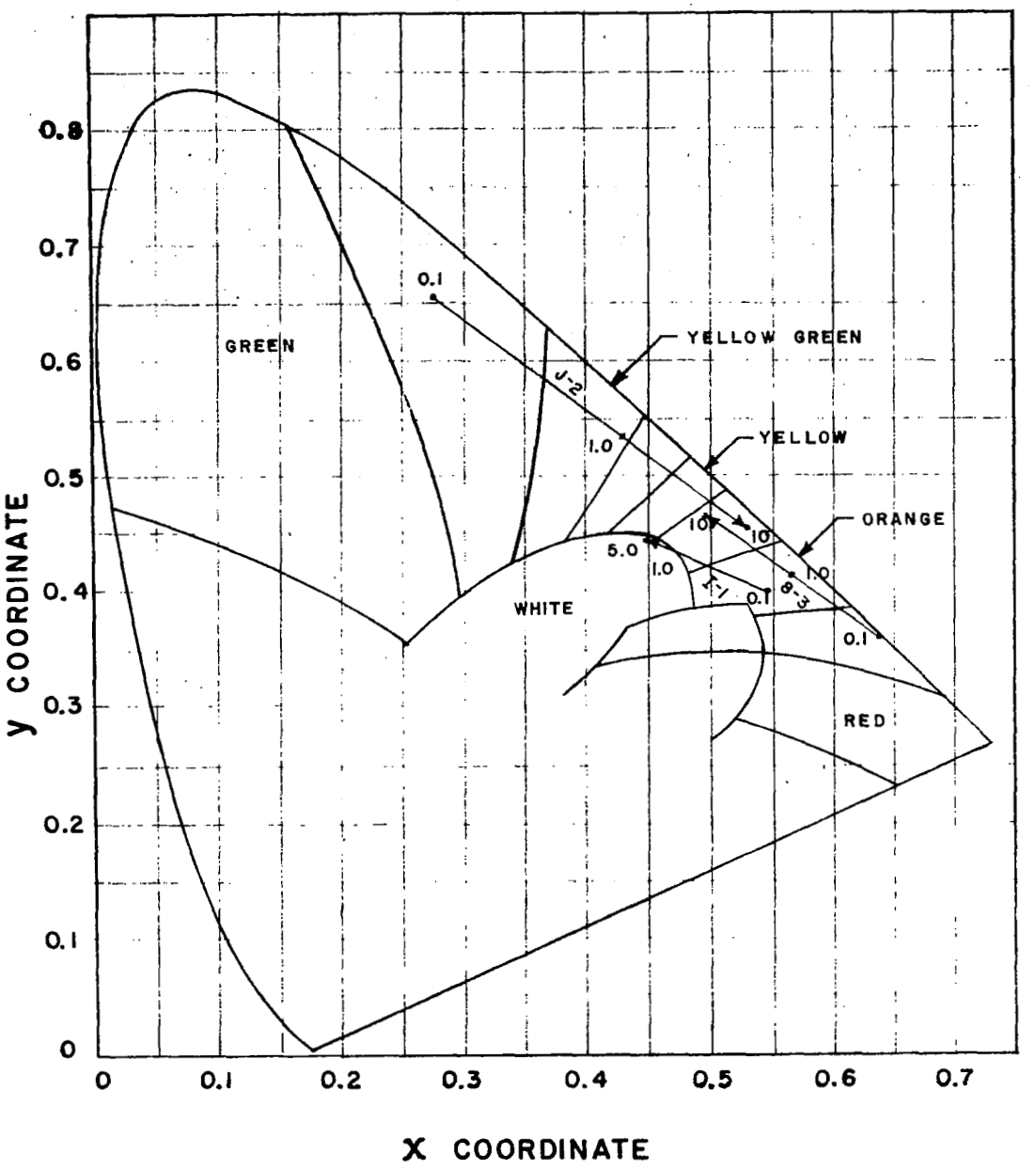

Figure 17 Color Shift For Several Experimental Tubes

CONCLUSIONS

The work done to date on this contract has demonstrated the feasibility of producing single-gun color cathode-ray tubes by combining a superlinear phosphor with a linear or sublinear phosphor of a different emission color. Tubes having a screen of this type provide a variation in emission color which is dependent on excitation current density. The major factor in producing screens of this type is the preparation of phosphors having superlinear intensity versus current density behavior. Phosphors having this behavior have been obtained by doping (ZnCd)S:Ag phosphors with a small amount of Ni; however, superlinear behavior in other phosphor systems has not been obtained.

Experimental screens and tubes which have been prepared give an indication of the degree of color shift which can be expected. Improvements have been made continuously in the properties of the phosphors used, and it seems likely that further improvements are possible and will result in greater color shifts. Tubes similar to some of the ones prepared to date would probably be suitable for display of many types of alphanumeric information.

Further work should be concentrated on improving the performance and reproducibility of the phosphors. Two particular goals should be to improve the superlinear behavior and to find better sublinear phosphors so that a greater color shift with less brightness difference can be obtained. Another important aspect is to determine, if possible, the mechanism responsible for the superlinear behavior. This should then make it easier to improve the performance and determine which other systems might give superlinear behavior.

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APPENDIX A

MEASUREMENT TECHNIQUES

The initial evaluation of experimental phosphors is carried out on powder samples in a demountable CRT system such as the one shown in Figure A-1. The powder samples are packed into depressions in an aluminum disc which holds nine samples. The disc can be rotated by means of a vacuum feedthrough gear arrangement in order to place the desired sample under the electron beam. A front surface mirror reflects the emitted radiation to the viewing port which has a Suprasil window. The samples are normally excited by a 1μa electron beam at 10 kv using a 2 cm^2 scanned raster. A 166 line scan with a repetition rate of 30 frames/sec is used.

For evaluation of experimental screens a demountable bulb such as the one shown in Figure A-2 is used. The holder has space for seven screens at one time. In this system the holder is stationary and the electron beam is deflected to excite the desired sample. The phosphors are deposited by conventional water settling techniques on 1 inch image tube faceplates, then the screens are filmed and aluminized. A 1 cm^2 raster is used at the desired screen current and voltage.

To obtain spectral distribution data, the radiation from powder samples or experimental screens was analyzed with a motor-driven Jarrell-Ash 0.25 meter monochromator (model 82-410). The detector used during the early part of the program was an EMI 9592B photomultiplier (S-10 surface); during the latter part of the program an ITTIL F4013 photomultiplier (S-20 surface) was used. The photomultiplier signal was amplified by a Keithly model 414 micro-microammeter and recorded with a Houston Instruments model HR197 X-Y recorder. The monochromator-photomultiplier combination was calibrated using a standard of spectral irradiance (quartz-iodine lamp) obtained from Eppley Laboratories. Corrected spectral energy distribution data and chromaticity coordinates were calculated by an IBM 1130 computer.

Measurement of the total emission intensity from powder samples was carried out with a photometer consisting of an RCA 1P21 photomultiplier (S-4 surface) and a Wratten 106 filter. This combination has a sensitivity which is very similar to that of the photopic eye and, thus, measures the relative luminous intensity. The response of this photometer has been measured and is shown in Figure A-3 compared to that of the photopic eye. A sample of commercial P-1 phosphor was run with each group of experimental phosphors for use as a comparison standard. The gain of the photometer was adjusted so that the P-1 gave a reading of 10μa when excited by a current density of 0.5 $\mu a/cm^2$. For some of the early samples, the intensity was measured with an ITTIL F4000 biplanar phototube (S-5 surface).

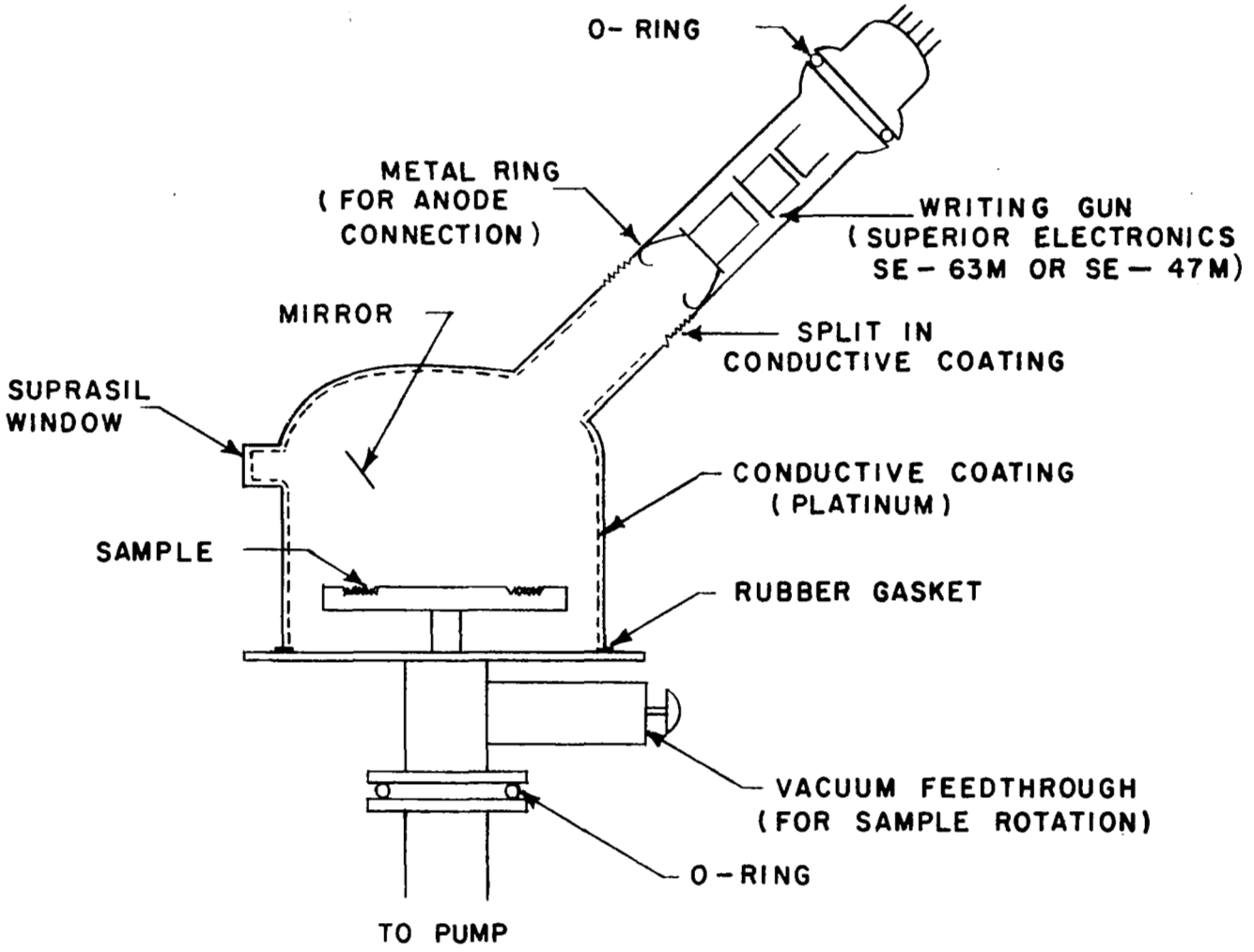

Figure A-1 Demountable CRT for Powder Sample Evaluation

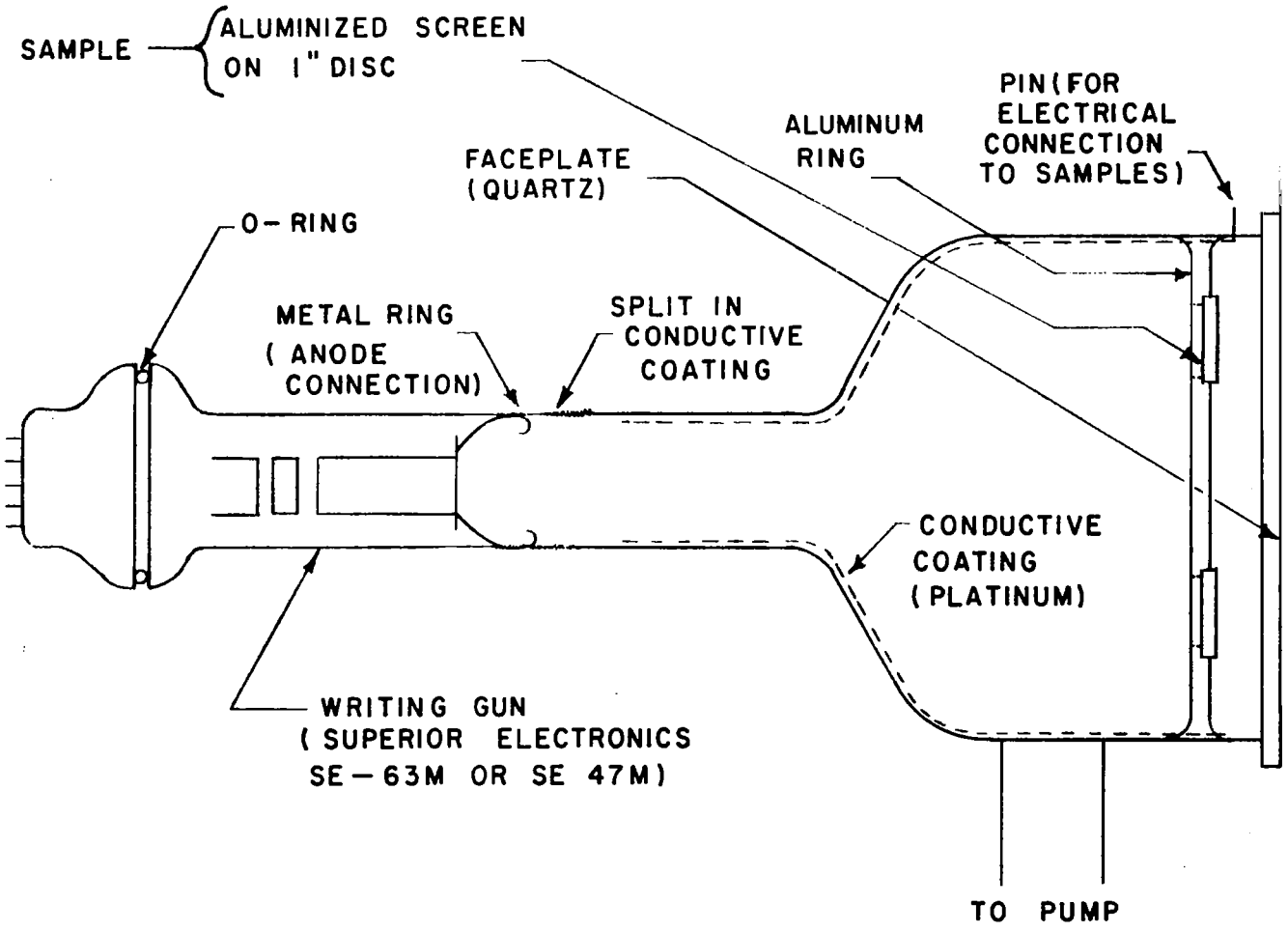

Figure A-2 Demountable CRT for Sample Screen Evaluation

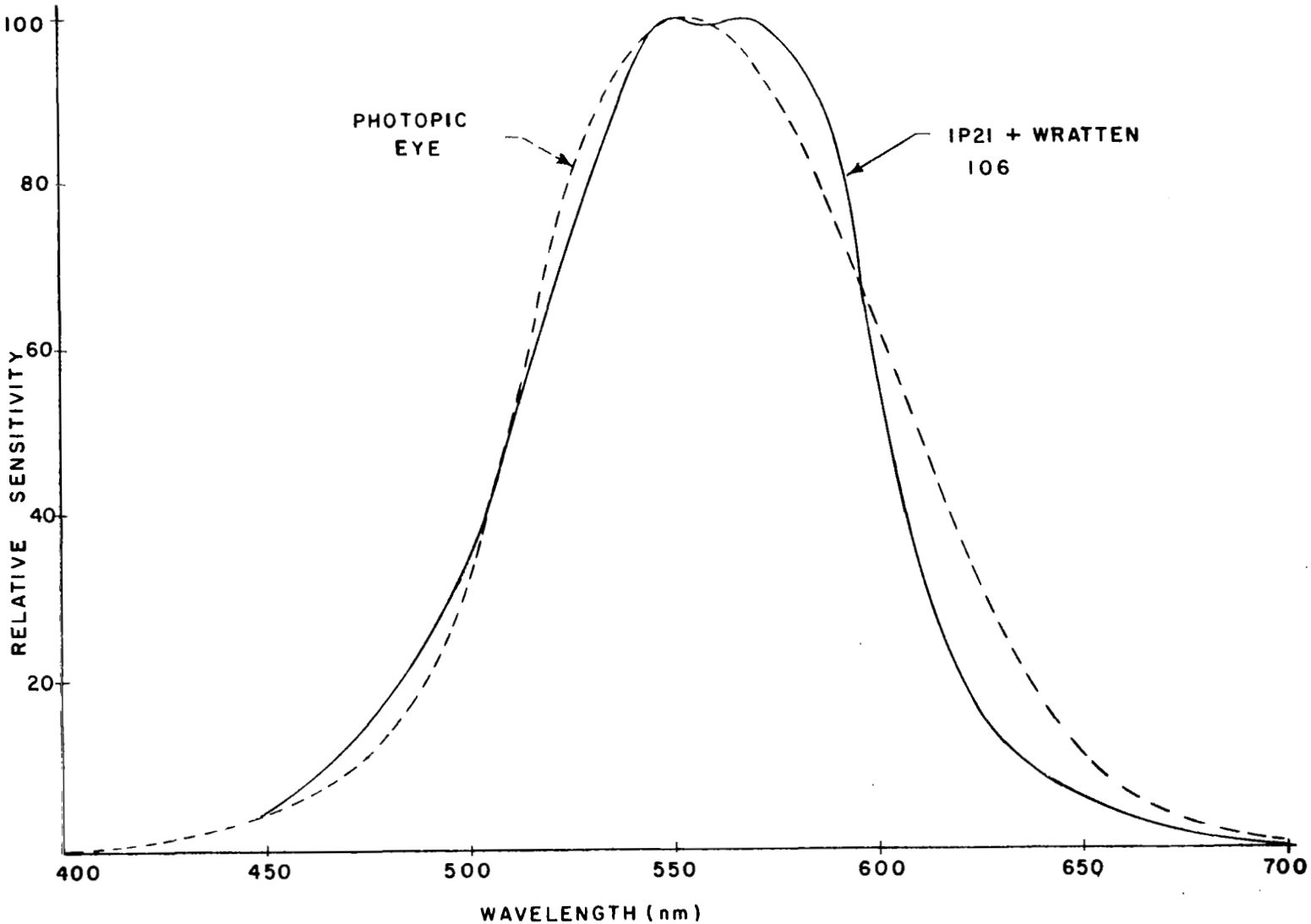

Figure A-3 Spectral Sensitivity of 1P21 Photometer

APPENDIX B

EXPERIMENTAL PHOSPHOR SAMPLES

Data are given for powder samples of the experimental phosphors which have been prepared. The samples are divided into several categories as indicated on the tables. For the sake of completeness, data are included on some samples prepared before work on this contract was started.

The ZnS:CdS ratios and activator and poison concentrations are all given on a weight basis. The peak wavelength is in nanometers and is an approximate value which is not corrected for instrument sensitivity. The luminous intensity was measured at $0.5 \mu a/cm^2$ with the IP21 photometer as described in Appendix A. The intensity ratio is the ratio of the luminuous intensity at $1.0\ \mu a/cm^2$ to that at $0.05\ \mu a/cm^2$ and gives an indication of the linearity of intensity as a function of current density. Where no data are given, either the intensity was quite low or no measurements were made for some other reason.

Table B-1

High Zn Samples with Simultaneous Incorporation of Ag & Ni

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
ZC-1	65:35	50	10	2 hrs. @ 850°	523	1.1	50
-2	65:35	50	1	2 hrs. @ 850°	522	14.0	16
-3	65:35	50	5	2 hrs. @ 850°	518	5.3	24
-4	65:35	50	7.5	2 hrs. @ 850°	520	1.6	87
-5	57:43	50	5	2 hrs. @ 700°	-	-	-
-6	57:43	50	10	2 hrs. @ 700°	-	-	-
-7	65:35	50	7.5	2 hrs. @ 850°	520		
-8	70:30	50	7.5	2 hrs. @ 850°	510		
-9	60:40	50	7.5	2 hrs. @ 850°	530	7.6	37
-10b	60:40	20	7.5	2 hrs. @ 850°	528	1.8	47
-11b	57.5:42.5	20	7.5	2 hrs. @ 850°	538	1.6	58
-12b	57.5:42.5	50	7.5	2 hrs. @ 850°	536	4.8	39
-12c	57.5:42.5	50	7.5	2 hrs. @ 850°	533	1.9	80
-13	90:10	50	7.5	2 hrs. @ 850°	466	1.0	25

Table B-1 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
ZC-14	80:20	50	7.5	2 hrs. @850°	483	1.0	27
-15	55:45	50	7.5	2 hrs. @850°	537	1.8	79
-15-2	55:45	50	7.5	2 hrs. @850°	546	6.5	45
-15-3	55:45	50	7.5	2 hrs. @850°	548	4.8	50
-16	50:50	50	7.5	2 hrs. @850°	558	2.9	52
-17	50:50	50	7.5	2 hrs. @850°	558	2.6	76
-18	50:50	50	7.5	2 hrs. @750° + 1 hr. @850°	558	3.8	54
-19b	55:45	50	2.5	2 hrs. @750°	548	10.7	13
-20b	55:45	50	5	2 hrs. @750°	547	7.2	21
-21b	55:45	50	7	2 hrs. @750°	547	0.65	27
-22b	55:45	50	2.5	2 hrs. @850°	549	13.3	13
-23b	55:45	50	5	2 hrs. @850°	549	8.3	22
-24b	55:45	50	7	2 hrs. @850°	548	0.29	18
-25	84:16	40	0	2 hrs. @750°	-	-	-

Table B-1 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
ZC-26	84:16	40	4.5	2 hrs. @ 750°	-	-	-
-27	84:16	40	9.0	2 hrs. @ 750°	-	-	-
-28	55:45	50	7.5	2 hrs. @ 850°	547	5.5	51
-29	55:45	50	7.5	2 hrs. @ 750°	548	5.6	46
-30a (Note 1)	55:45	50	7.5	2 hrs. @ 850°	551	2.1	65
-30b (Note 1)	Portion of 30a refired			1 hr. @850°	555	0.61	56
-30c (Note 1)	Portion of 30a refired			2 hrs. @ 850°	559	0.30	32
-31	55:45	50	6.2	2 hrs. @ 750°	547	9.1	39
-32	55:45	50	7.5	2 hrs. @ 750°	545	5.4	50
-33	55:45	50	6.2	2 hrs. @ 850°	547	2.9	73
-34 (Note 2)	55:45	33	0	2 hrs. @ 750°	551	21.2	18
-35	55:45	33	0	2 hrs. @ 750°	549	22	18

Note 1 Ni added to slurry before adding Ag.

Note 2 Sample pre-fired 3 hrs. @850° before adding Ag.

Table B-2

High Zn Samples with Other Poisons (Note 1)

Sample No.	ZnS:CdS Ratio	Poison - ppm	Firing	Peak λ	Lum. Int.	Int. Ratio (Note 2)
ZC-Fe-1	65:35	Fe - 10	2 hrs. @850°			18
-2	65:35	Fe - 50	2 hrs. @850°			23
-3	65:35	Fe - 5	2 hrs. @850°	518		17
-4	65:35	Fe - 20	2 hrs. @850°			20
-5	65:35	Fe - 100	2 hrs. @850°			27
ZC-Co-1	65:35	Co - 10	2 hrs. @850°			12
-2	65:35	Co - 50	2 hrs. @850°			17
-3	65:35	Co - 20	2 hrs. @850°			16
ZC-Co,Fe-1	65:35	Co - 20 Fe - 10	2 hrs. @ 850°			17
ZC-Fe,Ni-1	65:35	Fe - 10 Ni - 10	2 hrs. @ 850°			42
ZC-V-1(Note 3)	65:35	V - 84	2 hrs. @ 850° (in H_2S)		Dead	
-2	65:35	V - 25	2 hrs. @ 850° (in H_2S)		Dead	

Table B-2 (cont)

Sample No.	ZnS:CdS Ratio	Poison - ppm	Firing	Peak λ	Lum. Int.	Int. Ratio
ZC-V-3	65:35	V - 12.5	2 hrs. @ 850° (in H_2S)		Dead	
-4	65:35	V - 2.5	2 hrs. @850° (in H_2S)		Dead	
ZC-V,Cl-1a (Note 4)	65:35	V - 12.5	2 hrs. @ 850°(H_2S) + 1 hr. @850°(N_2)			
-1b	65:35	V - 12.5	2 hrs. @850°(H_2S) + 1 hr. @850°(H_2S)	504		
-2 (Note 5)	65:35	V - 12.5	1 hr. @ 850°(H_2S) +1 hr. @ 850°(H_2S)	504		
-3 (Note 6)	65:35	V - 12.5	1 hr. @850°(H_2S) +1 hr. @ 850°(N_2)	504		
-Fe-40 (Note 7)	55:45	Fe - 10	3 hrs.@ 950° +2 hrs. @750°	559	6.2	21 (Note 8)
-Co-41 (Note 7)	55:45	Co - 10	3 hrs. @ 950° +2 hrs. @ 750°	559	19.3	17(Note 8)
- V -42 (Note 7)	55:45	V - 100	3 hrs. @ 950° +2 hrs. @ 750°	555	21.5	17(Note 8)

Note 1. All samples have 50 ppm Ag and simultaneous addition of Ag and Ni unless otherwise noted.
Note 2. Data obtained with biplanar phototube (S-4 surface) unless otherwise noted.
Note 3. Used 180 ppm Ag.

Table B-2 (cont)

Note 4. Sample ZC-V, C1-1 had V + NaCl added before 1st firing, washed and split into -1a and 1b before second firing.

Note 5. NaCl added before 1st firing; V added before 2nd firing.

Note 6. V added before 1st firing; NaCl added before 2nd firing.

Note 7. Poison added before 1st firing; Ag added before 2nd firing.

Note 8. Data obtained with 1P21 photometer.

Table B-3

High Zn Samples with Separate Incorporation of Poison and Activator

Sample No.	ZnS:CdS Ratio	1st Addn. ppm	1st Firing	2nd Addn. ppm	2nd Firing	Peak λ	Lum. Int.	Int. Ratio
ZC - p1a (Note 1)	55:45	Ni - 7.5	3 hrs. @850°	Ag-50	2 hrs. @750°	570	3.9	72
-p1b					2 hrs. @850°	570	3.6	23
-p1c					3 hrs. @850°	566	4.4	74
-p2a (Note 1)	55:45	Ni - 7.5	3 hrs. @850°	Ag-50	2 hrs. @650°	561	3.7	55
-p2b					2 hrs. @700°	573	4.0	69
-p2c					2 hrs. @750°	568	3.7	69
-p3a (Note 1)	55:45	Ni - 7.5	3 hrs. @950°	Ag-50	2 hrs. @750°	566	2.0	81
-p3b					2 hrs. @800°	561	2.4	73
-p3c					2 hrs. @850°	559	2.8	74
-p4a	55:45	Ag - 50	3 hrs. @950°			544	11.8	16

Table B-3 (cont)

Sample No.	ZnS:CdS Ratio	1st Addn. ppm	1st Firing	2nd Addn. ppm	2nd Firing	Peak λ	Lum. Int.	Int. Ratio
ZC -p4b	Each sample (p4b thru p4e) represents a Ni addition and refiring of the previous sample. Ni conc, based on original sample wt.			Ni - 5	1hr. @750°	556	3.5	35
-p4c				Ni - 4	1hr. @800°	544	1.7	75
-p4d				Ni - 4	1hr. @800°	555	0.20	57
-p4e				Ni - 4	1hr. @800°	538	0.39	17
-p4f	Each sample (p4f thru p4jb) represents additional firing of the previous sample.			-	6hrs. @850°	538	0.43	12
-p4g				-	6 hrs. @850°	517	0.009	14
-p4h				-	6 hrs. @850°	514	0.14	16
-p4i				-	6 hrs. @850°	526	0.20	18
-p4ja				-	24hrs. @850°	-	0.04	14
-p4jb				-	24hrs. @850°	-	0.06	14
ZC -p6a	55:45	Ag-50	3hrs. @950°			548	21.0	20
-p6b				Ni-10	1hr. @850°	563	3.8	82

Table B-3 (cont)

Sample No.	ZnS:CdS Ratio	1st Addn. ppm	1st Firing	2nd Addn. ppm	2nd Firing	Peak λ	Lum. Int.	Int. Ratio
-p6c					1hr. @850°	551	2.6	115
-p6d	Each sample (p6c through p6g) represents additional firing of previous sample.				1hr. @850°	551	2.4	128
-p6e					1hr. @850°	555	2.3	146
-p6f					1 hr. @850°	561	1.9	147
-p6g					1 hr. @850°	553	2.1	147
-p8a (Note 1)	55:45	Ni-7.5	2.5 hrs@950°	Ag-45	1 hr. @750°	572	5.7	51
-p8b					2 hrs. @750°	590	4.0	52
-p8c					3 hrs. @750°	582	4.6	30
-36a (Note 2)	55:45	Ni-7.5	3 hrs. @950°			Dead		
-36b				Ag-50	2 hrs. @750°	555	1.8	58
-37a (Note 2)	55:45	Ni-7.5	3 hrs. @950°			Dead		
-37b				Ag-50	2 hrs. @750°	543	0.49	31
-38a (Note 2)	55:45	Ni-7.5	3 hrs. @950°			Dead		
-38b				Ag-50	2 hrs. @750°	556	1.3	44

Table B-3 (cont)

Sample No.	ZnS:CdS Ratio	1st Addn. ppm	1st Firing	2nd Addn. ppm	2nd Firing	Peak λ	Lum. Int.	Int. Ratio
-39-1	60:40	Ni - 7.5	2 hrs. @950°	Ag-50	2 hrs. @750°	539	5.2	51
-39-2	60:40	Ni - 7.5	3 hrs. @950°	Ag-50	2 hrs. @750°	545	3.4	63

Note 1. Sample split into 3 parts (a, b, c) before 2nd firing.

Note 2. Samples ZC-36, -37, and -38 are the same except for the fluxes used; the b samples were prepared from the a samples.

Table B-4
ZnS:Cu, Ni with Separate Incorporation of Cu and Ni

Sample No.	1st Addn. ppm	1st Firing	2nd Addn. ppm	2nd Firing	Peak λ	Lum. Int.	Int. Ratio
ZC-p5a	Cu - 10	1 hr. @ 850°			539	22	15
-p5b			Ni-5	1/2 hr @850°	540	15	19
-p5c	Each sample (p5b through p5d) represents a Ni addn. and refiring of the previous sample.		Ni-5	1 hr. @850°	537	10.6	20
-p5d			Ni-5	1 hr. @850°	538	6.8	22
-p5e	Each sample (-p5e thru -p5pl represents additional firing of the previous sample.			1 hr. @850°	538	6.5	22
-p5f				1-1/2hrs@850°	539	5.9	21
-p5g				1-1/2hrs@850°	540	6.0	21
-p5h				1-1/2hrs@850°	541	5.6	20
-p5i				1-1/2hrs@850°	537	5.6	20
-p5j				1-1/2hrs@850°	539	5.9	13
-p5k				1-1/2hrs@850°	540	3.8	16
-p5l				1-1/2hrs@850°	537	3.8	16
-p5m				2 hrs. @850°	533	3.4	16
-p5n				1-1/2hrs@850°	536	3.0	15
-p5o				1-1/2hrs@850°	534	3.0	16
-p5p				1-1/2hrs@850°	531	1.9	14

Table B-5

High Cd Samples with Simultaneous Incorporation of Ag & Ni

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-1	14:86	50	5	2 hrs @700°		-	14 (Note 1)
-2	14:86	50	10	2 hrs @700°		-	14 (Note 1)
-2a	14:86	50	10	2 hrs @850°	652		
-2b	14:86	50	10	2 hrs @800°	652		
-20	15:85	40	1	1 hr @750°	635	1.9	18
-20b	15:85	40	1	1 hr @850°	636	2.4	30
-20c	15:85	40	1		632	1.6	15
-21	15:85	40	5	1 hr @750°	638	1.3	21
-21b	15:85	40	5	1 hr @850°	641	1.8	30
-21c	15:85	40	5		636	1.0	18
-22	15:85	40	10	1 hr @750°	641	0.5	20
-22b	15:85	40	10	1 hr @850°	638	0.74	30
-22c	15:85	40	10		641	0.34	20
-23	15:85	4	1	3 hrs @700°	630	0.71	≈ 12

Table B-5 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-24	15:85	4	5	3 hrs @700°	645	0.06	≈ 6
-25	15:85	4	10	3 hrs @700°	632	-	-
-26	15:85	8	1	3 hrs @700°	627	1.2	15
-27	15:85	8	5	3 hrs @700° +1 hr @700°	645	0.05	6
-28	15:85	8	10	3 hrs @700° +1 hr @700°	636	0.012	10
-29	15:85	16	1	1 hr @650° + 1 hr @ 700°	628	1.7	15
-30	15:85	16	5	1 hr @650° +1 hr @700°	636	0.32	29
-31	15:85	16	10	1 hr @650°			
-32	15:85	0	1	1 hr @ 650°	635	0.19	≈ 8
-33	15:85	0	5	1 hr @ 650°	630	-	-
-34	15:85	0	10	1 hr @ 650°	Dead	-	-
-38	40:60	50	7.5	2 hrs @750° +1 hr @ 850°	586	1.35	90
-39-1	30:70	50	7.5	2 hrs @750° +1 hr @850°	612	0.52	56

Table B-5 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-40-1	20:80	50	7.5	2 hrs @750^{o} +1 hr @ 850^{o}	637	0.36	20
-41	35:65	50	7.5	2 hrs @850^{o}	580	0.76	89
-42a	22.5:77.5	38	5.5	2 hrs @ 700^{o}	623	1.9	22
-42b	22.5:77.5	38	5.5	1 hr @ 900^{o}	625	1.8	22
-42c	22.5:77.5	38	5.5	1 hr @ 1100^{o}	620	0.84	25
-43a	18.5:81.5	38	5.5	2 hrs @ 700^{o}	633	1.2	20
-43b		38	5.5	1 hr @ 900^{o}	634	1.1	17
-43c		38	5.5	1 hr @ 1100^{o}	630	0.93	18
-44a	16.5:83.5	37	5.4	2 hrs @700^{o}	637	0.78	18
-44b	16.5:83.5	37	5.4	1 hr @ 900^{o}	637	0.90	18
-44c	16.5:83.5	37	5.4	1 hr @ 1100^{o}	633	0.84	19
-45a	14.5:85.5	37	5.4	2 hrs @700^{o}	647	0.67	17
-45b	14.5:85.5	37	5.4	1 hr @900^{o}	639	0.73	17
-45c	14.5:85.5	37	5.4	1 hr @1100^{o}	636	0.73	19
-46a	12.5:87.5	37	5.3	2 hrs @ 700^{o}	655	0.55	16

Table B-5 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
ZC-46b	12.5:87.5	37	5.3	1 hr @ 900°	650	0.56	16
-46c	12.5:87.5	37	5.3	1 hr @ 1100°	642	0.59	15
-47a	11:89	36	5.3	2 hrs @700°	656	0.32	14
-47b	11:89	36	5.3	1 hr @ 900°	649	0.42	16
-47c	11:89	36	5.3	1 hr @1100°	643	0.39	14
-48b	18.5:81.5	38	1.5	1 hr @ 650°	657	1.6	17
-49b	18.5:81.5	38	3.4	1 hr @ 650°	661	1.2	19
-50b	18.5:81.5	38	4.5	1 hr @ 650°		1.0	19
-51b	18.5:81.5	38	1.5	1 hr @700°		1.8	19
-52b	18.5:81.5	38	3.4	1 hr @ 700°		1.1	20
-53b	18.5:81.5	38	4.5	1 hr @700°		0.98	22
-54b	18.5:81.5	38	1.5	1 hr @900°		1.6	18
-55b	18.5:81.5	38	3.4	1 hr @900°		1.0	20
-56b	18.5:81.5	38	4.5	1 hr @900°	660	0.86	21
-57	14.5:85.5	40	0	2 hrs @750°	661	1.5	17

Table B-5 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^{+}	Ppm Ni^{++}	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-58	14.5:85.5	40	0.4	2 hrs @750^{o}	661	1.5	18
-59	14.5:85.5	40	0.9	2 hrs @750^{o}	661	1.2	16

Note 1. Measurements on peak intensities using monochromator - photomultiplier combination.

Table B-6

High Cd Samples with Other Poisons (Note 1)

Sample No.	ZnS:CdS Ratio	Ppm Ag^+	Poison ppm	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-14	15:85	40	Fe - 1	1 hr @ 750°	634	1.9	16
-14b	15:85	40	Fe - 1	1 hr @ 850°	638	1.3	17
-14c	15:85	40	Fe - 1	1 hr @ 950°	638	1.9	18
-15	15:85	40	Fe - 5	1 hr @ 750°	634	1.8	17
-15b	15:85	40	Fe - 5	1 hr @ 850°	638	1.2	16
-15c	15:85	40	Fe - 5	1 hr @ 950°	636	1.8	16
-16	15:85	40	Fe - 10	1 hr @ 750°	634	1.7	15
-16b	15:85	40	Fe - 10	1 hr @ 850°	638	1.3	18
-16c	15:85	40	Fe - 10	1 hr @ 950°	636	1.6	17
-17	15:85	40	Co - 1	1 hr @ 750°	642		
-17b	15:85	40	Co - 1	1 hr @ 850°	637	2.9	15
-17c	15:85	40	Co - 1	1 hr @ 950°	632	1.8	17
-18	15:85	40	Co - 5	1 hr @ 750°	634		
-18b	15:85	40	Co - 5	1 hr @ 850°	634	2.9	15

Table B-6 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^+	Poison ppm	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-18c	15:85	40	Co - 5	1 hr @ 950°	638	1.7	17
-19	15:85	40	Co - 10	1 hr @ 750°	635	1.8	17
-19b	15:85	40	Co - 10	1 hr @ 850°	634	2.9	14
-19c	15:85	40	Co - 10	1 hr @ 950°	636	1.5	17
-35a (Note 2)	20:80	20	Pd - 20	1 hr @ 700°	629	2.3	20
-35b				1 hr @ 850°	633	2.2	18
-36a (Note 2)	20:80	20	Pd - 75	1 hr @ 700°	630	2.0	18
-36b				1 hr @ 850°	633	1.9	18
-37a (Note 2)	20:80	20	Pd - 300	1 hr @ 700°	629	1.5	18
-37b				1 hr @ 850°	630	1.5	17

Note 1. Used simultaneous addition of Ag and poison in all cases.

Note 2. Samples CZ -35b, -36b, and -37b prepared by refiring the a samples.

Table B-7

(CdZn)S: Ag, Cu Samples

Sample No.	ZnS:CdS Ratio	Ppm Ag^+	Ppm Cu^+	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-Cu-1	14.4:85.6	40	23.5	1 hr @ 750°	636	0.19	14
-2	14.4:85.6	40	47	1 hr @ 750°	636	0.05	
-3	14.4:85.6	40	94	1 hr @ 750°			
-4	14.4:85.6	80	23.5	1 hr @ 750°	643	0.16	15
-5	14.4:85.6	80	47	1 hr @ 750°	652	0.02	
-6	14.4:85.6	80	94	1 hr @ 750°			
-7	14.4:85.6	160	23.5	1 hr @ 750°			
-8	14.4:85.6	160	47	1 hr @ 750°			
-9	14.4:85.6	160	94	1 hr @ 750°			
-10	14.4:85.6	40	0	1 hr @ 750°	633	1.8	16
-11	15:85	40	1	1 hr @ 750°	634	1.7	16
-11b	15:85	40	1	1 hr @ 850°	631	1.2	17
-11c	15:85	40	1	1 hr @ 950°	632	1.6	17
-12	15:85	40	5	1 hr @ 750°	634	0.77	19

Table B-7 (cont)

Sample No.	ZnS:CdS Ratio	Ppm Ag^+	Ppm Cu^+	Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-Cu-12b	15:85	40	5	1 hr @ 850°	631	0.73	18
-12c	15:85	40	5	1 hr @ 950°	635	0.87	14
-13	15:85	40	10	1 hr @ 750°	634	1.1	17
-13b	15:85	40	10	1 hr @ 850°	631	0.88	18
-13c	15:85	40	10	1 hr @ 950°	636	1.0	18

Table B-8

High Cd Samples with Separate Incorporation of Poison & Activator

Sample No.	ZnS:CdS Ratio	1st Addn. ppm	1st Firing	2nd Addn. ppm	2nd Firing	Peak λ	Lum. Int.	Int. Ratio
CZ-60-1	35:65	Ni-7.5	2 hrs @ 950°	Ag-50	2 hrs @ 750°	610	2.6	50
-60-2	35:65	Ni-7.5	3 hrs @ 950°	Ag-50	2 hrs @ 750°	616	1.3	73
-61-1	30:70	Ni-7.5	2 hrs @ 950°	Ag-50	2 hrs @ 750°	631	1.7	44
-61-2	30:70	Ni-7.5	3 hrs @ 950°	Ag-50	2 hrs @ 750°	634	1.0	60
-61-3	30:70	Ni-7.5	3 hrs @ 950°	Ag-50	2 hrs @ 750°	630	0.64	48
-61-4	30:70	Ni-7.5	3 hrs @ 950°	Ag-50	2 hrs @750°	631	0.70	50
-61-5	30:70	Ni-7.5	3 hrs @950°	Ag-50	2 hrs @ 750°	633	0.62	56
-61-6	30:70	Ni-7.5	3 hrs @ 950°	Ag-50	2 hrs @ 750°	638	0.70	54
-61-7	30:70	Ni-7.5	3 hrs @ 950°	Ag-50	2 hrs @ 750°	622	0.74	65
-61-8	30:70	Ni-5	3 hrs @ 950°	Ag-50	2 hrs @ 750°	626	2.2	39
-61-9	30:70	Ni-7.5	3 hrs @ 1000°	Ag-50	2-1/2 hrs @800°	626	1.4	43
-61-10	30:70	Ni-7.5	3 hrs @ 1000°	Ag-50	2-1/2 hrs @800°	626	1.8	31
-62 (Note 1)	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 650°	661	1.2	17

Table B-8 (cont)

Sample No.	ZnS:CdS Ratio	1st Addn. ppm	1st Firing	2nd Addn. ppm	2nd Firing	Peak λ	Lum. Int.	Int. Ratio
-63	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 700°	665	0.74	11
-64	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 750°	661	0.90	12
-65	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 800°	661	0.98	11
-66	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 650°	661	0.79	11
-67	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 700°	663	0.91	12
-68	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 750°	669	1.1	
-69	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 800°	669	1.0	
-70	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 650°	667	0.55	10
-71	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 700°	658	0.75	11
-72	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 750°			
-73	18.5:81.5	Ni-6	3 hrs @ 850°	Ag-75	2 hrs @ 800°			

Note 1. Samples CZ-62 thru -73 consist of 3 groups of 4 samples with different sodium halide fluxes.

Table B-9

Sublinear Zn_2SiO_4:Mn Samples

Sample No.	Mole % Mn	Firing	Peak λ	Lum. Int.	Int. Ratio
Z_2S-1	1.2	2 hrs. @ 1250°	523	-	-
-2	0.05	2 hrs. @ 1250°	523	4.0	14
-3	0.1	2 hrs. @ 1250°	523	6.5	14
-4	0.5	2 hrs. @ 1250°	522	6.7	17
-5	0.01	2 hrs. @ 1250°	524	1.1	7.6
-6	0.001	2 hrs. @ 1250°	524	0.7	7.9

APPENDIX C

EXPERIMENTAL SCREENS

Data on all the screens prepared for demountable evaluation are included. Table C-1 lists the composition while Table C-2 gives the chromaticity coordinates as a function of current density. Chromaticity coordinates were not calculated for all the screens so that Table C-2 does not include all the screens which are listed in Table C-1. In general, the screens for which chormaticity coordinates were not obtained either had very little color shift or less color shift than other screens with a similar composition.

Data for Table C-2 were taken on aluminized screens at 10 kv unless otherwise noted. Variations in values for screens of same composition do not necessarily represent lack of reproducibility in calculations. Some discrepancies could be due to errors in transferring data from recorder plots to punched cards for computer or else to non-uniformities in settling of screens.

Table C-1

Composition of Experimental Screens

Screen No.	Superlinear Phosphor	Linear or Sublinear Phosphor	Ratio Superlinear: Linear
39	ZC-4 (green)	ZnS: **Ag**, Ni (blue)	1:2
40	ZC-4(green)	ZnS:Ag, Ni (blue)	1:1
41	ZC-4 (green)	ZnS:Ag, Ni (blue)	2:1
42	ZC-4 (green)	ZnS:Ag, Ni (blue)	5:1
47	ZC-9 (green)	YVO_4:Eu (red)	2:3
48	ZC-9 (green)	YVO_4:Eu (red)	1:1
49	ZC-9 (green)	YVO_4:Eu (red)	3:2
57	ZC-9 (green)	YVO_4:Eu (red)	11:9
61	ZC-12b (green)	YVO_4:Eu (red)	11:9
62	ZC-12b (green)	YVO_4:Eu (red)	1:1
63	ZC-12c (green)	YVO_4:Eu (red)	11:9
64	ZC-12c (green)	YVO_4:Eu (red)	1:1
* 65	ZC-9 (green)	YVO_4:Eu (red)	11:9
66	ZC-12b (green)	YVO_4:Eu (red)	9:11
67	ZC-12c (green)	YVO_4:Eu (red)	3:2
68	ZC-15 (green)	CZ-35b (red)	1:1
69	ZC-15 (green)	CZ-35b (red)	5:7
70	ZC-15 (green)	CZ-35b (red)	7:5
71	CZ-41 (red)	$InBO_3$:Tb (green)	2:1
72	CZ-41 (red)	$InBO_3$:Tb (green)	1:1
73	CZ-41 (red)	$InBO_3$:Tb (green)	7:5
74	CZ-41 (red)	Zn_2SiO_4:Mn (green)	5:1
75	CZ-41 (red)	Zn_2SiO_4:Mn (green)	3:1
76	CZ-41 (red)	Zn_2SiO_4:Mn (green)	2:1
77	CZ-41 (red)	Z_2S-Ni-2 (green)	3:1
78	CZ-41 (red)	Z_2S-Ni-2 (green)	2:1
79	CZ-41 (red)	Z_2S-Ni-2 (green)	7:5
80	ZC-15 (green)	CZ-35b (red)	7:8
81	CZ-41 (red)	ZC-Ag_1Co-2 (green)	2:1
82	CZ-41 (red)	ZC-Ag_1Co-2 (green)	3:2
83	CZ-41 (red)	ZC-Ag_1Co-2 (green)	1:1
84	CZ-41 (red)	$Y(BO_2)_3$:Tb, Gd (green)	2:1
85	CZ-41 (red)	$Y(BO_2)_3$:Tb, Gd (green)	3:2
86	CZ-41 (red)	$Y(BO_2)_3$:Tb, Gd (green)	1:1
87	ZC-15 (green)	YVO_4:Eu (red)	1:1
88	ZC-15 (green)	YVO_4:Eu (red)	3:2
89	CZ-41 (red)	$Y(BO_2)_3$:Tb, Gd (green)	5:1
90	CZ-41 (red)	$Y(BO_2)_3$:Tb, Gd (green)	11:4

Table C-1 (cont)

Screen No.	Superlinear Phosphor	Linear or Sublinear Phosphor	Ratio Superlinear:Linear
1a	ZC-33 (green	CZ-57 (red)	1:1
2a	ZC-33 (green)	CZ-59 (red)	1:1
3a	ZC-30 (green)	CZ-57 (red)	1:1
4a	ZC-30 (green)	CZ-59 (red)	1:1
5a	CZ-61 (red)	Z_2S-2 (green)	1:1
6a	CZ-61 (red)	Z_2S-2 (green)	3:2
7a	CZ-61 (red)	Z_2S-2 (green)	2:1
8a	CZ-61 (red)	Z_2S-2 (green)	5:1
9a	CZ-61 (red)	$Y(BO_2)_3$:Tb, Gd (green)	1:1
10a	CZ-61 (red)	$Y(BO_2)_3$:Tb, Gd (green)	3:2
11a	CZ-61 (red)	$Y(BO_2)_3$:Tb, Gd (green)	2:1
12a	CZ-60 (red)	Z_2S-2 (green)	2:1
13a	CZ-60 (red)	Z_2S-2 (green)	5:1
14a	CZ-60-2 (red)	Z_2S-5 (green)	1:1
15a	CZ-60-2 (red)	Z_2S-5 (green)	2:1
16a	CZ-60-2 (red)	Z_2S-6 (green)	1:1
17a	CZ-60-2 (red)	Z_2S-6 (green)	2:1
18a	CZ-61-2 (red)	Z_2S-5 (green)	1:1
19a	CZ-61-2 (red)	Z_2S-5 (green)	2:1
20a	CZ-61-2 (red)	Z_2S-6 (green)	1:1
21a	CZ-61-2 (red)	Z_2S-6 (green)	2:1
22a	CZ-61-2 (red)	Z_2S-5 (green)	17:13
23a	CZ-61-2 (red)	Z_2S-5 (green)	19:11
24a	CZ-61-2 (red)	Z_2S-6 (green)	17:13
25a	CZ-61-2 (red)	Z_2S-6 (green)	19:11
26a	CZ-61-8 (red)	Z_2S-5 (green)	5:7
27a	CZ-61-8 (red)	Z_2S-5 (green)	1:1
28a	CZ-61-8 (red)	Z_2S-5 (green)	7:5
29a	CZ-61-8 (red)	Z_2S-6 (green)	5:7
30a	CZ-61-8 (red)	Z_2S-6 (green)	1:1
31a	CZ-61-8 (red)	Z_2S-6 (green)	7:5
32a	CZ-61-9 (red)	Z_2S-5 (green)	2:1
33a	CZ-61-9 (red)	Z_2S-5 (green)	7:5
34a	CZ-61-9 (red)	Z_2S-6 (green)	2:1
35a	CZ-61-9 (red)	Z_2S-6 (green)	7:5
36a	CZ-61-8 (red)	Z_2S-5 (green)	3:2

* Screen No. 65 was settled together with the screen for tube No. I-2.

Table C-2

Experimental Screen Chromaticity Coordinates

Beam Current Density ($\mu a/cm^2$)

Screen No.	0.01 x	0.01 y	0.1 x	0.1 y	1.0 x	1.0 y	10 x	10 y
48 (Note 1)			0.517	0.420	0.454	0.453	0.435	0.460
49 (Notes 1 & 2)			0.495	0.427	0.430	0.468	0.404	0.468
			0.466	0.447	0.423	0.449	0.424	0.458
57 (Notes 1 & 2)			0.516	0.421	0.448	0.462	0.430	0.471
			0.518	0.413	0.453	0.453	0.456	0.443
			0.506	0.419	0.460	0.450	0.456	0.457
			0.535	0.402	0.459	0.451	0.444	0.460
61 (Note 2)			0.491	0.448	0.434	0.481	0.439	0.478
			0.507	0.431	0.450	0.475	0.448	0.477
	0.563	0.393	0.486	0.454	0.440	0.483	0.428	0.492
62 (Note 2)			0.518	0.433	0.471	0.463	0.466	0.465
	0.584	0.377	0.520	0.428	0.472	0.465	0.456	0.478
			0.521	0.431	0.473	0.462	0.461	0.473
63 (Note 2)	0.630	0.342	0.593	0.368	0.516	0.436	0.502	0.442
	0.625	0.349	0.583	0.378	0.497	0.444	0.476	0.462
			0.598	0.364	0.516	0.425	0.492	0.449
64 (Note 2)			0.602	0.367			0.513	0.434
	0.628	0.342	0.612	0.358	0.538	0.416	0.520	0.433
			0.546	0.393	0.465	0.448	0.512	0.436

Table C-2 (cont)

Beam Current Density ($\mu a/cm^2$)

Screen No.	0.01 x	0.01 y	0.1 x	0.1 y	1.0 x	1.0 y	10 x	10 y
65 (Note 2)	0.598	0.365	0.537	0.403	0.480	0.442	0.464	0.450
			0.535	0.406	0.468	0.449	0.465	0.451
66 (Note 2)	0.548	0.412	0.468	0.465	0.438	0.491	0.443	0.490
	0.549	0.406	0.495	0.454			0.440	0.495
67 (Note 2)	0.609	0.354	0.546	0.402	0.455	0.475	0.434	0.493
	0.608	0.352	0.552	0.399	0.451	0.475	0.437	0.490
68	0.635	0.358	0.583	0.402	0.498	0.475	0.446	0.518
69	0.636	0.358	0.593	0.395	0.510	0.467	0.468	0.502
70	0.612	0.376	0.563	0.418	0.465	0.501	0.427	0.535
71	0.352	0.598	0.351	0.605	0.418	0.550	0.466	0.511
72	0.348	0.603	0.360	0.594	0.418	0.548	0.446	0.528
73	0.351	0.603	0.383	0.581	0.443	0.532	0.470	0.510
84	0.322	0.619	0.328	0.614	0.400	0.560	0.427	0.538
87	0.636	0.354	0.606	0.382	0.542	0.429	0.525	0.439
88	0.626	0.361	0.582	0.398	0.488	0.466	0.480	0.464

Table C-2 (cont)

Beam Current Density ($\mu a/cm^2$)

Screen No.	0.01		0.1		1.0		10	
	x	y	x	y	x	y	x	y
89	0.327	0.613	0.337	0.608	0.422	0.541	0.467	0.507
90	0.320	0.615	0.332	0.607	0.414	0.546	0.448	0.521
1a	0.578	0.396	0.501	0.463	0.440	0.517	0.411	0.540
2a	0.532	0.430			0.407	0.538	0.377	0.564
3a	0.589	0.388	0.525	0.449	0.463	0.502	0.443	0.515
4a	0.576	0.403	0.484	0.480	0.427	0.530	0.410	0.540
19a	0.379	0.527	0.415	0.532	0.539	0.449	0.557	0.436
20a	0.296	0.608	0.280	0.642	0.446	0.518	0.525	0.459
21a	0.355	0.516	0.381	0.544	0.534	0.446	0.574	0.418
22a	0.213	0.696	0.222	0.693	0.300	0.632	0.405	0.548
23a	0.218	0.698	0.244	0.676	0.361	0.583	0.466	0.501
24a	0.263	0.653	0.303	0.626	0.488	0.483	0.553	0.434
25a	0.232	0.683	0.271	0.651	0.455	0.510	0.556	0.432

Table C-2 (cont)

Beam Current Density ($\mu a/cm^2$)

Screen No.	0.01		0.1		1.0		10	
	x	y	x	y	x	y	x	y
32a (Note 3)	0.229	0.678	0.274	0.651	0.425	0.535	0.520	0.461
32a					0.348	0.594		
33a (Note 3)	0.252	0.671	0.338	0.604	0.470	0.501	0.539	0.446
34a (Note 3)	0.262	0.665	0.334	0.610	0.512	0.467	0.570	0.422
35a (Note 3)	0.263	0.665	0.362	0.586	0.530	0.453	0.578	0.416
36a (Note 3)	0.278	0.652	0.394	0.560	0.489	0.485	0.572	0.417
							0.570	0.418

Notes: 1. First set of values for these screens is from unaluminized screen.
2. Each set of readings is from separate screen; screens were all settled together.
3. Readings taken at 15kv.

APPENDIX D

EXPERIMENTAL TUBES

Table D-1 lists the screen composition while Table D-2 gives the chromaticity data.

Table D-1

Experimental Tubes Screen Composition

Tube No.	Superlinear Phosphor	Linear or Sublinear Phosphor	Ratio Superlinear: Linear
*I-1 & I-2	ZC-9 (green)	YVO_4:Eu (red)	11:9
8-1	ZC-12c (green)	YVO_4:Eu (red)	3:2
8-2 & 8-3	ZC-15 (green)	CZ-35b (red)	6:7
8-4, 8-5, 8-6	CZ-61-2 (red)	Z_2S-5 (green)	19:11
8-7 & 8-8	CZ-61-8 (red)	Z_2S-5 (green)	1:1
8-9	CZ-61-9b (red)	Z_2S-6 (green)	19:11
*J-1 & J-2	CZ-61-9b (red)	Z_2S-6 (green)	19:11

* I-1, I-2, J-1, and J-2 are 5 inch round tubes; the others are 8 inch rectangular tubes.

Table D-2

Experimental Tubes Chromaticity Coordinates

Beam Current Density ($\mu a/cm^2$)

Tube No.	0.05		0.1		1.0		10	
	x	y	x	y	x	y	x	y
I-1 (10kv)	0.631	0.352	0.542	0.399	0.452	0.441	0.442*	0.445*
8-3 (10kv)	0.639	0.357	0.635	0.359	0.566	0.417	0.495	0.466
8-5 (10kv)			0.227	0.689	0.260	0.665	0.316	0.622
	0.01$\mu a/cm^2$							
J-1 (10kv)	0.237	0.684	0.267	0.660	0.420	0.541	0.517	0.464
J-1 (15kv)**			0.297	0.636	0.454	0.512	0.539	0.447
J-2 (15kv)	0.231	0.681	0.275	0.654	0.427	0.534	0.529	0.453

* These values are for 5.0$\mu a/cm^2$

** Operation was somewhat erratic; therefore, current density values are approximate.

APPENDIX E

NEW TECHNOLOGY

Improved Phosphor Screens for Single Gun Color Cathode Ray Tubes - p. 23

This work has resulted in the filing of a patent application covering the composition of phosphor screens for single-gun color cathode ray tubes.

Method for Preparing Improved Superlinear Phosphors - p. 11

A patent disclosure has been submitted to the ITT Patent Department covering this method; however, further action will be dependent on definitely establishing that this preparation procedure does result in improved superlinear behavior.