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FOR CATHODE RAY TUBE

January 31, 1967

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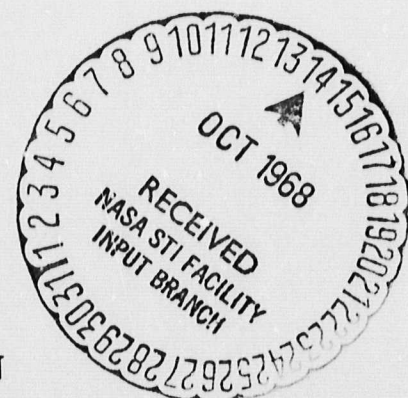
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Prepared under Contract No. NAS 4-1084

PanAura Corp.
Pennsauken, New Jersey

for

Flight Research Center
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION



NASA CR-96002

**EXPERIMENTATION PROGRAM FOR DEVELOPMENT OF PHOSPHOR
FOR CATHODE RAY TUBE**

January 31, 1967

Prepared under Contract No. NAS 4-1084 by
Pan Aura Corp.
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Flight Research Center
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ERRATA TO EXPERIMENTAL PROGRAM FOR
DEVELOPMENT OF PHOSPHOR FOR CATHODE RAY TUBE

FINAL REPORT ON CONTRACT NO. NAS 4-1084 FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
FLIGHT RESEARCH CENTER
P. O. BOX 273
EDWARDS, CALIFORNIA 93523

Page 17, Paragraph 3, Line 5 - Should read: "125 nanosec." rather than
"125 u sec."

Page 17A - ADD: Block Diagram of Hamner Electronics Co., Inc. Model NA-12
Delay Line Amplifier

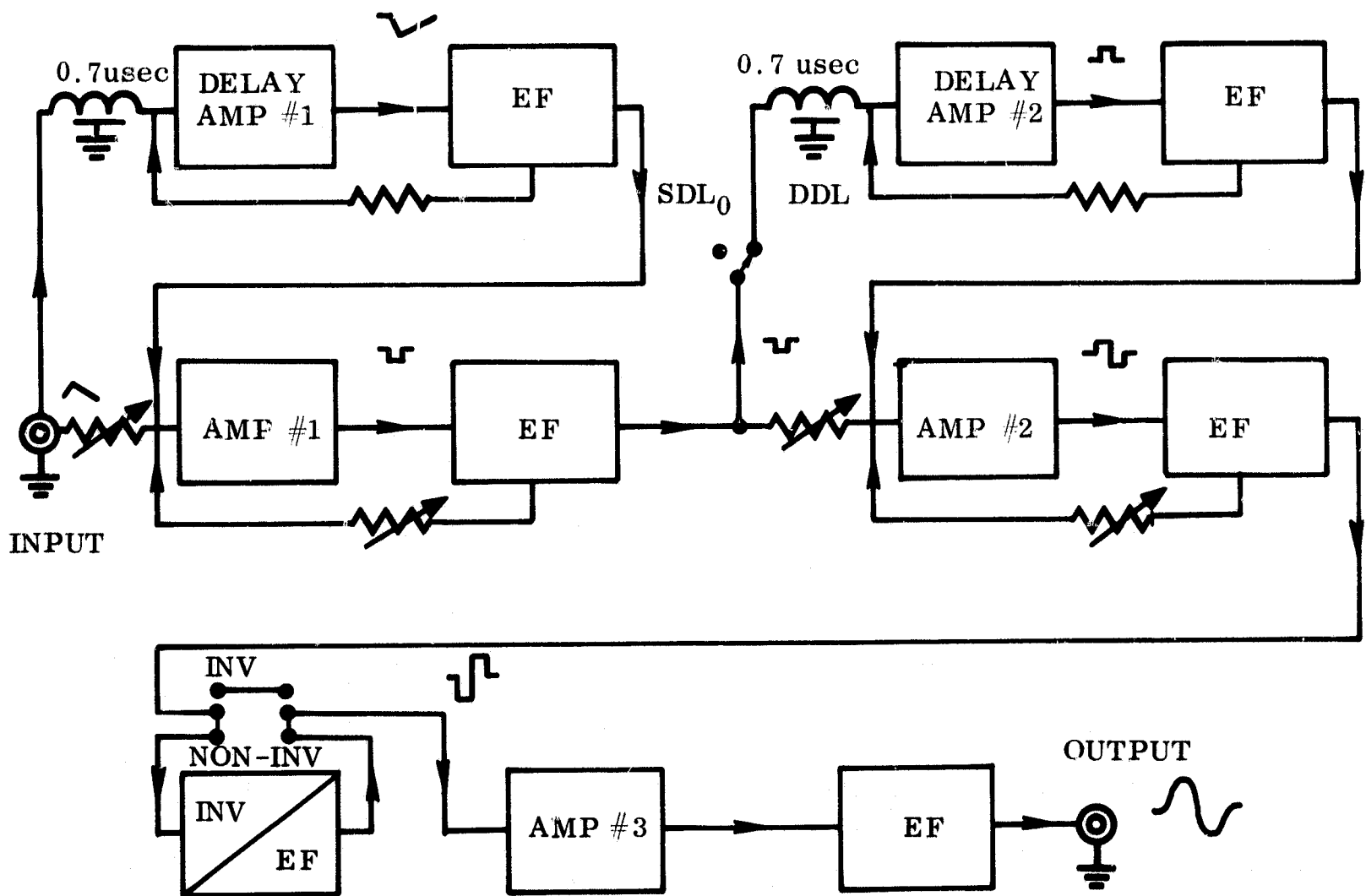


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EXPERIMENTATION PROGRAM FOR DEVELOPMENT OF

PHOSPHOR FOR CATHODE RAY TUBE

(Contract NAS4-1084)

FINAL REPORT

JANUARY 31, 1967

I. INTRODUCTION

The goal of this effort was to develop an improved phosphor which could be used in a cathode ray tube for a full color flying spot scanner system, which with the appropriate signal conditioning would produce a high resolution, high contrast display with good color fidelity. The specific goals are described in the contract work statement as follows:

"The Contractor shall conduct all necessary study and experimentation necessary to determine the feasibility of developing a suitable phosphor for this application. Short decay time, wide light spectrum, and durability shall be the major consideration of this effort. The desired result is a phosphor whose light can be split into 3 non-overlapping colors by suitable dichroics, the colors being approximately red, green, and blue. The light output and the decay time should be such that a 10 megacycle pulse rate can be reproduced with a 10,000 to 1 signal-to-noise ratio measured at the output of a suitable photomultiplier tube with appropriate signal conditioning. It is desired that this signal-to-noise ratio be obtainable in all 3-color channels when the spot on the CRT is not larger than 0.00007 of the screen diameter".

"The Contractor shall investigate advanced signal processing techniques designed to extract the highest possible signal-to-noise ratio from a flying-spot scanner camera. The best technique or techniques investigated shall be incorporated as a part of the above required demonstration".

To achieve this goal requires several things of the phosphor. It must have an efficient emission over a wide spectrum and must resist burn so that a strong signal can be generated in each of the three primary colors. It must be very evenly distributed on the CR tube face so that there is no variation in signal strength as the fine spot moves from point to point. And finally the luminescent decay must be extremely rapid so that the afterglow from one spot does not smear the next spot generated. For example, in a display with 1000 vertical and 1000 horizontal line resolution there are 1,000,000 dots generated 30 times a second. To avoid smear the decay should, therefore, be much faster than 0.03 μ sec.; and no such phosphor exists. The fastest available phosphors are P-16 with a blue emission which decays in about 0.2 μ sec. and P-24 with a fairly broad emission centered in the green with a decay of about 0.6 μ sec. No phosphors are commercially available with red emissions which decay in less than 10 milliseconds. P-24 is thus the phosphor usually employed in color scanning systems; but the red tail of its emission is very faint and has a decay of about 5 microseconds; and the red information channel is thus very noisy.

The emphasis, was therefore concentrated on the red channel. Efforts were made to improve the red emission of existing rapid decay phosphors and to develop new phosphors having efficient red emissions with rapid decay. It was then intended to produce these phosphors in the form of evaporated films in order to reduce "screen" noise.

Evaporated screens have previously been produced of a variety of phosphors in both transparent and translucent form. When transparent, evaporated screens are less bright than powdered screens by a factor of 4 to 6 but have high contrast, are perfectly uniform, and have a resolution capability of better than 200 line pairs per mm. If this amount of light loss cannot be tolerated without having noise in the detection circuit becoming the limiting factor, grain size of the evaporated screens can be increased which increases optical scattering among the grains. The films are then less transparent, contrast is reduced, and spot size increases; but brightness increases and uniformity is still good. On two phosphors (P-1 and P-5) where sufficient effort has been made, translucent evaporated screens have been made which were as bright as thinly settled powder screens and which retained substantial advantages in terms of uniformity (screen noise), spot size and contrast.

It was thus reasonable to hope that either red signal strength could be increased in available fast decay phosphors or a new red with faster decay could be developed; and that in either case, spot size and screen noise could be reduced and contrast could be improved--if the improved phosphor could be made in the form of evaporated films.

It was not reasonable to hope that decays faster than 0.03 μ sec. would be achieved in view of many years of previous effort resulting in nothing faster than 0.1 μ sec. In fact, on the basis of both theoretical grounds (not adequate for precise predictions) and all previous experience, it seemed unlikely that a red emitting phosphor would be developed with a decay as fast as existing blues.

Thus, it appeared from the start that the best phosphors which could be hoped for would have decays 10 to as much as 1000 times longer than required to avoid smear in a high rate scanner system.

Thus the phosphor development needed to be accompanied by a study of means of signal processing which would eliminate the smear, if there was to be a substantial improvement in scanning systems.

This was an extremely ambitious program on which to expect substantial results in the time frame and with the money allocated; but PanAura had a substantial body of pertinent experience and an internal interest in these problems that created a reasonable probability of achieving the goals. As the initial termination date approached, it became obvious that a small amount of additional effort would produce more definitive answers to a number of crucial questions. A sixty day extension was requested and granted during which PanAura continued the work at the same level of effort with no additional cost to the government. At the present date of termination, significant contributions have been achieved; and definitive answers can be deduced concerning most but not all, of the problems. While it is not a requirement of the contract, PanAura will continue its efforts in this area of development at its own expense; and if successful in certain specific tasks, will supply to NASA at no cost, a supplement to this Final Report containing the information relating to the goals of this contract.

II. SUMMARY

The contract effort produced a number of significant contributions to useful phosphors. These, when combined with the signal processing techniques which were demonstrated,

will result in significant improvements over existing flying spot scanner systems, both monochrome and full color. Thus while all the specific goals were not achieved, it was a highly productive, valuable effort.

Concerning phosphor development, there were three principal directions of effort. One was to extend the spectral emission of the $\text{CaMgSiO}_3\text{:Ce}$ (P-16) and related phosphors from blue toward red. A similar effort was made on ZnO (P-15; P-24) phosphors. The third effort was concerned with exploring the little known bismuth activated alkaline earth phosphates. In each case considerable effort was made to produce high quality evaporated films of the best composition.

In the case of the P-16 type, all of the composition changes and impurities activators which produced substantial emission broadening resulted in decay rates in the range of milliseconds. These attempts to achieve considerable emission broadening were abandoned early in the contract, and efforts were then concentrated on producing high quality films with whatever spectral shift could be achieved without an appreciable increase in decay rate. Despite considerable previous effort, which had appeared promising, it proved to be extremely difficult to perfect the technique for consistently good films of these materials. The technique was verified as reproducible only during the last month of the contract, and the specimen chosen for evaluation was not of the ideal composition. It was slightly shifted toward the visible blue, slightly brighter and appreciably slower (2 μ sec.) than the best P-16 powders. It was, however, highly transparent; would be useful as it is for moderate rates of scan and would

produce sharp definition, high contrast, and low screen noise compared to powdered phosphors. Having conquered the technique we are confident that with additional effort compositions with 0.2 μ decay and a range of grain sizes up to emissions as bright as powdered phosphors can be achieved.

The ZnO family of phosphors also resisted substantial broadening of the spectral emission without accompanying increases in persistence; and they totally resisted all efforts to produce good quality thin films by simple evaporation of the phosphor compound. Good quality films ranging in character from P-15 to P-24 were finally obtained in the last two weeks of effort by evaporating only the metal and depending on air bake for the oxygen content. The sample selected for evaluation showed a spectral emission slightly broader than P-24 and a decay of 0.3 μ sec. The specimen tested was very thin; but again we are confident that with sufficient effort it can be produced in a range of compositions and degrees of graininess to perform better than powders of either P-15 or P-24 in terms of brightness, contrast, screen noise and burn resistance.

Work on the alkaline earth phosphates is described in considerable detail in the subsequent "Technical Discussion" because it is a very interesting and useful family of phosphors which has not been previously very much explored. Briefly, we were not able to obtain good quality films by any means; but a number of the compositions produced powdered phosphors that are efficient, more deeply saturated red and much faster decay than any previously available red phosphor. The whole family deserves to be much more thoroughly explored than was possible in the time

frame of the contract effort, both because of the information it would provide on the mechanism of luminescence and because one of the family will be very useful in full color flying spot scanner systems. The choice of the most useful was narrowed during this study to one of four compositions, any one of which is greatly improved over previous phosphors for color scanner applications. The characteristics obtained are not necessarily the best that can be achieved. In each case the decays reported (from 3 to 6 μ sec.) can probably be reduced by a factor of three to ten, but probably at the expense of efficiency. The final choice of the best to use in powder form will depend on a lengthy, detailed study of efficiency at various excitation levels, saturation, burn resistance, ease of preparation, ease of grinding, settling characteristics, etc. Even without further study, however, any one of the four could be mechanically mixed with available P-15 powder and produce a scanner tube which (if subject to the signal processing developed in this effort) would substantially improve color scanning systems. It is our hope, of course, that continued effort will produce one of this family in the form of a transparent film which in a dual layer with the ZnO film would represent the ultimate in a high resolution color scanner tube.

Concerning signal conditioning, several approaches were considered and two were explored in some depth. One involved pulsing the cathode (more properly the grid) of the tube at a rate much faster than the rate of generating discrete bits (dots) of information. The sum of the build ups and decays would approach a saw tooth form of light output which could be converted to a series of square waves, the height of which would represent a signal to

noise advantage over a steady signal with a slow decay. The ultimate value of this form of signal conditioning was really not established.

The second approach was the more conventional feedback from a delay line for clipping of the undesired portion of the signal. This too requires some very fancy circuitry and an exotic delay line to operate well at the rate required for a high resolution color scan system. The beneficial effect was shown dramatically at a slower rate; and it is clear that this method is do-able with effort, and that the improvement which can be achieved in system performance is very large.

III. TECHNICAL DISCUSSION

A. Phosphor Development

The most interesting work by far from the viewpoint of phosphor chemistry was that on the alkaline phosphates and related compounds; and for this we are deeply indebted to Professor F. A. Kroger, both for suggesting and guiding this work. Before discussing these compounds we will dispose of those which are better known chemically, and on which most of the effort was concerned with producing good films.

(1) ZnO

The phosphor characteristics of ZnO (P-15 and P-24) are pretty well established. Additional information concerning electronic behavior of the solid will be obtained from work now in progress on improved crystals; but the behavior of phosphor particles prepared in a variety of ways has been pretty well studied. A little more time was spent trying to get a fast red emitting ZnO than was

probably justified because of some recent claims concerning a new P-24 with a stronger red emission. Our conclusion is that P-24 with a red emission is just dirty-- and that the red part is dim and slow.

There are several ways to get a red emission from ZnO which are interesting in the laboratory, but not ultimately useful. The easiest is to just run it very hot (about 500°K); but the new emission band which is generated is not bright; it decays slowly, and the phosphor burns. You can also get red emissions from a ZnO with a number of impurity atoms. We tried pure ZnO with a trace of MgO, with Boron and Mn, with Cd and SiO and all exhibited emissions which were somewhat red but were dim, and slow. We also tried adding Bi, Ce, Ti and some rare earths without achieving red emissions.

It is easy to be misled in this type of experiment because emission bands can be induced or can be killed by a few parts per million impurity atoms. For example, the red generated by ZnO plus Mg might be from Mn impurity atoms in the Mg; or Bi may not have worked because of a little Fe in the Bi.

Care must also be taken with the measurements. Many photomultipliers are sensitive only in the blue and do not detect that the red emission is much slower. In any event, if there is a good way to make a fast, red ZnO, we did not find it.

We attempted to make evaporated ZnO films starting with commercial P-15 and P-24 powders and with some pure ZnO prepared by burning Zn in oxygen. We tried evaporating ZnO from Pt, Ta, Mo, Carbon and ZrO boats and by using an electron gun. The resulting films were tested with a Tesla coil before and after firing, and none were luminescent. Presumably the film deposits in the wrong crystal structure.

The results finally achieved were obtained by producing a film of pure zinc metal and forming the ZnO by baking in situ on the glass. Brightest emission was obtained by baking at 1100° for two hours. The emission band for this film is slightly broader than normal for P-24 which might be because a surface layer has reacted with the glass substrate. However, the difference is not significant in terms of sufficient blue and red for a color scan system. The decay rate with no filter was 0.3μ sec., a bit faster than typical P-24 powder. With a red filter, the signal was too weak to read. This family of transparent phosphors will be very useful for high contrast, low noise monochrome scanner systems; and when it can be accompanied with a fast, transparent red film, will be the ideal combination for color scanners.

(2) $\text{CaMgSiO}_3:\text{Ce}$ (P-16)

It may have been slightly presumptuous to even try to get a fast decay, red emission from this family of chemicals in view of all the previous work on this phosphor system. To justify having made the effort, PanAura has produced films with bright red emission from the old classic $\text{ZnSiO}_4:\text{Mn}$ (P-1) green. This was achieved by altering the firing conditions to change the crystal structure. With P-16 we had no such luck. Addition of Bi and Mn produced long decays, and the whole effort to produce a fast decay red emission was abandoned early in the program.

Most of the effort on P-16 type phosphors was thus concentrated on producing transparent evaporated films. This proved to be extremely difficult, and after it was achieved it is difficult to say just what we did right.

Briefly, concerning the background of chemistry known about the P-16 type phosphors, the composition desired for rapid decay is $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2 : \text{Ce}^{+3}$ (5 mol percent). Changing the relative proportions of Ca and Mg changes the brightness, and the decay rate. For example, $1\text{CaO} \cdot 1\text{MgO}$ gives higher brightness but the decay is slower by an order of magnitude. $3\text{CaO} \cdot 1\text{MgO}$ is both less bright and slower. The delicate balance between the chemical stoichiometry and the emission characteristics presumably accounts for the fact that commercial P-16 powdered phosphors rarely decay in 0.16μ sec. claimed. It should also be noted that the Phillips group at Eindhoven under Dr. Kroger developed a variation in which the MgO is replaced with Al_2O_3 . The resulting Gehlemite has roughly the same brightness and decay rate as the Akermite (P-16) but the emission peak is shifted from $3850\text{\AA}^0$ to $4050\text{\AA}^0$.

Concerning the evaporation technique, we have tried for four years with our own personnel and employed other thin film groups in an effort to make transparent P-16, and on occasion produced a film of reasonably good quality; but could not reproduce it. Usually the films were very foggy and uneven. We tried evaporating the whole powder, the constituents individually with a variety of techniques, a variety of evaporation of boats and crucibles, a variety of baking cycles. Now that we are producing clear films consistently we are not sure why, and in fact the procedure that works is somewhat different in two different evaporators. The evaporation is from Tantalum boats onto Vycor which is baked for one hour at 1100°C . In one evaporator it helps to produce a thin film of the MgO before the other constituents are evaporated.

The ability to control composition precisely and to control grain size remains to be developed. The specimen that was chosen for evaluation is probably a little rich in MgO. The visible blue emission is bright; but the decay rate is about 2 μ sec.

The obvious value of a bright, fast decay, transparent P-16 screen makes it important for this effort to be continued.

(3) Alkaline Earth Phosphates

All of the effort on this interesting family of chemicals was performed on a subcontract basis by Sigmatron under the guidance of Professor Kroger. Efforts to produce transparent films were not successful; but the powders are both interesting and useful. The Sigmatron work is well described in their own report which is attached as Appendix I.

Briefly, some fifty compositions were prepared and tested from a related family of chemicals in which the cation comprised either alkali or alkaline earth metals (Ca, Sr, Ba, Na, Li, K or Mg) singly and in combination; with the anion comprising several forms of phosphate, borate, arsenate and sulfate; all activated by Bismuth.

With all the data which was obtained on this family of phosphors, it is very tempting to draw conclusions about the mechanism of the luminescent process based, for example, on such factors as the shift of the emission peak with successive atoms of different atomic weight and ionic radius, and Professor Kroger could have been enlisted to interpret the results with authority. We resist the temptation to be profound at this time, however, because more effort should be spent on a number of the phosphors before the data is

accepted as representative. Small variations in composition and small changes in the preparation technique can have a profound effect on phosphor characteristics; and the specimens prepared in this survey are not guaranteed to be typical; and are certainly not the best that can be done.

What is very gratifying is that there four compositions, any one of which is already substantially better than previously available phosphors for the red channel of color scanning systems. These four are the meta and the pyro phosphates respectively of calcium and strontium ($\text{CaP}_2\text{O}_6\text{:Bi}$; $\text{Ca}_2\text{P}_2\text{O}_7\text{:Bi}$; $\text{SrP}_2\text{O}_6\text{:Bi}$, $\text{Sr}_2\text{P}_2\text{O}_7\text{:Bi}$). The emission peaks are all in the range from 6300 to 6500Å⁰, and all are reasonably bright. The decay rates range from 3 to 6 μ sec., and it is probable that these rates can be reduced, for example, with larger amounts of the bismuth activator or with "poisons". An improvement by a factor of from two to as much as ten might be expected in shorter decay, but probably at the expense of efficiency.

Aside from these four, there are a number of compositions among the whole group which are intriguing for other reasons. For example, $\text{CaSO}_4\text{:Bi}$ shows two emission peaks which together cover the visible spectrum better than any single phosphor with a rapid decay. $\text{SrB}_2\text{O}_4\text{:Bi}$ changed from primarily blue to primarily red during bombardment. $\text{Mg}_2\text{P}_2\text{O}_7\text{:Bi}$ is a bright, fast blue. All of these deserve more attention.

This whole family of chemicals thus deserves a thorough study, a task which would occupy a good phosphor group for more than a year. A substantial amount of additional work must be done just on the four which now appear most promising to be sure which is best in terms

of the whole spectrum of requirements; efficiency, color, decay, burn resistance, and settling properties. One of these four, combined with P-15, and subject to proper signal conditioning, will result in a color scanning system far better than now available. It will be a high performance system in every respect except for "screen noise" inherent with powdered phosphors.

It is disappointing that none of this family of phosphors could be prepared as transparent films. Sigmatron personnel have outstanding ability in film production and worked very hard on several compositions with no success. PanAura personnel got equally no place. Phosphate ions dissociate more completely on heating than any of the compounds from which transparent phosphors have been successfully made, and the phosphates are hygroscopic, especially when dissociated. PanAura encountered this problem previously in connection with zinc orthophosphate which is the saturated red which produces the most pleasing commercial color TV picture. The meta and pyro phosphates are even less stable, so additional difficulty is not surprising. Thus we cannot guarantee that this problem can be solved; but certainly a substantial effort will be made.

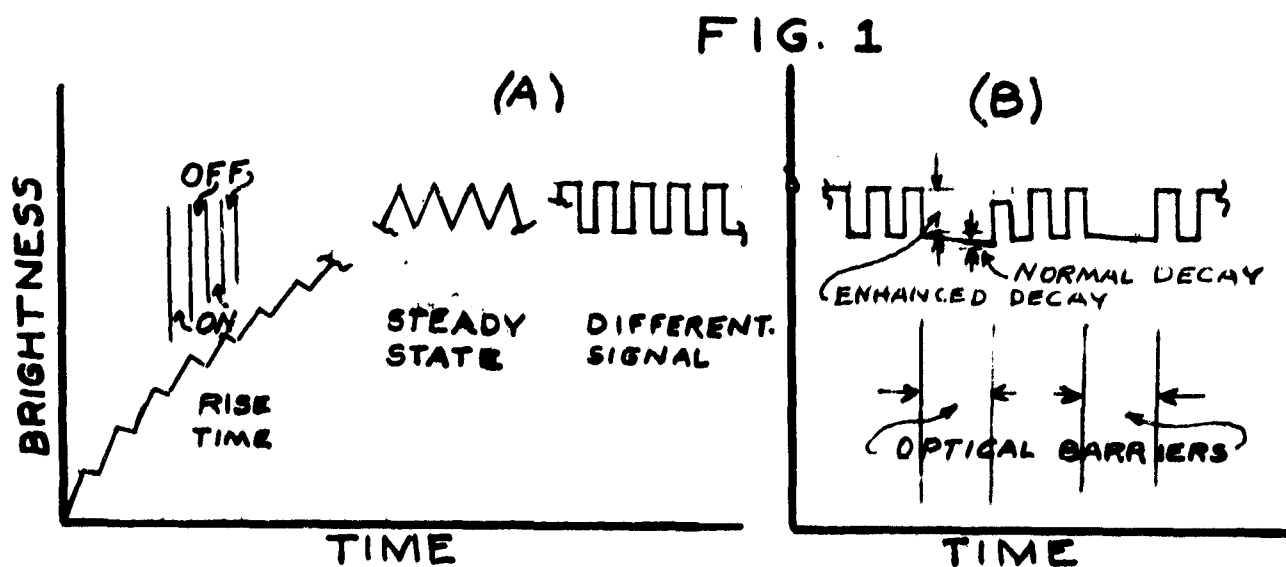
B. Signal Processing

The need for signal processing arises, as previously mentioned, from the fact that the decay rate of even the fastest phosphors is ten to a thousand times longer than it should be; and therefore produces a smear in the vertical resolution. Conventional practice in signal conditioning of scanner systems has employed tuning coil feedback and amplification of only the high frequency

portion of the signal; much the same approach as suppressing the bass response in audio systems. The advantage obtained in well designed systems of this type is about a factor of five--where we need a hundred or more.

Study of this problem brought forth two approaches which are novel either in concept or execution. One involves chopping the signal from the scanner tube and the other, auto-correlation of the signal from the photo-detector.

The concept behind chopping the signal from the scanner takes advantage of summing a series of small decays in intensity from the phosphor in the initial, fastest part of the decay curve. The principal is illustrated in Fig. 1.



Signal from Rapidly Pulsed CR Tube

When the electron beam is chopped rapidly with a 50% duty cycle, rapid compared to the decay time of the phosphor, the accumulated intensity rises, falls slightly, and repeats until the sum of the rises and the sum of the falls (decays) reaches a saw tooth variation in emission brightness which can be differentiated in the signal train from the detector

to produce a series of square waves. The effect of optical modulation from the target (a dense spot on the transparency being scanned) is shown in Fig. 1 (b). The signal emerging from the detector circuit drops to the "off" position of the square wave and decays from that point, adding the height of the square wave to the normal decay of the phosphor emission, thus increasing signal-to-noise ratio by that amount.

For this to be effective, the beam must be chopped at a rate faster than the sweep time of a horizontal bit of information. Thus in a 1000 horizontal line raster with each line resolved into 1000 vertical bits, there are a million dots repeated 30 times a second. The electron beam must therefore be chopped at a rate higher than 30 megacycles. Since there are several thousand volts and a few Mfd. in the beam, chopping clearly at that rate is a major circuit design problem in itself. Synchronizing the chopper and the detector circuit, converting to video and amplifying with the necessary bandwidth all pose design problems that push the ability of available components. The first version of this complete system has been set up and it appears that all existing deficiencies are correctable. The performance is not adequate at this date however to determine the value of this approach.

The other approach, clipping the noise by autocorrelation techniques has been applied with a high degree of success to other noise problems. Application to this system is in part easier and in part more difficult than in previous applications. The bandwidth requirements again involve designs and component performance that pushes the state of the art. The thing that is favorable is that

the shape and duration of the noise signal is well known since it is the decay curve of the phosphor screen, which is readily determined.

The problem thus reduces to designing a delay element which exactly matches the phosphor decay and amplifying the correlated signal with sufficient bandwidth. Designing the delay element is relatively straightforward if the phosphor decay is a simple exponential and otherwise becomes a fairly sophisticated problem. Fortunately each channel is handled separately so the delay element does not have to handle the several decay characteristics from a mixture of phosphors. Each of the phosphors now planned for use has a relatively simple decay curve so the effectiveness of this approach to signal conditioning is expected to be extremely high.

This approach was demonstrated using an available delay line with an effective pulse width of 700 nanoseconds on the 3 μ sec. decay from the new red phosphor; and the results are quite dramatic. Utilizing a delay element with a pulse width of 125 μ sec. will permit a bandwidth of 8 megacycles for each channel.

IV. RESULTS

A. Phosphor Emission Curves

The first set of data is the spectral emission curves from each of the significant phosphors. The phosphors were excited by the electron beam of approximately 5 KV in a demountable cathode ray tube. The emission curves were taken with a Beckman DK-2A Recording Spectrophotometer. Calibration was verified using a Jedec Standard P-22R red phosphor in the demountable CR tube.

Relative peak brightness from curve to curve is only a rough indication of relative efficiency of the respective phosphors because thickness of the phosphor layer was not identical in every case.

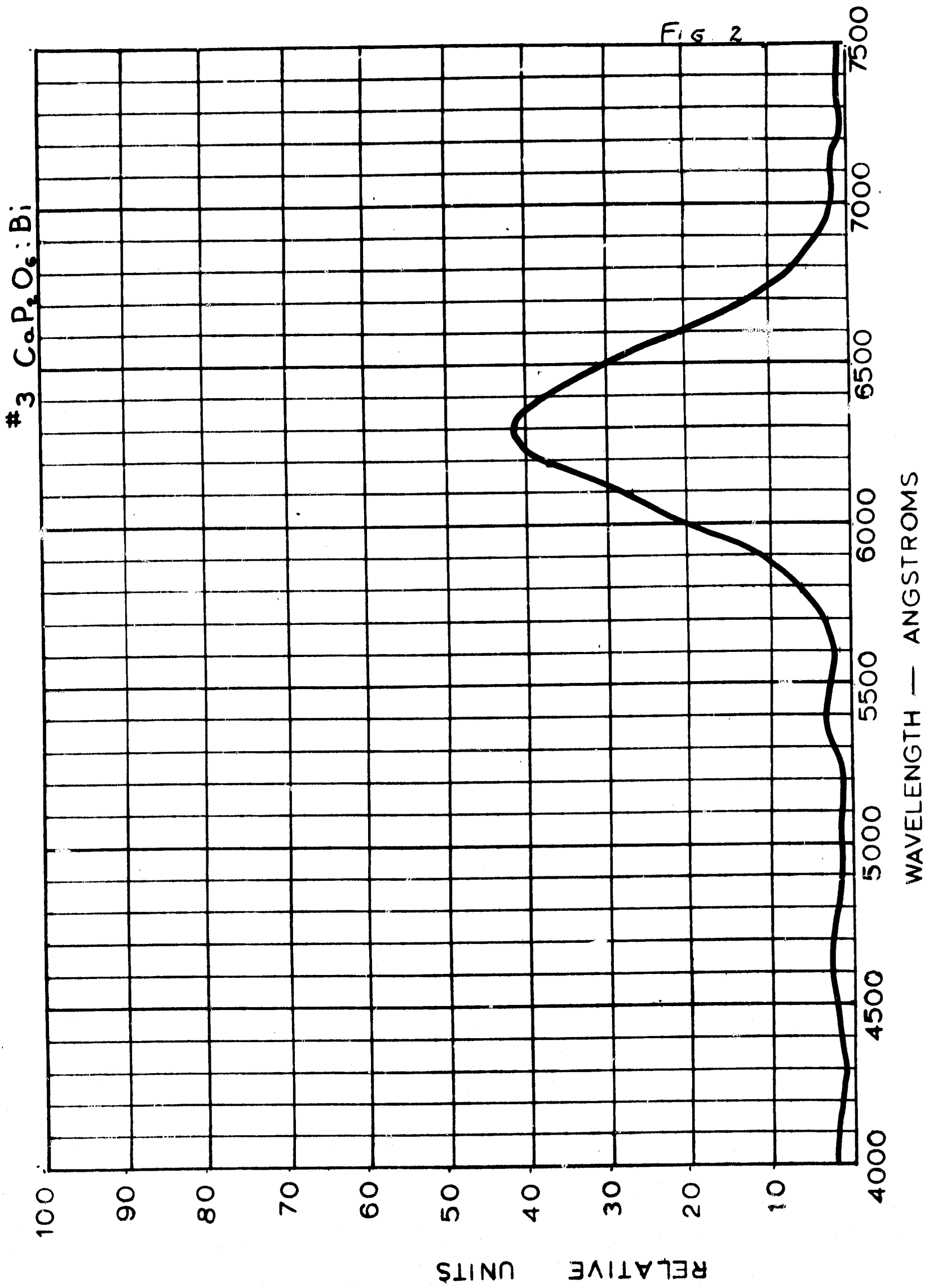
The first group of curves are those from the powdered phosphors prepared at Sigmatron. The heading, in addition to the chemical composition shows the Sigmatron sample numbers so that the results may be referred to the Sigmatron report attached as Appendix I. These sample numbers have no other significance, and are not related to standard Jedec phosphor numbers. Sample 7 for example, is not the commercial phosphor F-7.

The first four curves are the phosphors considered most promising for the red channel of a color scanner. The spectral response and relative brightness are not sufficiently different at the present state of development to serve as a basis of selection between them. All of them are good reds which would provide far more signal than is available in present scan tubes and all have decays which can be clipped. None of the four have emissions which extend far enough to use for a good signal even for the green channel, much less the blue.

The next curve, Fig. 6 is Sigmatron Sample 8, $\text{BaP}_{206}\text{:Bi}$. This is included primarily for phosphor chemists to note the trend of emission peaks with atomic number.

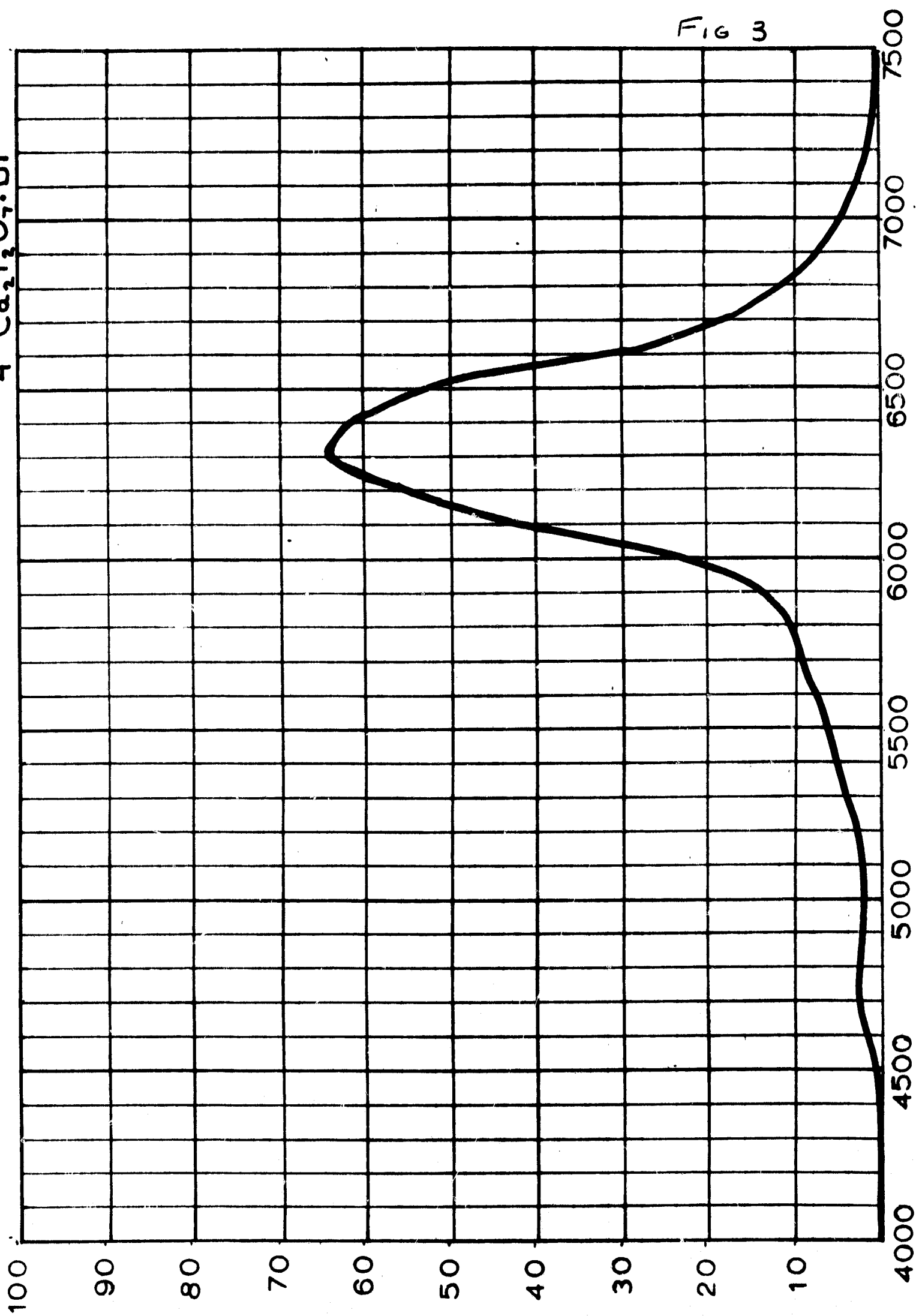
The curve of Sample 28, $\text{SrB}_{204}\text{:Bi}$ Fig. 7 is included because this composition behaved strangely, and further because it may be more amenable to film formation than the phosphates.

The following two curves Fig. 8 and Fig. 9 show the broad but weak emission from the sulfates. The last



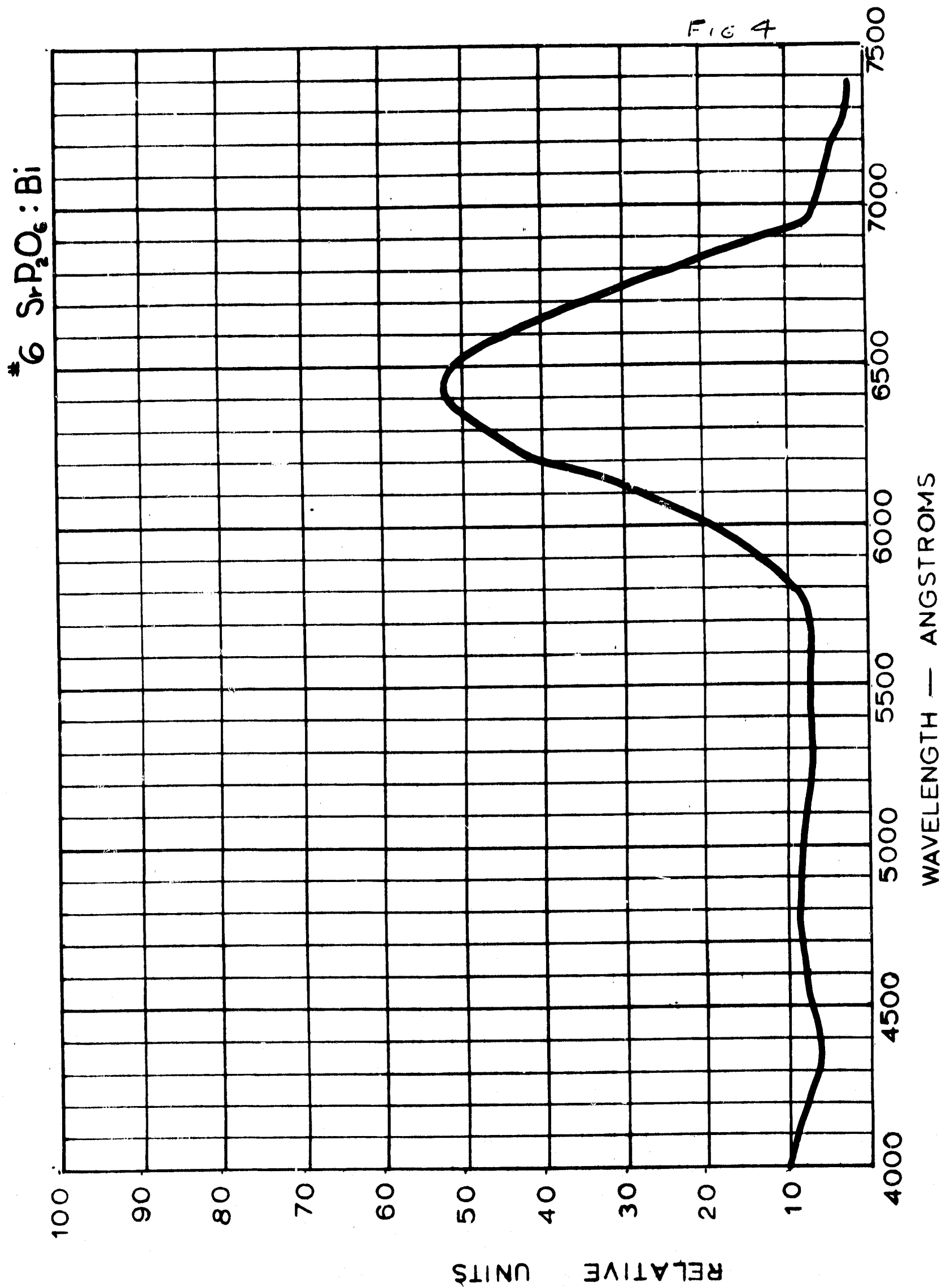
#4 $\text{Ca}_2\text{P}_2\text{O}_7\text{:Bi}$

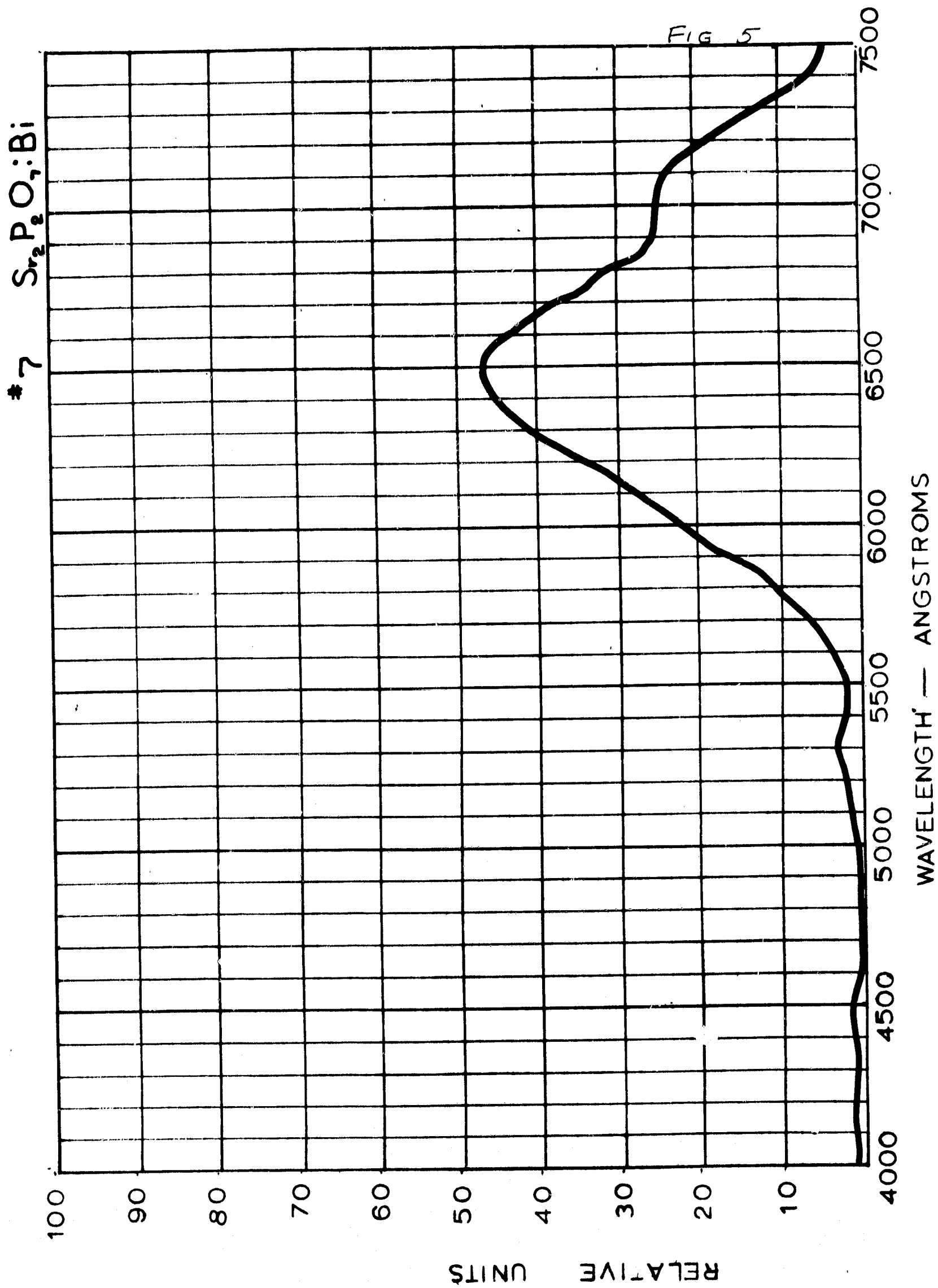
Fig 3



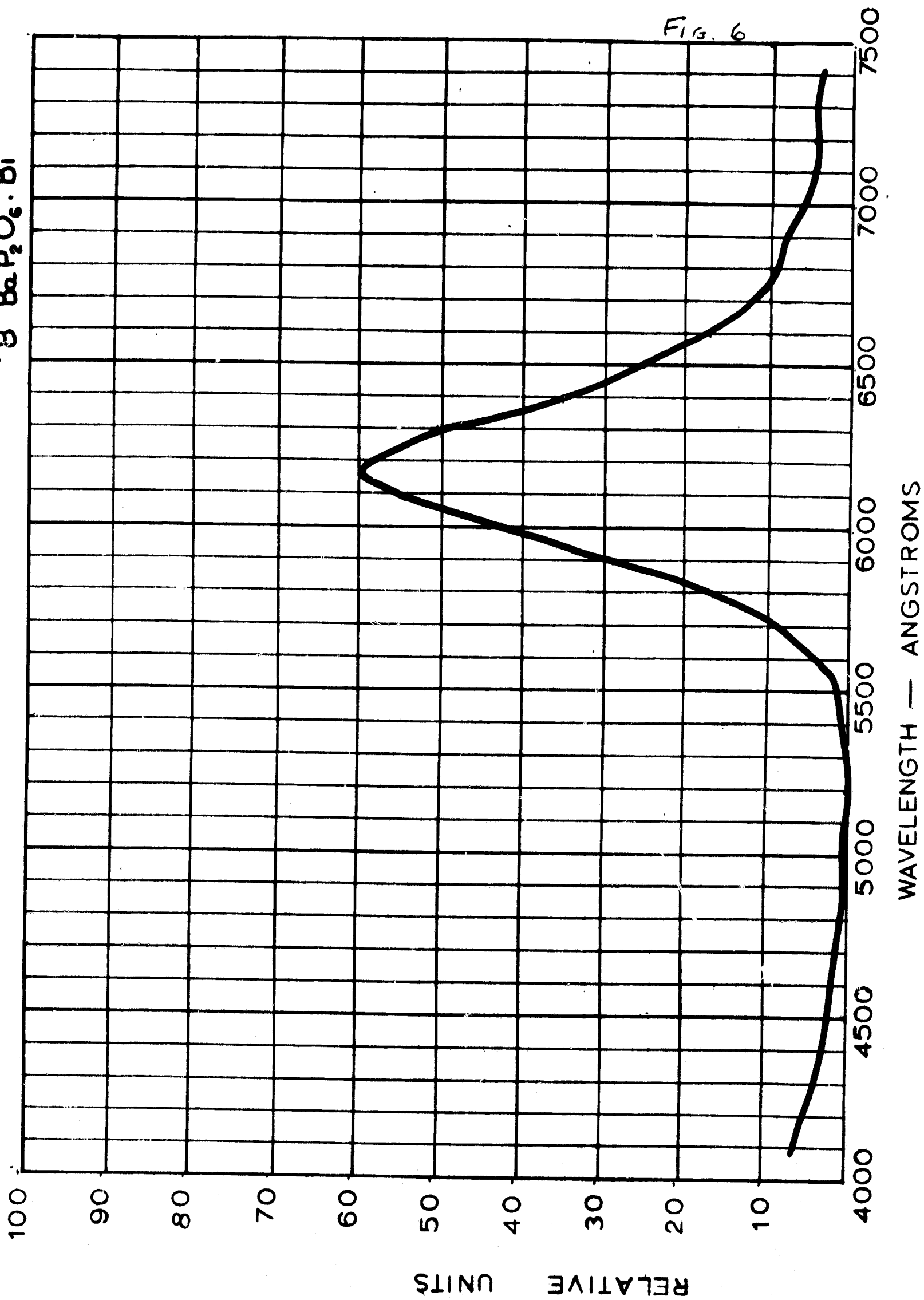
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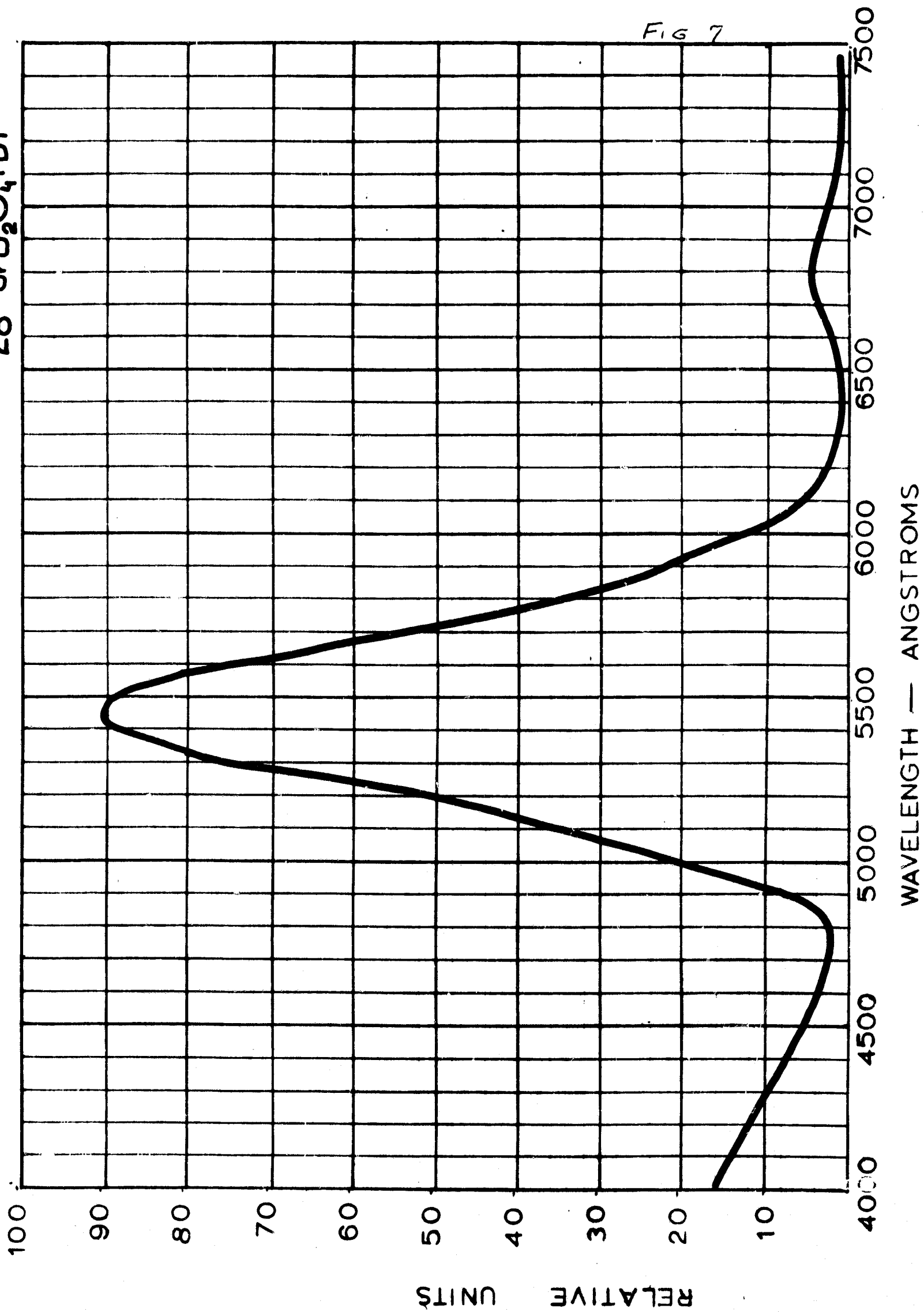


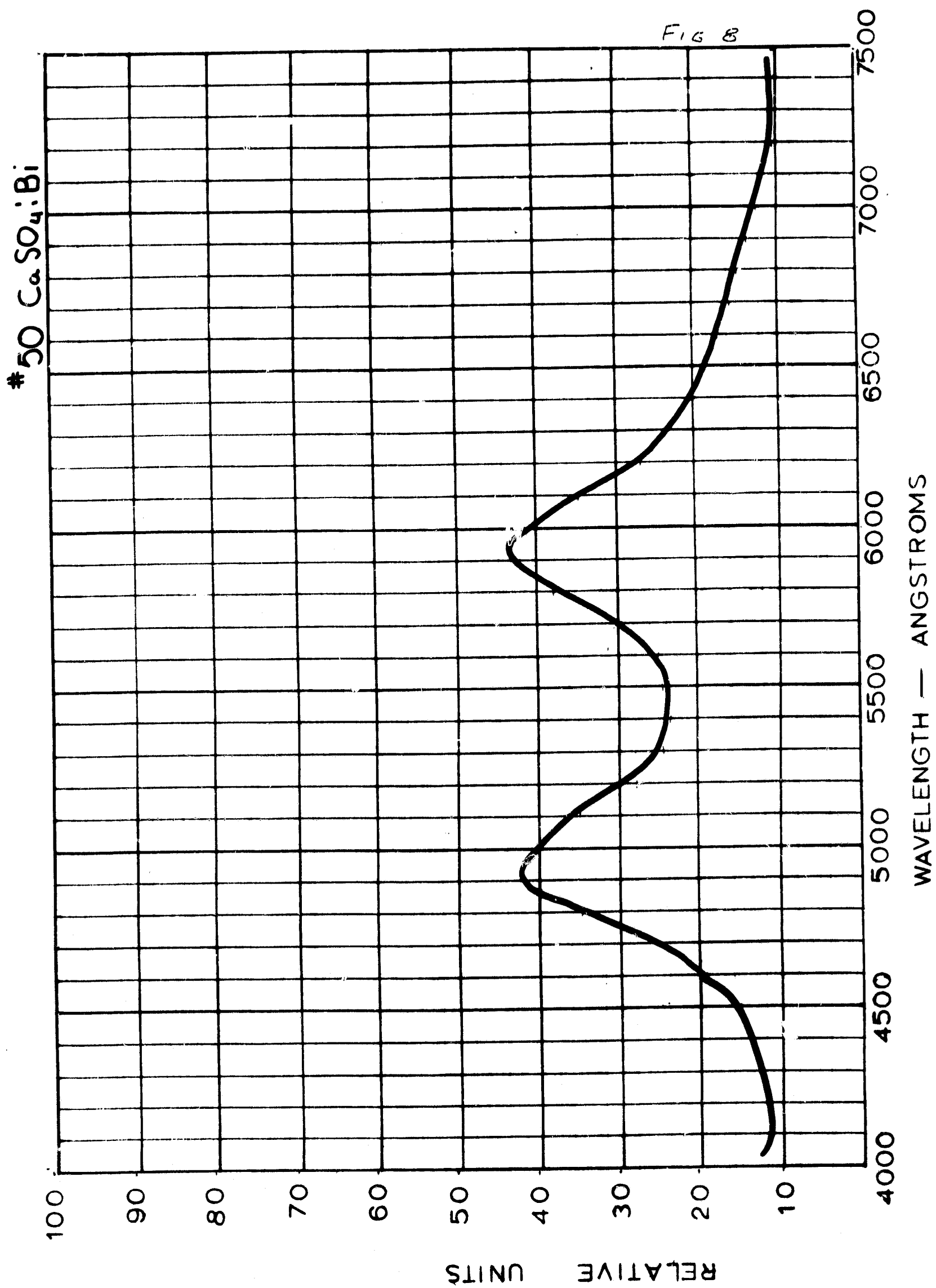
#3 BaP₂O₆:Bi

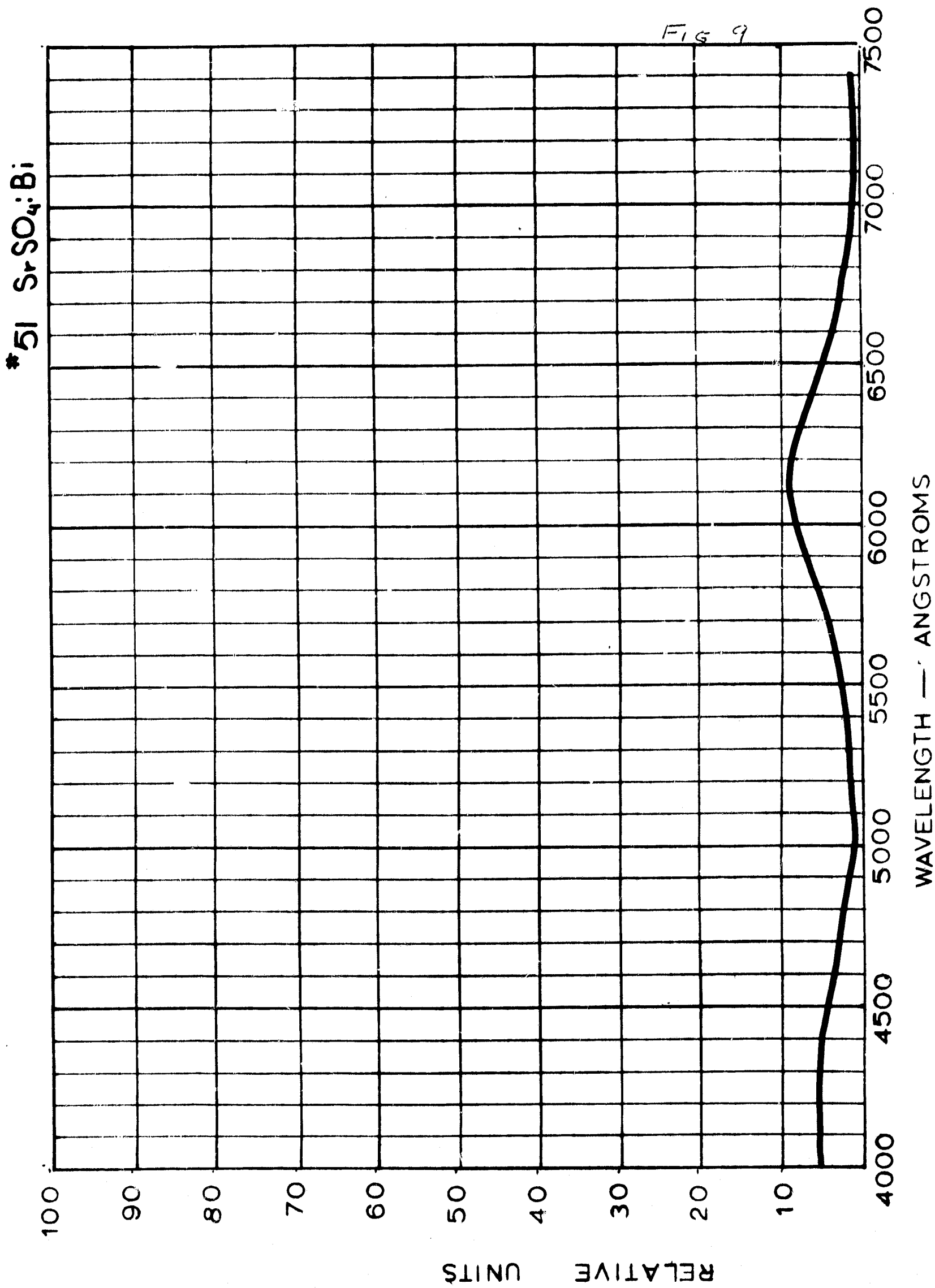


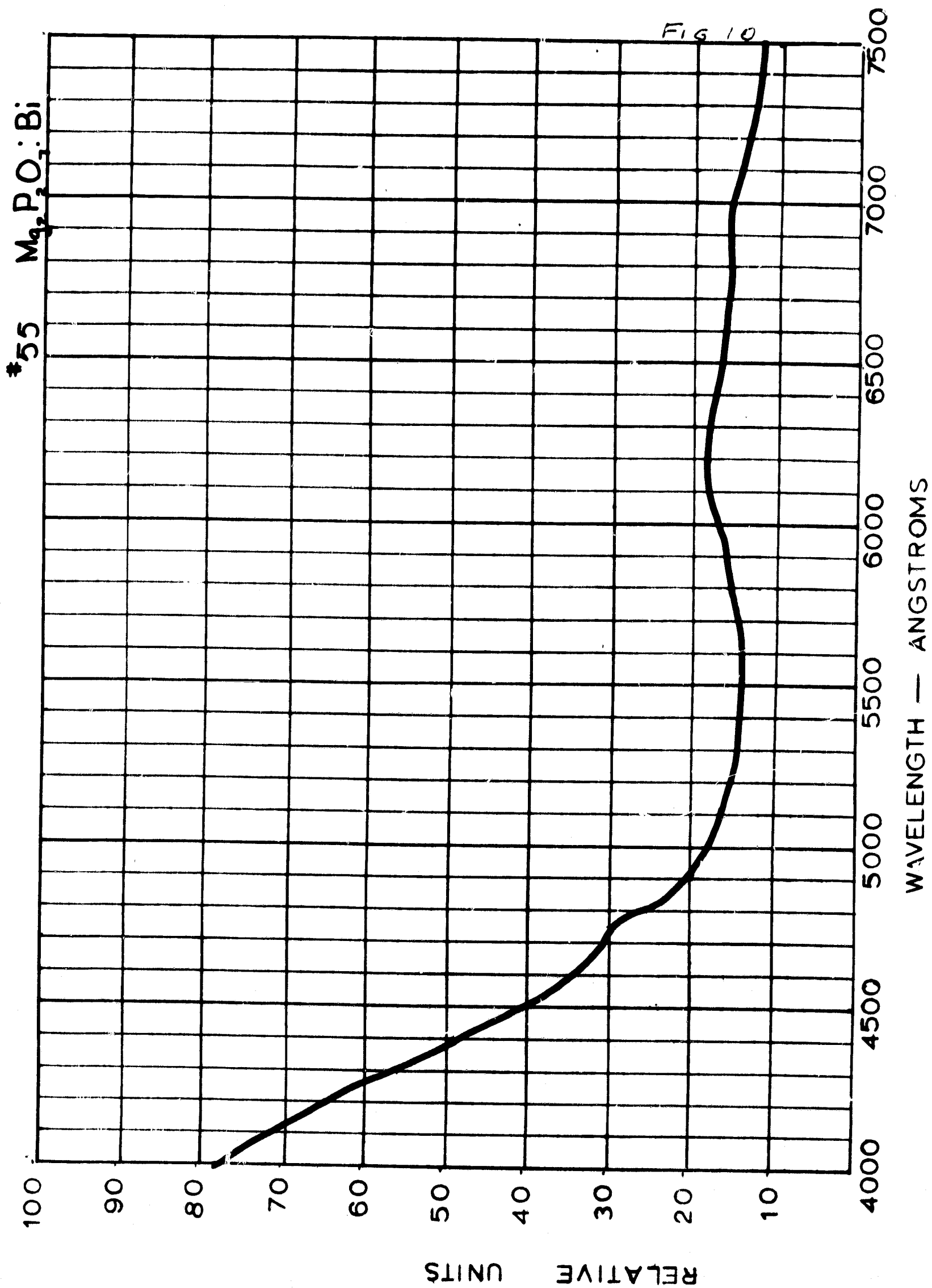
#28 $\text{SrB}_2\text{O}_4:\text{Bi}$

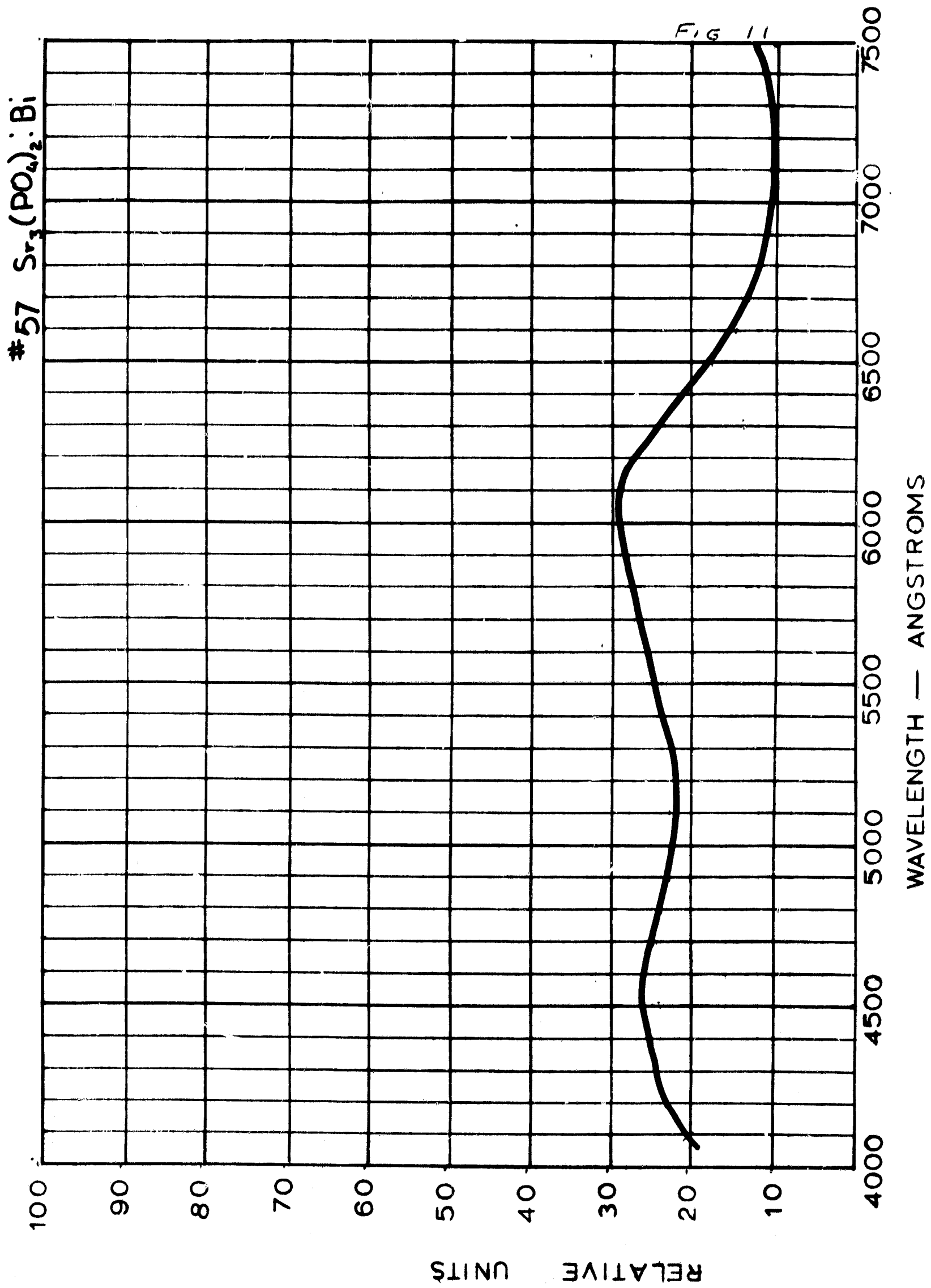
FIG 7

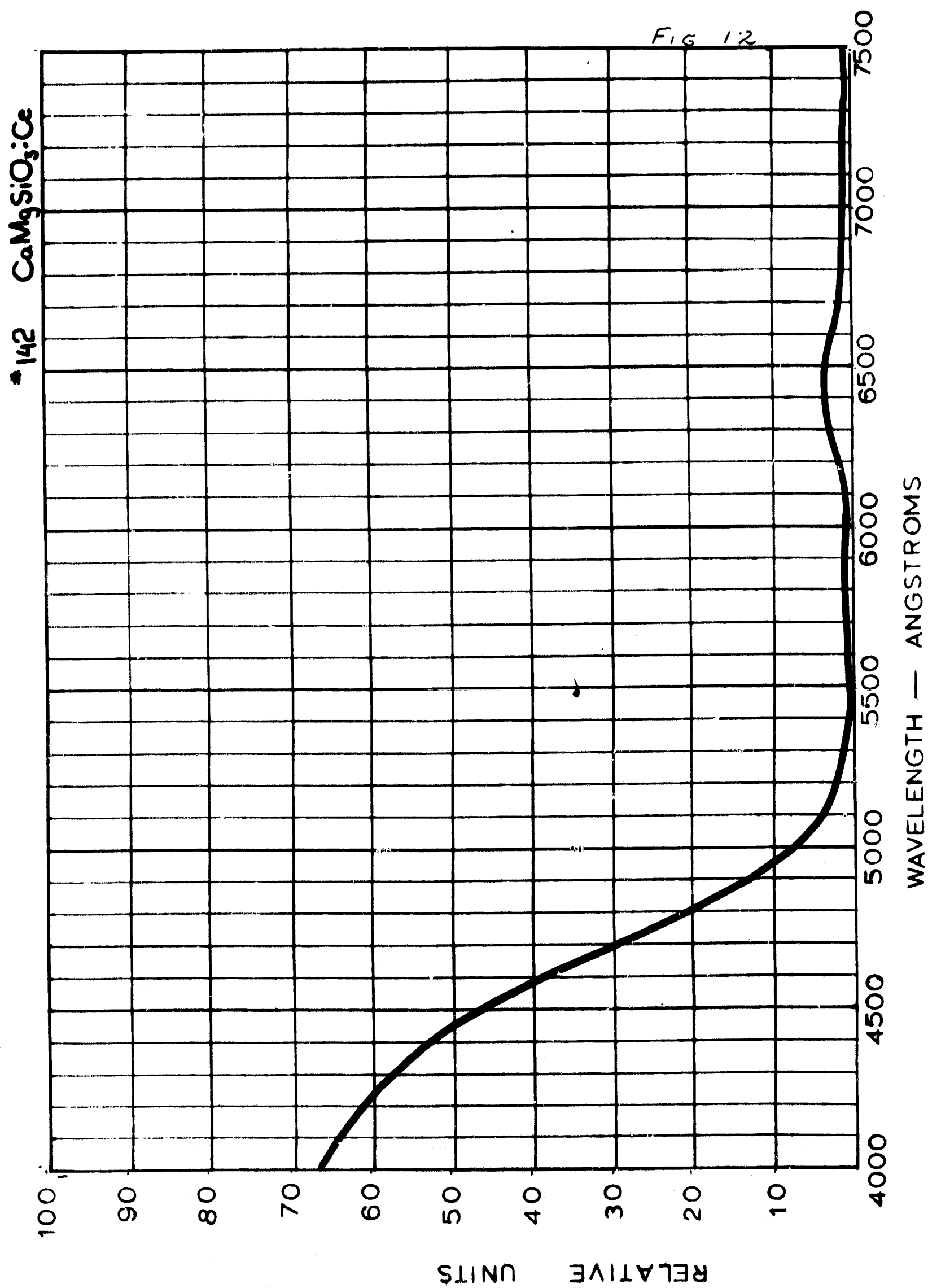






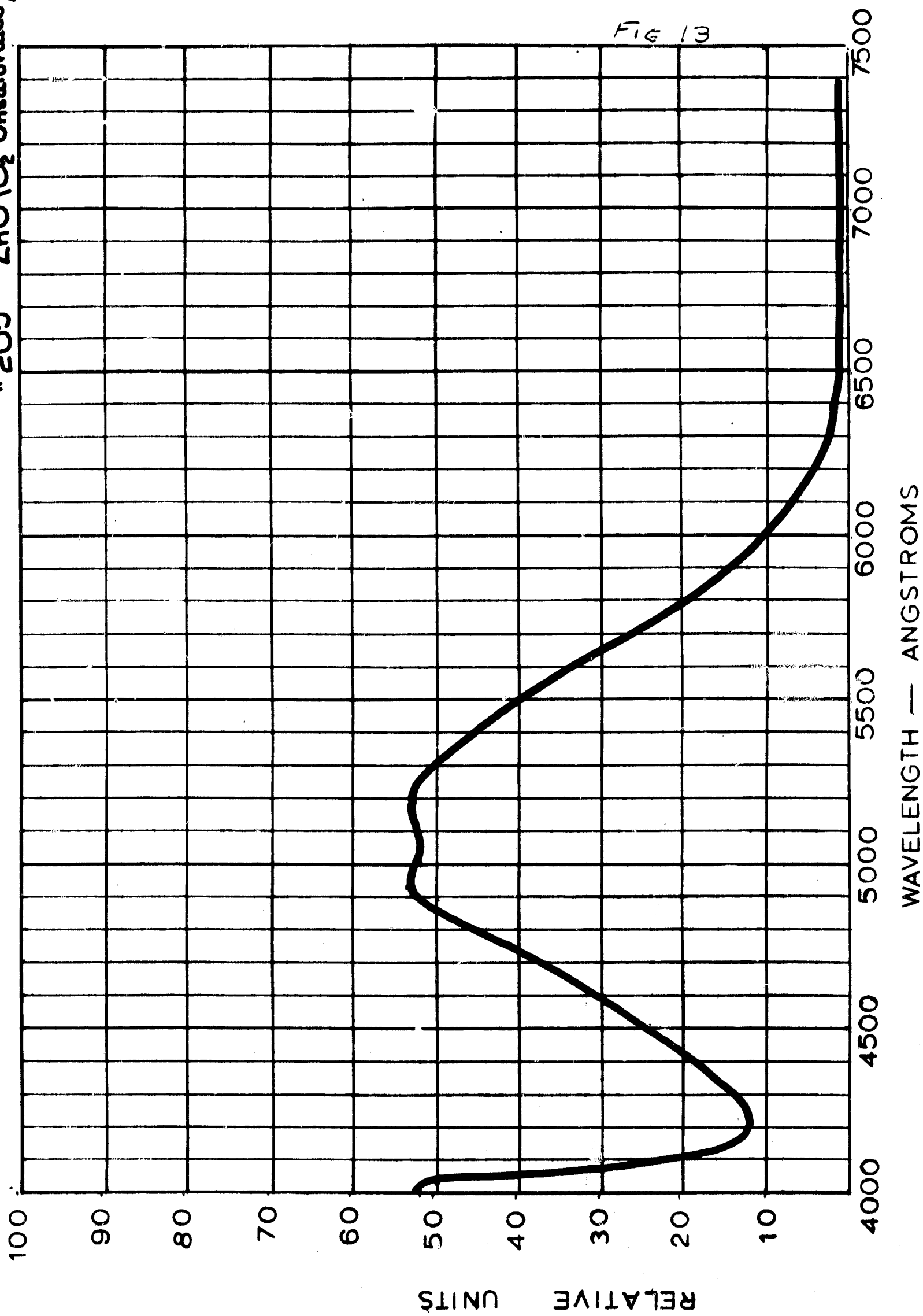


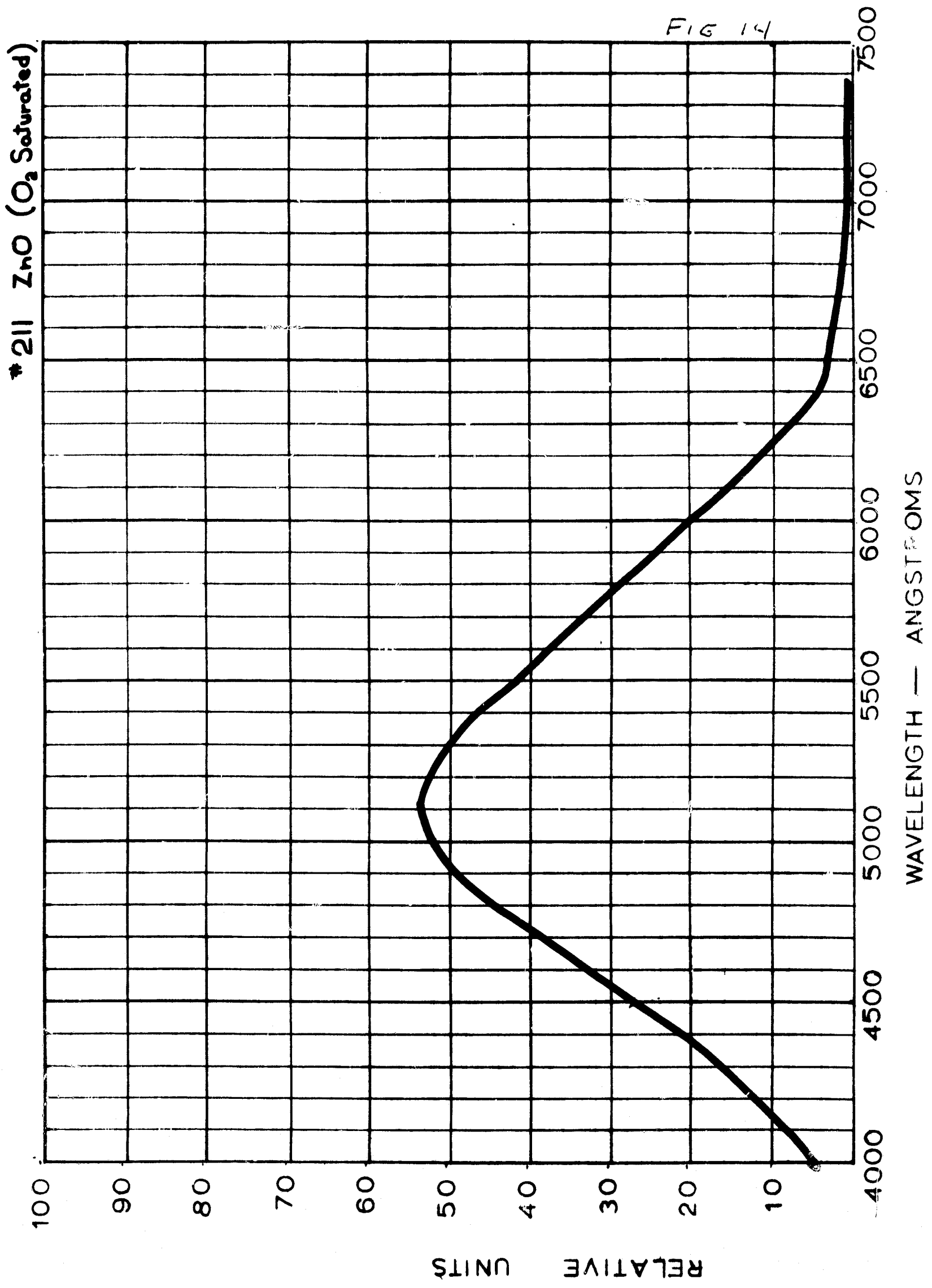




#205 ZnO (O₂ Unsaturated)

FIG 13





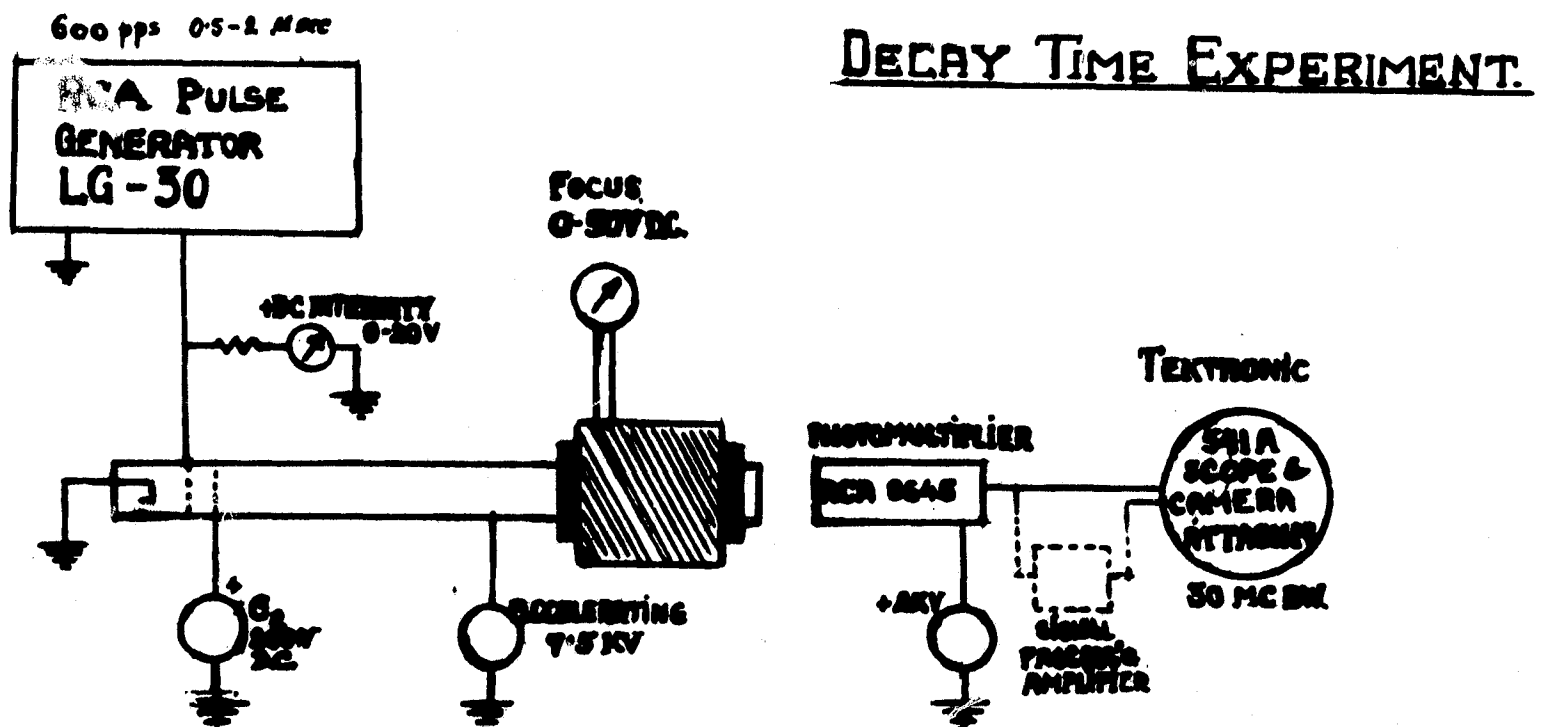
two, Fig. 10 and Fig. 11 are of little interest except to show where in the progressive shift of the periodic array of atoms, the emission has shifted to the blue end of the spectrum.

The remaining curves are of the transparent films. Fig. 12 of composition similar to P-16 has an emission very little different from a P-16 containing a small excess of Mg. Fig. 13 and Fig. 14 show simply that ZnO films can be obtained with emission similar to both powders P-15 and P-24.

B. Decay Measurements

Decay rates on the powdered samples were screened by Sigmatron and on this basis the samples were selected for putting into hard tubes to permit more accurate measurements by Dr. Hitt at the University of Detroit, utilizing the equipment shown in Fig. 15.

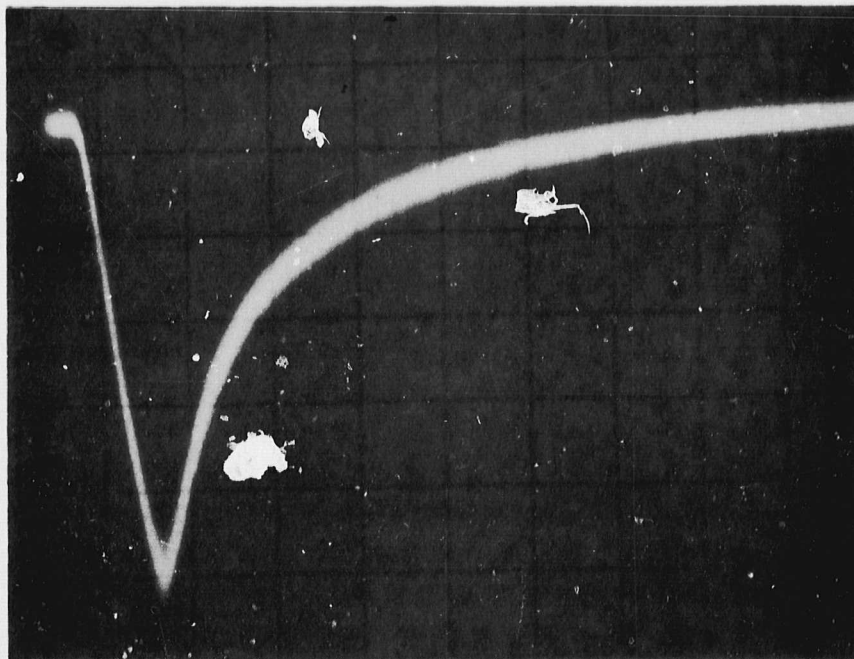
Fig. 15



The cathode ray tube used is PanAura's ultra high resolution tube which produces an electron beam with a spot size approaching 1/10 mil. The emission created by a pulsed signal was collected by a camera lens, focussed on a low noise photomultiplier and the signal observed on a scope. The correlation processing with the characteristics previously described could be introduced.

The samples which were accorded this treatment were the four powders, Samples 3, 4, 6 and 7 which were judged about equally useful on the basis of brightness and spectral response. The four phosphate powders had astonishingly similar decay rates ranging from 3 to 6 μ sec. The fastest is $\text{Sr}_2\text{P}_2\text{O}_7:\text{Bi}$, (Sigmatron Sample 7). Fig. 16 shows the decay without signal processing.

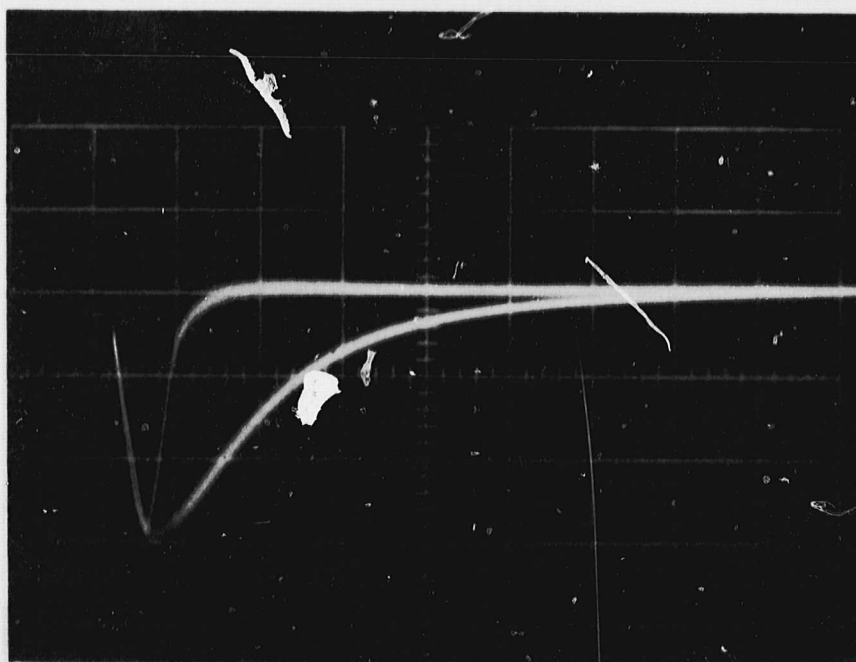
Fig. 16.



Decay Curve - $\text{Sr}_2\text{P}_2\text{O}_7:\text{Bi}$
Sweep Rate - 1 μ sec./cm.

The effect of the signal conditioning treatment using a delay line for autocorrelation is shown in Fig. 17. The bottom trace is the unprocessed decay curve as shown in the previous figure, except for a faster sweep rate. The top trace shows the effect of the signal processing. For this experiment a lens was added to the equipment shown in Fig. 15. The lens used was a conventional camera lens (Richoh 1:1.4) with a spacing that resulted in an approximate effective aperture of $F=1$. The tube was pulsed at 600 pp's and the pulsewidth of the delay line in the signal processing system is 700 nano sec.

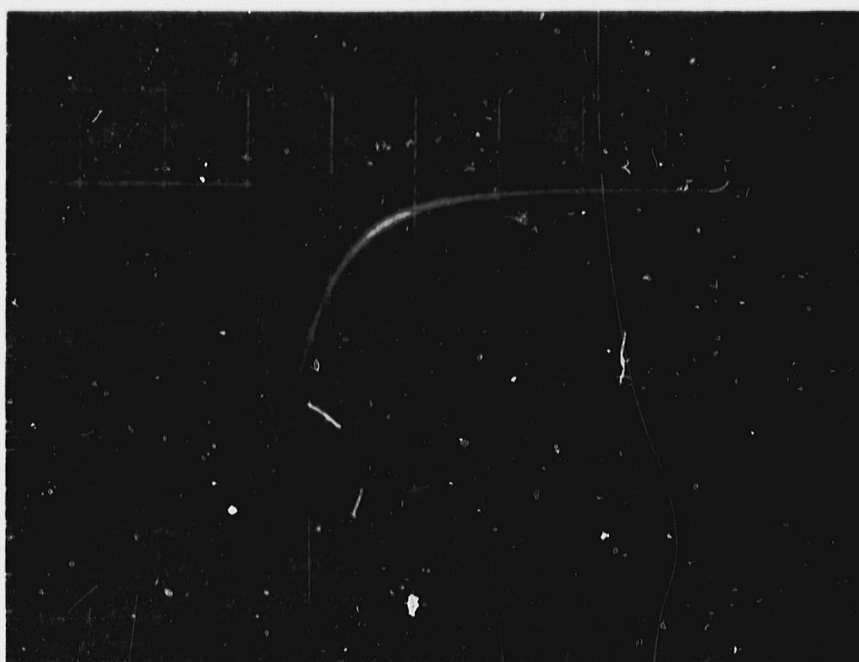
Fig. 17.



Decay Curves - $\text{Sr}_2\text{P}_2\text{O}_7:\text{Bi}$
Top Trace - Processed
Bottom Trace - Unprocessed
Sweep Rate - $2 \mu \text{ sec./cm.}$

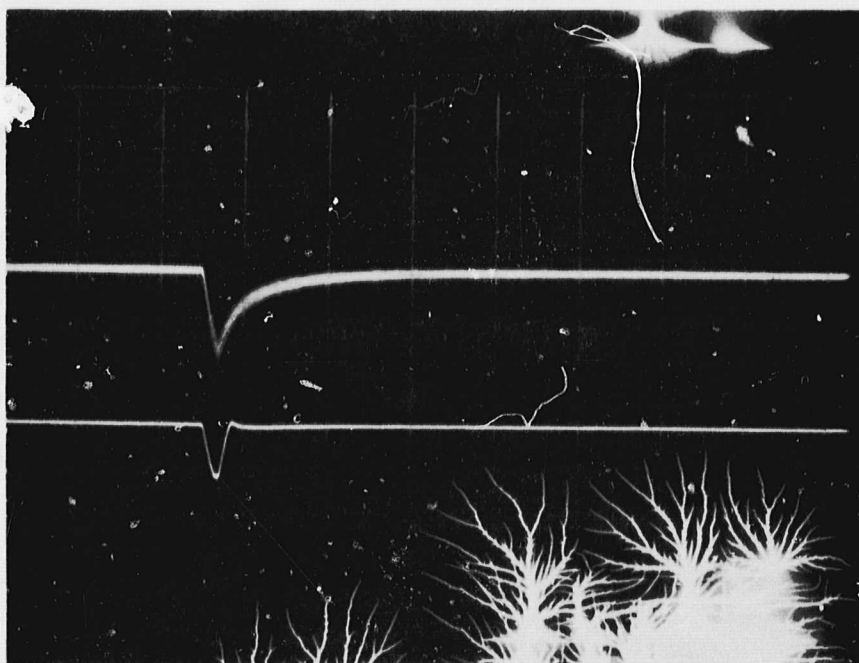
Transparent P-16 decay is shown unprocessed in Fig. 18 and the effect of the delay line correlation treatment is shown in Fig. 19.

Fig. 18.



Decay Curve - Transparent P-16
Sweep Rate - 5 μ sec./cm.

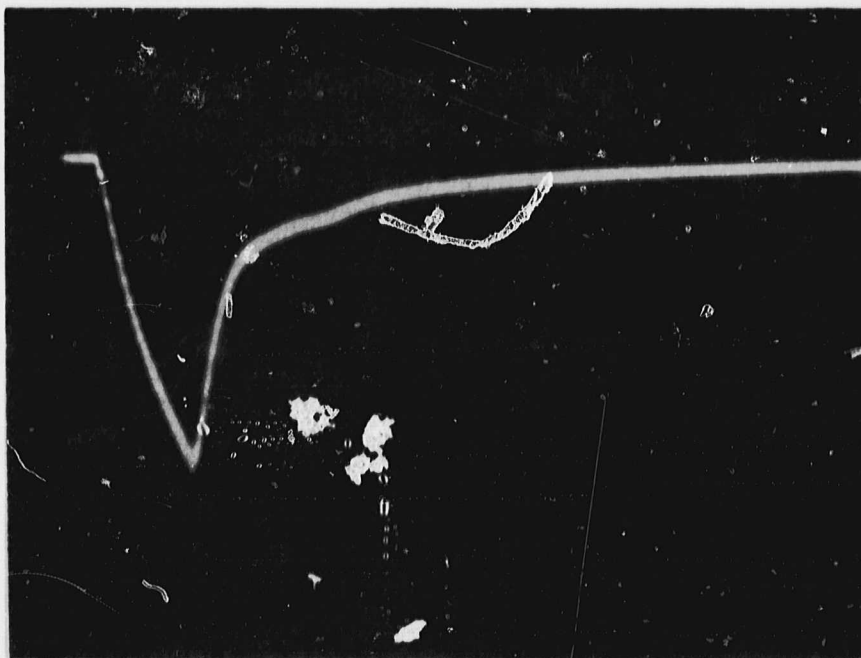
Fig. 19.



Decay Curves - Transparent P-16
Sweep Rate - 5 μ sec./cm.
(A) Unprocessed Signal
(B) Processed Signal

Transparent P-24 decay is shown in Fig. 20. Signal processing with the 700 nano sec. delay line had little effect on this short decay.

Fig. 20.



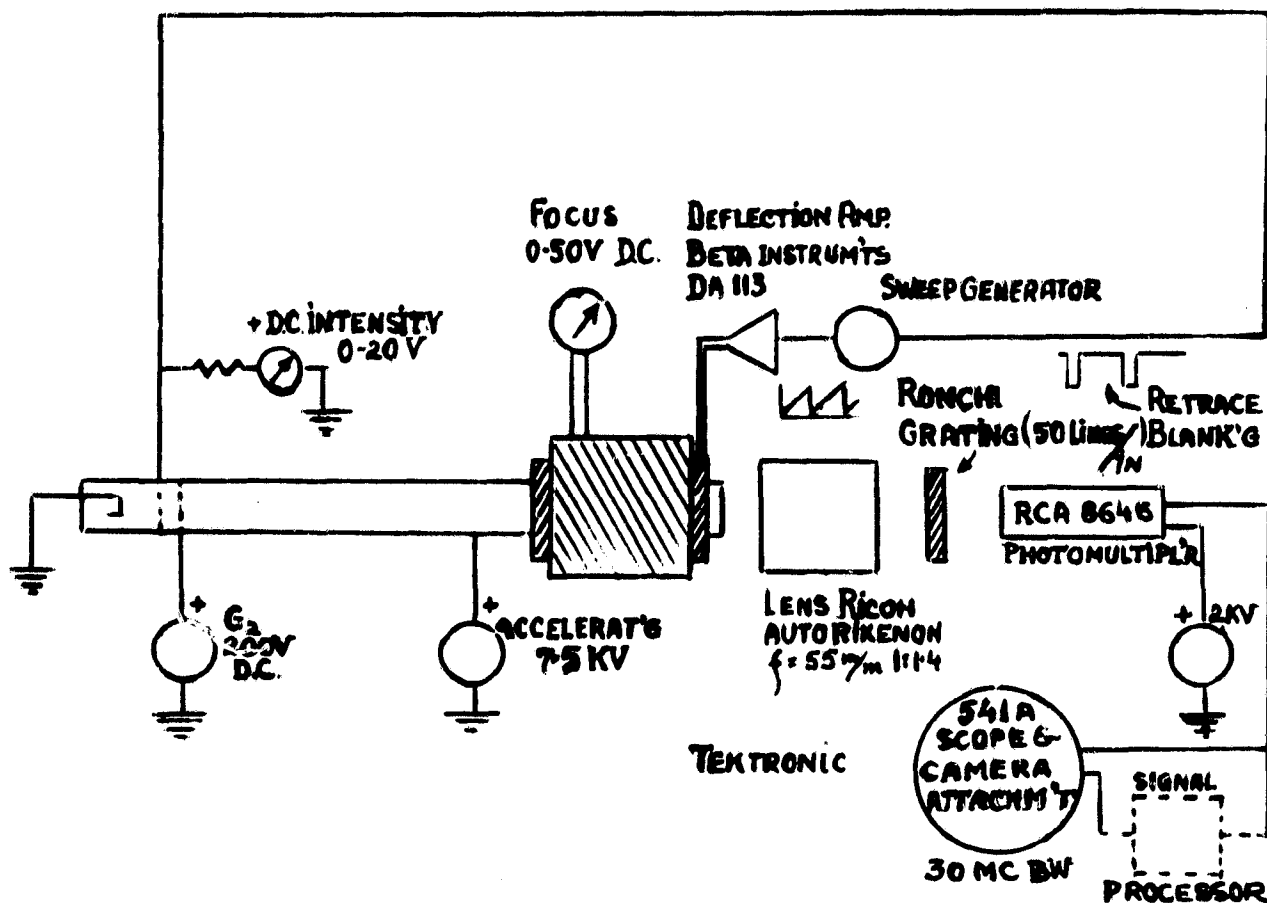
Decay Curve - Transparent P-24
Sweep Rate - $1 \mu \text{ sec./cm.}$

C. Signal-Noise Measurements

Signal-noise measurements suffered from equipment limitations to the point where their validity is doubtful. The principal reason is that the extremely tiny spot size and low voltage of the CR tube illuminated such a small volume of phosphor that the total light flux in the signal was extremely small. Moreover, the light tight box in which the measurements were conducted leaked at several points and provided a rather high background.

The equipment arrangement is shown in Fig. 21. A sweep generator deflected the tiny spot across the 1" face of the CR tube. The signal was collected by a camera lens and was interrupted by a Ronchi grating of fifty opaque stripes per inch, equal in size to the spaces; each bar and each space thus being ten mils wide.

Fig. 21



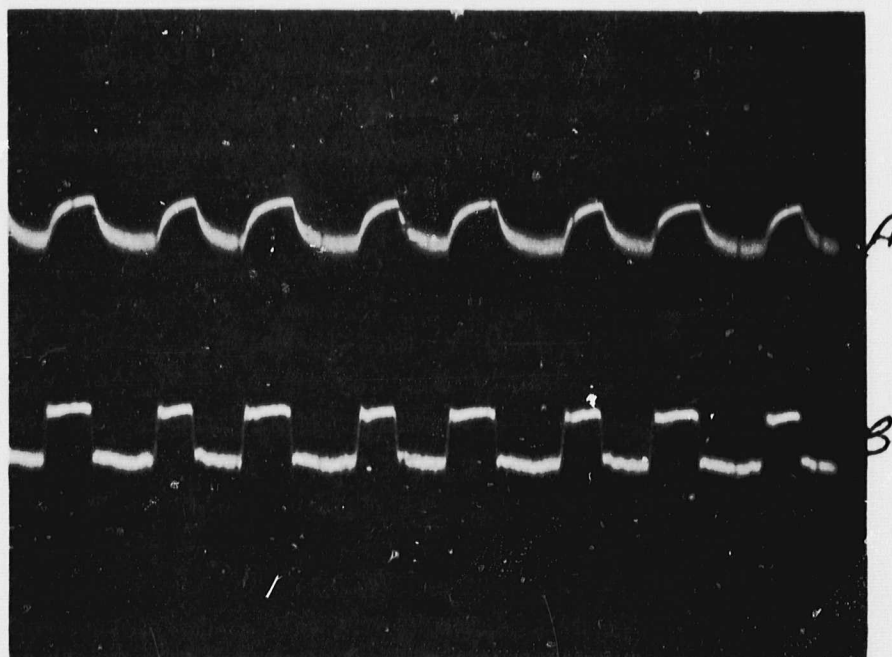
Signal-Noise Ratio Experiment

The powdered screen of $\text{Sr}_2\text{P}_2\text{O}_7:\text{Bi}$ produced screen noise comparable to the modulation from the Ronchi grating. Operating voltage was increased to 10 KV at which the beam size is close to 0.1 mil and the spot brightness is estimated at 30 ft. L. but the optical scatter among the phosphor grains was so high that the small bars and spaces of the Ronchi grating produced no measurable modulation of the signal reaching the photodetector.

Noise measurements on the ZnO (P-24) are not meaningful because of inadequate brightness. This film was extremely thin, and the accelerating voltage had therefore to be kept below 1200V to prevent the beam from penetrating into the glass substrate which emits a blue, slow decay luminescence. The spot size was about 0.2 mil and the total light flux reaching the detector was therefore not enough brighter than the background to produce a significant signal-noise ratio.

Measurements on the transparent P-16 shown in Fig. 22 are thus the only signal-to-noise measurements which are meaningful. The tube was operated at 4 KV with a spot size of about 0.15 mil and produced sufficient signal to get a little above the background noise. Also the decay rate is such that the signal conditioning is operative. Fig. 22 thus shows the results of optical modulation with the Ronchi grating with and without signal processing.

Fig. 22.



Signal-Noise - Transparent P-16
A. Unprocessed
B. Processed
Sweep Rate - $1 \mu \text{ sec./cm.}$
Effective Aperature - $F=2$

It is useful in this case to extrapolate to the level of signal-to-noise which might reasonably be expected in a perfected system, starting with the value of 5 or 6 to 1 that is shown in Fig. 21. The first obvious improvement would be in generating higher brightness from the tube. Brightness increases linearly with voltage in this operating range, and thicker films can be produced which would permit operation up to 20 KV. Higher brightness would thus increase the signal strength by a factor of five and because of the low screen noise of transparent screens, total noise would increase by no more than 5% of the signal increase. Signal-to-noise should, therefore, become 25 or 30 to 1 while maintaining the same small spot size.

So small a spot size is needed only for crowding 1000 lines into a $\frac{1}{4}$ " square raster. Most scanning systems operate with 1.5 mil spots, a factor of 100 increased area of lighted phosphor, which is 100 times increase in signal strength with no increase in the relative proportion of noise.

Thus, if the same optical efficiency as used in the test procedure can be maintained when using a 5 to 7" diameter tube, it is reasonable to expect a transparent P-16 screen, operating at 20 KV with a spot size of 1.5 mil to produce a signal-to-noise ratio better than 2000 to 1.

Similar extrapolations can be reasonably applied to the results that could be expected from thicker films of ZnO (P-24) based on the fact that the emission brightness of transparent P-24 is at least equal to transparent P-16. Thus 0.15 mil spots at 20 KV should produce signal-to-noise of 25 to 1 in ultra high resolution systems, and a

spot size of 1.5 mil should produce a signal-to-noise of 2500 in scan systems with conventional resolution.

Settled screens of the new red phosphors, even with the best settling techniques will not generate small enough spots of uniform brightness for an ultra high resolution system. Screen noise will be a limitation even with 1.5 mil spots. Phosphor burn of the red powders appears to be comparable to P-16 powders. For rapid scan systems the longer decay of the red can be clipped to produce less smear than the fastest P-16. Thus the new red powders can be expected to produce a signal-to-noise ratio in the red channel equal to that now obtained in the green channel with powdered P-24 or in the blue channel with powdered P-16.

V. Summary and Conclusions

(1) Phosphor Developments completed during the contract effort include:

a. A series of four related phosphor compositions in powdered form each with a saturated red emission and fairly rapid decay. Any one of the four is useful as is in scan systems of conventional spot size to produce a good signal in the red channel of a color scan system at moderate scan rates and in fast scan systems with the addition of signal processing. To be useful in ultra high resolution systems (0.1 to 0.2 mm spot size), it will be necessary to produce these phosphors in the form of transparent films, and the success of this step cannot at present be guaranteed.

b. Techniques were developed which for the first time produced ZnO phosphors with the spectral emission and decay characteristics of both P-15 and P-24

in the form of transparent films. The small spot size and low screen noise of these films can be utilized to convert systems now using these phosphors to ultra high resolution systems.

c. Techniques were developed for producing transparent films similar to but with slower decay than P-16 powders. The films are useful as is for converting present P-16 scan systems to ultra high resolution systems at moderate scan rates, or with signal conditioning to rapid scan systems. The probability of achieving, with additional effort, decay rates comparable to the powders is very high.

(2) Signal Processing

The autocorrelation approach to signal processing was shown to be adequate to eliminate the effect of smear from phosphor decay with phosphors with decays as long as several microseconds for use in 1000 line scan systems.

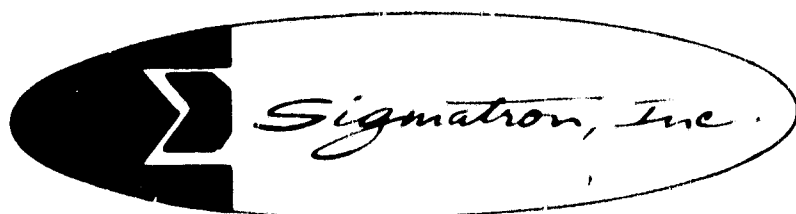
A combination of the foregoing achievements makes possible a color scan system with 500 to 700 line resolution and good signal-to-noise in all three channels, or it makes possible a monochrome scan system with 1000 line resolution in a small area with a very high signal-to-noise ratio.

Recommendations

The first obvious step toward taking advantage of the achievements of this effort is to upgrade the quality of present color scan systems. This requires only substituting a new CR tube for the one now employed and applying signal conditioning to the photodetection on the red channel. The new CR tube could presumably have the same geometry and electronic operating characteristics as the existing tube so that no modification of the driving circuits or the optical system would be required. The screen of the new CR tube would be a settled mixture of P-15 and the new red. P-15 provides a good blue signal with a very rapid decay ($0.1 \mu \text{ sec.}$) and a good green signal with a moderately fast decay ($0.8 \mu \text{ sec.}$). The new powder incorporated in the mixture would provide a good red signal with a slower decay which would be optically filtered from the other two color channels and smear in the red channel would be eliminated by signal conditioning. Thus a substantial improvement in the performance of the existing system should be achieved with relatively minor changes.

The second step indicated is to develop a high resolution, high signal-to-noise monochrome system. The basic approach to design of the electron gun is available; the necessary screen can be produced, and the technique for signal processing is known. A moderate amount of engineering of the driving circuits and of amplifying the processed signal would be required and possibly a new optical system.

The final stage of improvement, an ultra high resolution system with high signal-to-noise ratio in color will have to wait for the outcome of efforts to produce the new red phosphors in the form of transparent films.



DEVELOPMENT OF A FAST RED PHOSPHOR

1.0 INTRODUCTION

The work described below covers a thirteen week effort to develop a rapidly decaying red phosphor suitable to meet specific requirements in these properties and be applied to glass as a transparent thin film. These requirements are dictated by an application for such a film ultimately layered with other phosphors to result in a very high resolution flying spot scanner tube screen wherein colors are selectively excited by electron beam penetration. Normally the super position of thin films of most phosphors which have counterparts in the bulk powders can be classified as an extended exercise (the results of which are usually at some slight variance to the bulk phosphor properties). In this case, however, a red phosphor is not known which has a sufficiently fast emission decay rate; such a decay rate requirement being the order of 0.1 microseconds to 10% initial brightness. Reasonably satisfactory phosphors do exist for the other required colors. This program then becomes one in which a search is first launched to produce new red phosphors, measure their pertinent properties, make films of the most likely candidates and measure their properties. On a hit-or-miss basis this would be a prodigious task. The task is considerably narrowed through the consulting aid of Professor F. A. Kroeger, an outstanding phosphor expert, and the combined thin film experiences of Pan Aura and Sigmatron.

2.0 PROGRAM

Through the guidance of Professor Kroeger, and based to a large



extent on some previous work by him, promising phosphors might be afforded through bismuth activation of host materials of the alkaline earth and mixed alkaline earth - alkali metals of phosphates, borate, and the alkaline earth compounds of arsenated, antimonates, aluminates and sulphates. ⁽¹⁾ Although the decay rates are influenced to perhaps a factor of ten by the extremes of permissible concentration in structure due to different phases and defect density such sophistications would be beyond this exploration. Briefly, the bulk phosphor effort involved quickly producing and screening a large number of phosphors. The preliminary screening evaluation consisted of tesla coil excitation in vacuum of the reacted cake retained in the boat and the ground powder adhered to tape. In addition, the cake was exposed to long and short wave ultraviolet light. It turned out that these tests were good for indicating incomplete reaction or alumina boat contamination. When either was apparent or the charge was inadvertently melted, the material was remade. Materials which look promising were electron bombarded in a demountable CRT and the color and emission decay measured. Representative materials of the promising phosphors were selected and attempts made to form films in vacuum. Thermal evaporation and a modified R-F sputtering were the vacuum techniques employed. Data resulting from this program is described briefly later and tabulated at the end of this report. Described below are the more important details of the preparations and measurements.

2.1 Bulk Phosphor Preparation

The phosphors were prepared by mixing the dry components

(1) F.A. Kroeger, et al. 96, 3, p. 132, J. Electrochem. Soc., 1949.



and then adding the activator in solution form. The metallic components of the phosphors were introduced as carbonates. The bismuth activator was introduced in solution as 1×10^{-3} gram atoms bismuth per mole phosphor. To keep the batch size small 0.03 mole batches were prepared. All component chemicals were reagent C. P. grade. The bismuth activator solution was made from the oxide and nitric acid which had to be made fresh each day due to precipitation of a hydrate. The weighed components were ground to a fine mix in a mortar and pestle after which the proper volume of activator solution was added. If this mixture was too dry to result in a fine paste on further grinding, distilled water was added to facilitate this wet grinding. Subsequently the ground paste was transferred to a drying or firing vessel. Two methods were used for reacting the phosphor materials.

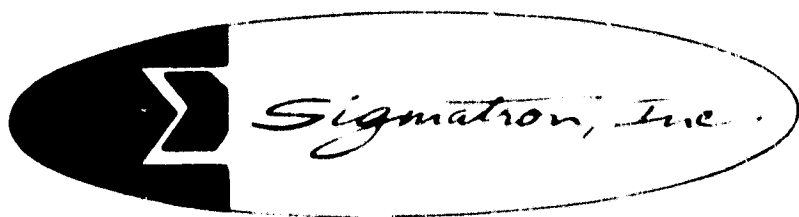
Case I.

1. Mix placed in type R A84 alundum combustion boat.
Use 2nd boat for cover.
2. Material dried for 1 hour at 150°C .
3. Raise temperature to 600°C for 1 hour.
4. Sinter at temperature for one hour. See tables for sintering temperature.
5. Cool in place to 400°C .

Case II.

This approach was the same as Case I except the wet mix was dried in a pyrex beaker then transferred to a alundum boat for remainder of firing. The technique is preferable as it minimized contamination from the boat.

Employing these techniques, sixty-one batches of phosphor were prepared of forty-eight compositions.



2.2 CRT Test Screen Preparation

Test screens were prepared using interesting phosphors by sintering or binding the powders to conductive tin oxide coated micro-sheet glass. In some cases dilute acids, such as phosphoric for phosphates or sulphuric for sulphates was used to cake dusted powder to the glass. In other cases a 1% solution of glyptal solution bonded the powders without noticeable vacuum outgassing or other interference.

2.3 Thin Film Phosphors Preparation

Attempts were made to deposit thin films in vacuum or four phosphate phosphors and the one borate phosphor which had shown red luminescence. Some of these thermal evaporations were several times with tungsten, platinum, iridium and tantalum boats. Boat materials can effect the degree of chemical dissociation of the evaporant. The vapors were received on glass substrates whose temperature in vacuum was controllable. When dissociation and or fractionation during evaporation was observed a technique was employed where many small quantities were evaporated to completion through a vibro-feed device.

Dielectric materials can be sputtered by alternately bombarding a source surface of the dielectric material alternately with ions and electrons from a plasma. RF alternating fields of several thousand volts are required for this technique and 1 megahertz induction heater was modified to attempt this type of sputtering from a sinter calcium phosphate electrode. It was not possible to obtain films with this equipment due to (a) inability to match impedance thus limiting the power available to the plasma and (b) low frequency; others using this technique find frequencies of 10 and 25 megahertz are required.



2.4 Color Measurement

The bonded powder phosphor screens described above were received in a demountable CRT evacuated through the test port of a Veeco Leak Detector. Such a vacuum system provided the mobility required for exposing the excited phosphor close to a window in the integrating sphere of a Beckman DK-2A Recording Spectrophotometer. Attempts were made to make rough intrinsic brightness measurements by replacing the phosphor with standard light sources at the integrating sphere. This was more complex than initially anticipated and shortly abandoned. To develop a confidence in the spectral measurements however, the red phosphor P-22 was incorporated among the series. The results correlated with published data. The brightnesses of the phosphors was generally low and our means for driving them inefficient which required operating the equipment at maximum sensitivity. This resulted in a high noise to signal ratio and a puzzling periodicity which is apparent in the curves. The data however is included and felt to be representative.

2.5 Emission Decay Measurements

The same demountable CRT and mobile vacuum system described above was rearranged to receive a PM-EMI 9502 photomultiplier. Within the tube a metal mask was interposed to intercept the cathode ray everywhere except at a photo etched slot 0.015 wide and 0.100 in. long. The sweep of an expanded raster past this hole bombarded the phosphor and provided the pulses of light whose emission decay was to be measured. The output of the detector was displayed and photographed on a Tektronix 545A oscilloscope.

The emission decay equipment was used to measure the decay characteristics of the seven interesting prepared phosphors. To build confidence in the measurements, a standard P-2 phosphor and measurements



of a discharge lamp (General Radio Strobtae Type 1531-A) were included in the series. It was generally concluded that the basic time constant for this system was close to 10 μ sec. for an ideal light pulse. The excitation technique was much less than ideal however, and only in the brightest phosphors was this resolution approached. Since these measurements were to provide rough screening for subsequent more sophisticated measurements, no attempt was made to further refine the technique.

3.0 Results

Described below are the results of the screening tests on sixty-one phosphor preparations of forty-four compositions. The extra preparations were undertaken when the first results were considered unsatisfactory.

3.1 Phosphor-Screening Tests

Tables 1a, 1b, 1c, and 1d show the results of the tesla coil, and UV excitations. All of the phosphates showed some luminescence to ion/electron bombardment and no significant luminescence to UV. Those considered suitable for further examination were the meta phosphates of calcium and strontium, and the tri strontium phosphate. In the Table 1 series, these are sample numbers, 3, 4, 6, 7, 8, 55, and 57.

Table 2 lists the results of screening tests applied to the arsenate compounds. No luminescence was evident for any of the compounds.

Tables 3 and 3b show a summary of the results of the borate phosphor tests. Of these preparations, only strontium borate, sample number 28 luminesced red to the tesla coil. (Sample number 28 was refired at a higher temperature later to become number 61). The strontium borate was selected for further testing. Eight other borate compounds were found to



emit in the blue under the tesla coil and two of these responded to UV excitation.

The sulphate phosphors all luminesce to some extent with the tesla coil but show no response to UV. A summary of these is shown in Table 4. Calcium and strontium sulphates were considered the only phosphors worth further testing here.

Some concern was felt that just the proper phosphor sought would be overlooked within this series as a result of firing at too low a temperature. Table 5 shows those phosphors reground and refired at higher temperatures. No important changes were noted except that magnesium arsenate; sample number 58 showed faint red luminescence by the tesla coil.

3.2 Vapor Deposition

Thin films formed by vapor deposition of the phosphates and the borate were attempted with the following results:

- a. Chemical reaction with the source boat occurred in every case. Tungsten, platinum, tantalum and iridium boats were used.
- b. The vapor deposition of the phosphates resulted in a deliquescent film on the substrate and a residue in the boat. If a post heat treatment of 800°C is applied without exposure to moisture, a hard non deliquescent film results.
- c. Strontium borate was evaporated from an iridium boat which yielded a durable film without post heat treatment, but a residue remained in the boat.
- d. No films resulting from the work exhibited any luminescence to the tesla coil excitation.



3.3 Phosphor Color and Emission Decay

Tables 7a and 7b summarize the results of spectrophotometer and emission decay characteristics of ten of the prepared phosphors and three standards. Most of the phosphors had a single peak in the red. Exceptions were noted for sample numbers 7, 28, 50 and 57. In the case of number 28 this phosphor changed color in CRT bombardment not observed in the tesla coil excitation. The two peaks were generated in the change. Sample number 55, magnesium pyrophosphate was strangely red when bombarded from the tesla coil and violet (4000A) in the CRT.

Calculated emission decay times shown in the table cannot be interpreted other than being of the order of 10u sec. to which all apparently qualify.

4.0 SUMMARY

During this program forty-eight phosphors were compounded from the bismuth activation of the alkali metal and alkali earth metal phosphates, arsenates, borates, and sulphates. Screening of these resulted in eight phosphates, one borate and two sulfates which luminesce red. The color peaks of the light emitted were measured during electron bombardment of the powdered phosphors in a demountable CRT. An attempt was made to measure the emission decay characteristics of each but time constant of the equipment was too long. Nine of the tested phosphors appeared to have emission decay to 10% in 10 to 50u sec. Formation of films of any of these materials was not possible by thermal evaporation in vacuum due to the thermal decomposition resulting from the high temperatures required and phosphor reaction with the boat materials. R.F. sputtering seems more promising.

Bulk Phosphor (Phosphates)

No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U.V. Long	U.V. Short	
1	CaP ₂ O ₆ :Bi (Meta) Batch 1		Red	No	No	Mat'l. white with gray crust.
2	CaP ₂ O ₆ :Bi (Meta) Batch 2	1050	Red Blue	No	No	Mat'l melted, therefore, fired to hot
3	CaP ₂ O ₆ :Bi (Meta) Batch 3	850	Red Blue	No	No	Mat'l gray-white, Homogeneous
4	CaP ₂ O ₇ :Bi B(Pyro)		Red Fuchsia	No	No	Mat'l white, Homogeneous
5	SrP ₂ O ₆ :Bi (Meta)	1050	Red Blue	No	No	Mat'l melted, therefore fired to hot
6	SrP ₂ O ₆ :Bi (Meta)	850	Red	No	No	Mat'l gray, Homogeneous
7	Sr ₂ P ₂ O ₇ :Bi B(Pyro)	850	Red Blue	No	No	Mat'l white, homogeneous
8	BaP ₂ O ₇ :Bi (Meta)	850	Pink	No	No	Mat'l white, homogeneous

Table 1a.

Bulk Phosphor (Phosphates Cont.)

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No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
9	$\text{Ba}_2\text{P}_2\text{O}_7\text{:Bi}$ (Pyro)	1050	Light-Blue (weak)	No	No	Mat'l white, homogeneous
10	$\text{MgP}_2\text{O}_6\text{:Bi}$ (Meta)	850	Red Blue Weak	No	No	Mat'l white-gray, fluorescence in center of mat'l only.
11	$\text{Mg}_2\text{P}_2\text{O}_7\text{:Bi}$ (Pyro)	850	Red Blue	White one spot	No	Mat'l white with gray areas. Not homogeneous. Fluorescence in white area only.

Table 1b.

Bulk Phosphor (Mixed Phosphates)

No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
12	LiCaPO ₄ :Bi	850	Red (Weak) Brighter Near boat	Pink and White	No	Mat'l white with yellow tint
13	LiSrPO ₄ :Bi	350	No	No	No	Mat'l very light blue, yellow residue on boat
14	LiBaPO ₄ :Bi	850	No	No	No	Mat'l Black and white mixture
15	NaCaPO ₄ :Bi	850	Red next to boat	No	No	Mat'l white, homogeneous
16	NaSrPO ₄ :Bi	850	Faint Red in big pieces	No	No	Mat'l light green, homogeneous
17	NaBaPO ₄ :Bi	850	No	No	No	Mat'l gray, homogeneous
18	KCaPO ₄ :Bi	850	Red next to boat. one green spot.	No	No	Mat'l white with spots of light yellow
19	KSrPO ₄ :Bi	850	No except faint red in one spot	No	No	Mat'l very light green. Mat'l reacted with boat

Table 1c.

Bulk Phosphor (Mixed Phosphates Cont. and Tri-Phosphates)

No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
20	$\text{KBaPO}_4\text{:Bi}$	850	No	No	No	Mat'l off white, homogeneous
21	$\text{Mg}_3(\text{PO}_4)_2\text{:Bi}$	850	Red in spots (weak)	No	No	Mat'l brown with white crust. Not homogeneous
22	$\text{Ca}_3(\text{PO}_4)_2\text{:Bi}$	850	Red (Strong)	White		Mat'l white, Fluorescence not uniform, i.e., a thin layer on surface of mat'l will fluoresce & remainder does not. Note: This sample will be reground, mixed with water & refired.
23	$\text{Sr}_3(\text{PO}_4)_2\text{:Bi}$	850	Red Strong next to boat	No	No	Mat'l white, yellow ring next to boat. Not Homogeneous
24	$\text{Ba}_3(\text{PO}_4)_2\text{:Bi}$	850	Blue	No	No	Mat'l white, homogeneous
25	$\text{Ca}_3(\text{PO}_4)_2\text{:Bi}$	850	Scattered Red Spots	No	No	Phosphor #25 is #22 which was ground & mixed with H_2O in a beaker. The H_2O was driven off at 100°C. Mat'l transferred to a lundum boat & fired @850°C for 2 hrs.

Table 1d.

Bulk Phosphor (Arsenates)

No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
41	$\text{Mg}_3(\text{AsO}_4)_2$: Bi	900	No	No	No	Mat'l white with pink tint
42	$\text{Ca}_3(\text{AsO}_4)_2$: Bi	900	No	No	No	Mat'l white, homogeneous
43	$\text{Sr}_3(\text{AsO}_4)_2$: Bi	900	No	No	No	Mat'l white, homogeneous
44	$\text{Ba}_3(\text{AsO}_4)_2$: Bi	900	No	No	No	Mat'l white, homogeneous

Table 2.

Bulk Phosphor (Borates & Mixed Borates)

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No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
26	MgB ₂ O ₄ :Bi	900	No	No	No	Mat'l white, homogeneous
27	CaB ₂ O ₄ :Bi	900	Light Blue	No	No	Mat'l white, homogeneous
28	SrB ₂ O ₄ :Bi	900	Red (Rose weak)	No	No	Mat'l white, homogeneous
29	BaB ₂ O ₄ :Bi	900	No	No	No	Mat'l white, homogeneous
30	LiCaBO ₃ :Bi	900	No	White	No	Mat'l white with gray residue next to boat. Appears to have reacted with boat.
31	LiSrBO ₃ :Bi	900	Blue one small area	Blue (Strong)	No	Mat'l white with yellow next to boat. Not homogeneous.
32	LiBaBO ₃ :Bi	900	No	No	No	Mat'l white with black streaks, reacted with boat.
33	NaCaBO ₃	900	Light Blue	No	No	Mat'l white, not homogeneous

Table 3a.

Bulk Phosphor (Mixed Borates, Cont.)

No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
34	NaSrBO ₃ :Bi	900	No	No	No	Mat'l gray
35	KCaBO ₃ :Bi	900	Light Blue spots in white area	No	No	Mat'l dark gray with white next to boat. Not homogeneous
36	KSrBO ₃ :Bi	900	Light Blue	Spots of blue	No	Mat'l white with a few green areas. Boat cracked, not homogeneous
37	KBaBO ₃ :Bi	900	Light blue on white area only	No	No	Mat'l gray with white next to boat. Boat cracked Not homogeneous
38	LiSrBO ₃ :Bi	900	No	No	No	Mat'l white with green residue
39	LiSrBO ₃ :Bi Batch #2	900	No	No	No	Mat'l light green. Note: This sample was sintered in a glazed porcelain boat. The mat'l reacted with boat. Mat'l melted, boat cracked.
40	LiSrBO ₃ :Bi	900	Light blue around edge	No	No	Mat'l was sintered in a platinum boat. Color is white and light brown
53	NaBaBO ₃ :Bi	900	Light blue spots in white area	No	No	Mat'l dark gray with white next to boat. Not homogeneous. Note: Phosphor number is not in order because sample was mis-placed.

Table 3b.

Bulk Phosphor (Sulphates)

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No	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
49	MgSO ₄ :Bi	1140	Red next to boat, weak	No	No	Mat'l appears to be homogeneous but does not fluoresce uniformly. <u>Note</u> : Mat'l sintered at 950°C, would not fluoresce. . resintered at 1150
50	CaSO ₄ :Bi	950	Orange (Weak)	No	No	Mat'l homogeneous, has slight pink tint.
51	SrSO ₄ :Bi	950	Orange (Strong)	No	No	Mat'l homogeneous, has light gray tint.
52	BaSO ₄ :Bi	1140	Blue	No	No	Mat'l homogeneous and white. <u>Note</u> : Mat'l sintered as per #49.

Table 4.

Bulk Phosphor (Material Remade)

No.	Phosphor	Sinter °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
54	$Mg_2P_2O_6:Bi$	1150	Red one spot. Rest area dead.	No	No	Material light brown, not homo. Material melted. Red spots fluoresce in boat bottom. (OLD #10).
55	$Mg_2P_2O_7:Bi$	1150	Red Blue	No	No	Material white & homo. Material fluoresce red except where it touches boat, some blue specks next to boat. (OLD #11)
56	$Ca_3(PO_4)_2:Bi$	1150	Red Specks	No	No	Material white & homogeneous. Fluoresce is evenly scattered. Material may not be properly mixed (OLD #22).
57	$Sr_4(PO_4)_2:Bi$	1150	Red	Blue-white	No	Material white & homogeneous. (OLD #23).
58	$Mg_3(AsO_4)_2:Bi$	1100	Red very weak	No	No	Material white & homo. Material sintered at 1000°C with no results. (OLD # 41).
59	$NaCaPO_4:Bi$	1100	Blue, one spot (weak)	Very light Blue	No	Material light green & homogeneous. (OLD # 15).
60	$KCaPO_4:Bi$	1000	Blue	No	No	Material green & is granular. (OLD # 18).
61	$SrB_2O_7:Bi$	1000	Red (fuchsia)	No	No	Material white & homogeneous. Material melted & fused with boat. (OLD # 28).

Table 5.

Vapor Deposited Phosphor Data

No.	Phosphor	Subst. temp. °C	Fluorescence			Comments
			Tesla-coil	U. V. Long	U. V. Short	
1	$\text{CaP}_2\text{O}_6\text{:Bi}$	Ambient Lab.	No	No	No	Film is deliquescent, has acid smell. Boat mat'l. tantalum. Mat'l reacted with boat.
4	$\text{Ca}_2\text{P}_2\text{O}_7\text{:Bi}$	Ambient Lab.	No	No	No	Film is deliquescent. Iridium boat. White substance remaining in boat, therefore, boat not hot enough.
6	$\text{SrP}_2\text{O}_6\text{:Bi}$	Ambient Lab.	No	No	No	Film deliquescent. Iridium boat. White residue.
12	$\text{LiCaPO}_4\text{:Bi}$	Ambient Lab.	No	No	No	Film deliquescent. Iridium boat. White residue.
28	$\text{SrB}_2\text{O}_4\text{:Bi}$	Ambient Lab.	No	No	No	Film is hard, transparent and appears to be hygroscopic. Iridium boat. White Residue
6	$\text{SrP}_2\text{O}_6\text{:Bi}$	200.	No	No	No	Iridium boat. Substrate fired in vacuum to 800°C. Mat'l fed into boat with Vibro-feed. Boat burnt out at about 2000°C. Film hard and transparent.

**Spectrophotometer and Emission Decay
Data**

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NO.	Phosphor	Wave Length Peaks	Emission Decay Time to 90%	Comments
1	CaP ₂ O ₈ :Bi (Meta) Batch 1	6300 A		No emission after one week in air
3	CaP ₂ O ₈ :Bi (Meta) Batch 3	6300 A	28 μ Sec.	
4	Ca ₂ P ₂ O ₇ :Bi (Pyro)	6360 A	16 μ Sec.	
6	SrP ₂ O ₈ :Bi (Meta)	6400 A	22 μ Sec.	
7	Sr ₂ P ₂ O ₇ :Bi (Pyro)	6500 A 7000 A	18 μ Sec.	
8	BaP ₂ C ₆ :Bi (Meta)	6200 A	14 μ Sec.	
28	SrB ₂ O ₄ :Bi	5400 A < 4000 A		Red with Tesla Coil Fuchsia faded to yellow in CRT
P-22	Zn ₃ (PO ₄) ₂ :Mn	6000 A		Used for color comparison

Table 7a

Spectrophotometer and Emission Decay Data (Cont.)

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No.	Phosphor	Peak Wave Length	Decay Time to 10%	Comments
50	CaSO ₄ :Bi	5000 Å 6000 Å	14 μ Sec.	
51	SrSO ₄ :Bi	6100 Å	12 μ Sec.	
55	Mg ₂ P ₂ O ₇ :Bi	< 4000 Å	12 μ Sec.	Red with Tesla coil Violet in CRT
57	Sr ₃ (PO ₄) ₂ :Bi	4300 Å 6100 Å	13 μ Sec.	
P-2	ZnS:Cu	5200 Å	54 μ Sec.	Used for decay comparison
S	Strobe Light		23 μ Sec.	

Table 7b.