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Investigation by an Improved Method of the Wave Lengths of Fluorescence of Lead Tungstate-Calcium Tungstate Mixtures Excited by Various Wave Lengths of Ultraviolet Light

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INVESTIGATION BY AN IMPROVED METHOD OF THE WAVE LENGTHS OF FLUORESCENCE OF LEAD TUNGSTATE—CALCIUM TUNGSTATE MIXTURES EXCITED BY VARIOUS WAVE LENGTHS OF ULTRAVIOLET LIGHT

by

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Date August 12, 1942
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To Dr. F. E. E. Germann I wish to express appreciation for suggestions and assistance in carrying through the present investigation. I also wish to thank Dr. R. G. Gustavson and Kenneth A. Gagos for their assistance and interest in this study. I desire also to express my most sincere appreciation to all those workers of the past whose lives, be they great or small, are blended together to make what we carelessly call civilization. Only through the kindness of my associates and through the contributions, both known and unknown, of the workers of the past was the present work made possible.
Investigation by an Improved Method of the Wave Lengths of Fluorescence of Lead Tungstate-Calcium Tungstate Mixtures Excited by Various Wave Lengths of Ultraviolet Light

A method of investigation was developed whereby the intensity of fluorescence was recorded as the density on a photographic plate; the wave length of the fluorescent light was recorded across the plate; and the wave length of the exciting light was recorded as the distance down on the plate. The method makes use of a monochromator and a spectrograph arranged so that the dispersion of one instrument is at right angles to the dispersion of the other. The visible part of the spectrum from the monochromator was not allowed to fall on the samples. The samples could easily and quickly be placed in position or removed. Thus before making the permanent photographic record, they were accessible to convenient visual observation as to intensity of fluorescence and wave length of ultraviolet producing the fluorescence.

Samples were made and examined for the composition range extending from pure CaWO₄ to pure PbWO₄. Several interesting things were observed: The sum of the fluorescent light of all wave lengths excited by ultraviolet of all wave lengths passed through a broad maximum in the neighborhood of a mole fraction of 0.02 PbWO₄ as had been reported by other investigators. The sum of the fluores-
cent light was found to pass through a second maximum near pure PbWO₄. It was found that the distribution of fluorescent light in the visible spectrum changes with mole fraction of PbWO₄ and also to a less extent with the wave length of exciting light. As the mole fraction of PbWO₄ is increased, the average wave length of the fluorescent light shifts toward the red—that is, the color changes from blue to a color which is more nearly white. As the wave length of the exciting light is increased, the average wave length of the fluorescence again shifts toward the longer wave lengths.

The wave lengths of ultraviolet that excite fluorescence vary with the mole fraction. As the mole fraction of PbWO₄ in the samples is increased, longer wave lengths of ultraviolet are able to excite fluorescence. Thus the maximum fluorescence excited by a single wave length is in general not at the same composition as the maximum of total fluorescence. For example, the ultraviolet line at 312 mμ does not show a maximum fluorescence at a mole fraction of 0.02 but shows a very strong maximum at a mole fraction of about 0.997 PbWO₄. The fluorescence exhibited by samples prepared with a mole fraction of about 0.999 was quite strong both by comparison with samples having a mole fraction of about 0.02 and with the fluorescent powders actually used in fluorescent lights.

This abstract of about 450 words is approved as to form and content. I recommend its publication.

Signed

[Signature]
Professor in charge of dissertation
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INTRODUCTION

This investigation was undertaken as an attempt to improve the methods of excitation and observation of fluorescence and to examine the fluorescence of mixtures of CaWO$_4$ and PbWO$_4$ over the entire composition range. The problem consists of the investigation of four variables: namely, the frequency of the exciting light, the frequency of the fluorescent light, the composition of the CaWO$_4$-PbWO$_4$ mixture, and the intensity of fluorescence at each frequency and composition.

Many investigators have worked on fluorescence, though most of the work consists of placing various naturally occurring substances under an ultraviolet light and describing the fluorescence in words. In spite of the importance of CaWO$_4$ as a material in fluorescent lights very little has been known about its fluorescence.

A very good discussion on the nature of fluorescent light is given by G. E. Inman. He discusses general design, operating characteristics, wiring diagrams, colors, and efficiency. He gives the approximate lumens per watt for white light of different sizes as: 18" x 1" = 30; 18" x 1½" = 30; 24" x 1½" = 32; and 36" x 1" = 35. He also gives the approximate lumens per watt for the various colors of the 24 inch lights as: daylight, 32; white, 32; red, 3; gold, 19; pink, 22; green, 65; and blue, 19. From

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this it can be seen that there is a very great difference in the efficiency of fluorescent substances used commercially.

Oday and Cissel⁷ also discuss the properties of fluorescent lights.¹ From a fifteen watt lamp they say that about 7.5 watts are concentrated in the line at 253.7 m, 0.2 watt in the visible lines of mercury, and 7.2 watts are dissipated as heat and infra red radiation. Of the 7.5 watts of energy in the ultraviolet line at 253.7 m, 1.8 watts are converted into visible light in a daylight lamp, and the other 5.8 watts are lost as heat.

J. W. Marden and George Meister investigated the effects of impurities on fluorescence.² Their method was as follows:

Fluorescent powders were prepared in the well known way by thoroughly mixing the purest ingredients and heating in clear silica dishes to appropriate temperatures as described in the literature. (British Pat. 494,299, Oct. 20, 1938)**

Each powder tested was then weighed out in two gram portions into clean porcelain dishes and the impurity added in the form of solution, usually a nitrate. The wet samples were dried and individually transferred to an agate mortar, thoroughly

1 A. B. Oday and R. F. Cissel, "Fluorescent Lamps and Their Applications", I. E. S. Trans., 34, p. 1166 (1941).

2 J. W. Marden and George Meister, "Effects of Impurities on Fluorescent compounds", I. E. S. Trans., 34, p. 505-513 (1939).

* Authors: Nela Park Engineering Department, General Electric Company, Cleveland, Ohio.

** This patent, issued to the British Thomson-Houston Co., Ltd., called for the addition of 0.5% to 1.5% lead as the acetate to 21 parts of CaO and 79 parts of WO₅. (C.A., 33, 2417.)
ground and mixed, and placed in clean silica dishes. They were arranged in boats so that several could be heated simultaneously in the furnace. The temperature of heating was the same as used for preparation; the borates at 700° C. and the silicates at 1200° C. The period of heating was a half hour in every case.

The samples were removed from the silica, again pulverized in an agate mortar, and a standard quantity placed in the brass measuring container. The readings were made with a photo cell. The difference between the readings with and without an interposed window glass, indicated the relative fluorescent response.

Thin window G-type mercury lamps which have high 2537 Å output were used to irradiate the samples. The lamps were allowed to stabilize before readings were taken. Small variations in lamp output of heat treatment, however, were not serious since a blank was always included with each set of readings.

All readings were corrected for reflections from the interposed glass surfaces. The corrected readings divided by the readings given by the blank and multiplied by one hundred gave the percentage response reported in the curves.1

Their curve2 for the addition of lead to CaWO₄ starts with a reading of 57 for pure CaWO₄, 57 for 0.001%, 56 for 0.01%, 60 for 0.1%, 77 for 0.2%, 100 for 1%, 90 for 2%, and 90 for 3%. This is as far as they carried the curve, and of course their work tells us nothing about the wave length of the exciting light, or the wave length of the fluorescent light or how these

1 Marden and Meister, op. cit., p. 506.
2 Ibid., p. 508.
vary with composition. It might be pointed out that their value for the fluorescence drops 10% when the lead content changes from 1 to 2%, but it does not change at all when the lead content goes from 2 to 3%.

Swindells\textsuperscript{1} investigated the effect of x-rays on mixtures of lead and calcium tungstates. His apparatus made use of a bakelite plate with holes drilled in it. A sheet of celluloid was glued to the bottom surface of this leaving little cylindrical pockets with transparent bottoms. This plate was placed on an x-ray film, the pockets filled with the powders and exposed from beneath. When the film was developed, the spots opposite the samples were darker than the main body of the film if the samples fluoresced. Swindells heated all samples to 1000° C. He found no fluorescence beyond a mole fraction of 0.5 PbWO\textsubscript{4}.

Oldham and Kunerth\textsuperscript{2} used a monochromator and spectroscope to study the effect of particle size on the fluorescence of "ZnBeSiO\textsubscript{5}". They used the monochromator only to secure monochromatic light of one wave length at a time. The one line of monochromatic light fell on the sample and the fluorescence was determined by photography. They found that the fluorescence increased linearly as the

\begin{enumerate}
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size of the particles was decreased. They explain this peculiar condition by assuming that the fluorescence is produced only at the surface.

Since the beginning of this investigation, Marden and Beese have published a photograph of one sample of CaWO₄ showing the wave lengths of ultraviolet light that produce fluorescence. (Fig. 1. See note* page 10) They did not investigate the wave length of the fluorescent light or the effect of PbWO₄ on the wave length of ultraviolet light producing fluorescence. They obtained their photograph by merely placing a filter to absorb ultraviolet in front of a photographic plate. The filter was coated with glue and the CaWO₄ was sprinkled on it. Then the assembly was put in an ultraviolet spectroscope so that the spectrum

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1 J. W. Marden and N. C. Beese, "Ultraviolet Excitation of Fluorescent Compounds", I.E.S. Trans., 56, 239 (Feb., 1947)

* Authors: Research Laboratory, Westinghouse Lamp Division, Broomfield, N. J.
would fall on the plate. When the ultraviolet light fell on the CaWO$_4$, fluorescent light was emitted, some of which penetrated the filter and exposed the photographic plate. This gives a somewhat blurred picture because of the diffusion of the fluorescent light and because of the difficulty of getting a thin filter that cuts out all of the ultraviolet light. Unless the film used has the same sensitivity to each color, their measurements will be in error, since the color of the fluorescence varies, and since according to their method nothing is known about the wave length of the fluorescent light so corrections could not be made. Also both the glue and the filter must not exhibit any fluorescence themselves.

The lamp used by these investigators was probably superior in some respects to the one used in the present investigation. Their description of it is as follows:

The lamp used in the experiments was constructed of Pyrex glass and had water cooling in the constricted portion. A spherical quartz bulb was sealed on the end of the lamp to pass the short wave length ultraviolet. This lamp had cold electrodes of rather large size and contained at sealing off about 5 or 6 mm. pressure of hydrogen. The discharge operated on A.C. at about 0.5 amperes and 1150 volts. Although the lamp gave a satisfactory output in the desired region, it became blackened and was badly discolored in 50 or 100 hours of operation.¹

¹ Marden and Beese, op. cit., p. 236-237.
METHOD OF INVESTIGATION

The first method considered was the use of a photo cell to measure the intensity of the fluorescent light. This left three variables: namely, the frequency of the exciting light, the frequency of the fluorescent light, and the composition. For each sample and each wave length of exciting light there would be an intensity of each wave length of fluorescent light. Thus, even if fairly wide wave length intervals were taken, the investigation would involve a very large number of measurements. For instance, if this method had been chosen for this investigation, and readings had been taken at intervals of 0.100 A, more than 9000 measurements requiring over 100 pages of tables would have been needed to record the data which would give less information than is given in the photographs shown on pages 29 to 36. Furthermore, the problem of getting a sufficiently intense beam of monochromatic fluorescent light from a monochromatic beam of ultraviolet light to affect a photo cell was considered impractical if not impossible.

A Hilger Model No. F 84302 ultraviolet monochromator was available for the work, and in the course of attempts to view the fluorescence of fine powders the idea was conceived of turning the instrument up on its side. The second slit was removed and the instrument was clamped in

such a position that the ultraviolet spectrum was projected down on to the powder, X, placed in a horizontal position. (Fig. 2) This was an ideal arrangement for viewing fluorescence. The samples could be held under the light and the wave lengths producing fluorescence could be recognized immediately. An ordinary camera was clamped in such a position that photographs could be taken of the fluorescence. This gave a fairly good record of the intensity of fluorescence excited by the various frequencies of ultraviolet light, but it did not give any indication of the wave length of the fluorescent light.

Next a Hilger constant deviation spectroscope No. D.10.3021 with a photographic attachment was clamped up on edge so that the collimator pointed down at the fluorescent powder, X. (Fig. 3) A lens, L5, was placed between the powder and the collimator so that an image of the powder would be focused on the slit, S2, of the spectroscope. The plane of the spectroscope was at right angles to the plane of the monochromator so that when the fluorescent light was focused on the slit of the spectroscope, the light excited by the longest wave lengths of ultraviolet would come to a focus on one end of the slit and that excited by the shortest wave lengths would come to a focus on the other end of the slit. When a photograph of this is made through the spectroscope, the top of the picture represents light produced by the shortest wave lengths of

Fig. 2—Monochromator.

Fig. 3—Spectrograph.
ultraviolet and the bottom of the picture represents light produced by the longest wave lengths. The distance across on the picture gives the wave lengths of the fluorescent light. Thus each picture presents a graph of three variables: a vertical section representing a plot of frequency of exciting light against intensity of fluorescence measured as the darkness of the picture, and a horizontal section representing a plot of the wave length of fluorescent light against its intensity which is again measured as the darkness of the picture.

Arrangements having some of the same features as this were used by early experimenters. Newton was probably the first to employ two prisms in the investigation of light. Figure 4, page 11, is a reproduction* of one of his experiments1.

The first systematic and thorough investigation of fluorescence was made by Stokes in 1852 and 1853. His papers are exceedingly interesting. The following is his description of his methods:

**Methods of Observation Employed.**

**FIRST METHOD.**—The sun's light was reflected horizontally through a small lens,

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1 Thomas Preston, *The Theory of Light*, p. 120 (1901).

* The method of reproduction used for Figures 1, 4, and 5 consists merely in placing a piece of sensitive photographic paper face down over the material to be copied, pressing it down tightly with a piece of glass, and exposing it through itself. This is developed and dried in the usual manner and used as a negative for the final reproduction. The exposure time in both cases is about five or six times as long as that required for printing an ordinary negative.
This image of the spectrum was coloured, being red at its least refracted end and violet at its most refracted end, and yellow and blue in the intermediate spaces.

I then placed a second prism immediately after the first in a cross position to it, that it might again refract the beam of the sun's light which came to it through the first prism. In the first prism the beam was refracted upwards, and in the second sideways. And I found that by the refraction of the second prism, the breadth of the image was not increased, but its superior part, which in the first prism suffered the greater refraction, and appeared violet and blue, did again in the second prism suffer a greater refraction than its inferior part, which appeared red and yellow, and this without any dilatation of the image in breadth.

Figure 4

which was fixed in a hole in a vertical board. The cone of emergent rays was allowed to enter the solid or fluid examined. A coloured glass or other absorbing medium was then placed, first so as to intercept the incident rays, and then between the substance examined and the eye. For shortness' sake these positions will be designated as the first and the second. Sometimes a coloured glass was allowed to remain in front of the hole, and a second glass was added, first in front of the hole and then in front of the eye.

SECOND METHOD.—The sun's light, reflected as before, was transmitted through a series of three or four Munich prisms placed one immediately after the other, and each nearly in the position of minimum deviation. It was then transmitted through a small lens in a board close to the last prism, and
so allowed to enter the body to be examined, which was generally placed so that the first surface coincided, or nearly so, with the focus of the lens. The diameter of the lens was much smaller than the breadth or height of the prisms, so that the lens was completely filled with white light, the component parts of which however entered in different directions. Regarding the image of the sun on the focus of the small lens as a point, we may conceive the light incident on the body under examination as consisting of a series of cones, corresponding to different refrangibilities, the axes of which lay in a horizontal plane and intersected in the centre of the lens, the vertices being arranged in a horizontal line near the surface of the body examined.

THIRD METHOD.—The sun's light was reflected horizontally through a vertical slit, and received on the prisms, which were arranged as before, but placed at the distance of several feet from the slit. A large lens of rather long focus was placed immediately after the last prism, with its plane perpendicular, or nearly so, to the beam of light which had passed through the prisms, and with its centre about the middle of this beam. The body examined was placed at the distance of the image of the slit, or nearly so.

FOURTH METHOD.—Everything being arranged as in the third method, a board with a small lens of short focus was placed at the distance of the image of the slit, or between that and the image of the sun, which was a little nearer to the prisms, inasmuch as the focal length of the large lens commonly employed, though much smaller, was not incomparably smaller than the distance of the lens from the slit. A second slit was generally added immediately in front of the small lens. The body examined was placed at the focus of
the small lens. The dispersed light was viewed from above and analysed by a prism, being refracted sideways.\(^1\)

In the fourth method the observations were made by holding the prism to the eye.\(^2\) No slit or lenses were used in connection with this prism.

Figure 5

Figure 5\(^3\) is a reproduction from Stokes original article. It was presented in connection with an


2 Ibid., p. 473.

3 Ibid., Plate XXV.
explanation of what was seen in method four.

This first paper by Stokes was used by Wood¹ in his discussion of fluorescence in his book on Physical Optics.

In a later paper² Stokes describes two other methods of investigating fluorescence which he recommends as superior. The first of these is to admit light into a darkened room through a filter which cuts out all wave lengths longer than a certain limit. He then views the sample through a filter which cuts out all wave lengths shorter than this same limit. If the first filter cuts out the entire visible spectrum, no second filter is needed. The two filters taken together are opaque, but the first may transmit light which excites fluorescence in the sample. According to Stokes' law the wave length of the fluorescent light is always longer than the wave length of the exciting light. Thus the fluorescent light will be visible through the second filter, if the limits of transmission of the filters are properly chosen. This is essentially the method used by most investigators at the present time. It gives very spectacular and beautiful results. It is very popular with amateur investigators. However, the method gives us very little information about the wave length of the exciting light or the wave length


of the fluorescent light, and in these respects it is inferior to Stokes' previous work. In fact it is doubtful if he would have discovered his law if he had used only this method. Stokes' law has since been disproved, but the intensity of the light emitted in violation of it is so slight as to be negligible in most cases.

The second method suggested by Stokes is to admit skylight into a darkened room through a narrow slit. A filter is put in behind the slit to absorb all but the shorter wave lengths. The image of the slit is focused on the samples and upon some white material placed beside it which is used for comparison. This is viewed by holding a prism up to the eye. The prism is held in such a way that the light will be refracted perpendicular to the image of the slit. The light is spread out into two spectra—one for the fluorescent material and one for the non-fluorescent standard. The non-fluorescing standard will show a short blue spectrum depending on the filter used. The fluorescent material will show the same blue spectrum, but in addition it will show fluorescent light of longer wave length. Thus if the proper filter is used, this gives the wave length of the fluorescent light, but it does not give the wave length of the light exciting the fluorescence. It does have one unique advantage not possessed by most methods and that is that it gives a relative measure of the absorption spectrum of the fluorescent material over the limited region transmitted.
by the filter, since its spectrum can be compared with the white standard.

Nichols and Merritt\textsuperscript{1} in their investigation of Stokes' law used a spectrophotometer in combination with a monochromator. They have this to say about the previous methods:

No attempt apparently has been made to apply the spectrophotometer to the study of fluorescence; yet it is obviously possible to determine both the limits and the maximum of a spectral region for which a curve of intensities can be plotted with far greater accuracy than by the method hitherto pursued by all observers, i.e. that of attempting to set the cross-hairs in the eye-piece of a spectroscope in a region of greatest brightness or at the point where the spectrum ceases to be visible.\textsuperscript{2}

In the set-up used by Nichols and Merritt the light from a monochromator entered a rectangular cell holding the solution to be investigated. The light entered near one edge of the cell and the fluorescent light produced was observed perpendicular to this edge—that is also perpendicular to the entering monochromatic light beam but parallel to its spectrum. The fluorescent light entered a spectroscope and was observed in the usual way. A source of light for comparison was introduced into the spectroscope by a mirror just in front of the prism. This

\begin{enumerate}
\item Ibid. p. 404.
\end{enumerate}
arrangement necessitates a separate reading for every wave length of fluorescent light produced by every wave length of ultraviolet light. The method is well adapted to the investigation of the fluorescence of liquids, especially if the fluorescent light is very nearly the same wave length as the exciting light as it was, of course, in their investigation of Stokes' law.

The set-up used in the present investigation gave very good results. Its chief drawbacks are the time required to expose a picture—usually two or three hours—and the difficulty of getting everything lined up, since the image of the fluorescent light is not strong enough to be visible to the eye. However, once the set-up is adjusted it is a comparatively simple matter to take the pictures, since all that is necessary is to smooth the sample down on top and set it under the light. The photographic plate is inserted in the camera and in two or three hours the light is turned off and the picture developed.

One of the worst difficulties encountered is that the focal plane of the monochromator is not perpendicular to the beam. That is, when the ultraviolet light from the monochromator was directed vertically downward on to the powder, one end of the spectrum would be out of focus. This difficulty is overcome in quartz spectrosopes by tipping the photographic plate. But in working with loose powders it is very difficult to get them exactly
level and flat and also to get them always at exactly the same height. Also the ultraviolet light penetrates the powder slightly by diffusion, and what is gained in sharpness by having a better focus is lost by these other difficulties. In the final set-up a compromise was used. The monochromator was tipped to partly correct the effect and the spectrum was brought to focus in the center leaving the two ends slightly out of focus. (Fig. 2, page 9) These difficulties account for the broadness of the ultraviolet lines across the pictures.

The light source used was a mercury arc\(^1\). It operated at a fairly high pressure and gave a fairly good distribution of light over the spectrum, although it was not continuous and there was not much light below 253.7 μm. It is probably the best source commercially available, but a continuous light source such as that used by Marden and Beese\(^2\) would probably give better results, since it would be easier to recognize sharp changes in sensitivity of the material to various wave lengths. The light was originally made to use with a large glass filter. There are two types of filters available for mercury lights. One is a non heat-resistant filter which can be used only with the low pressure arcs; the other is a heat-resistant filter which is used with this light. The heat-resistant filters do not transmit short enough wave lengths to

\(^1\) Uviarc Laboratory Outfit, Code No. ACA—HD—SK.1314-D, General Electric Vapor Lamp Co., Hoboken, N. J.

\(^2\) J. W. Marden and N. C. Beese, op. cit., p. 236-237.
excite any fluorescence in CaWO$_4$. Many attempts were made to prepare samples of CaWO$_4$ that would fluoresce under this light before the cause of the difficulty was discovered.

To adapt the light as a source of ultraviolet for the monochromator a metal plate was made to slip into the housing instead of the glass filter. This plate was provided with a small hole in the center so that the monochromator could be put up close to prevent stray light from escaping into the room. The plate was made of two layers and water was circulated between them to keep the apparatus cool. Sheet aluminum was used for the inner layer so that as much ultraviolet as possible would be reflected back and forth till it entered the slit of the monochromator.

It is necessary to make only one picture of each sample, since from this picture one can observe the intensity of each wave length of fluorescent light produced from each wave length of ultraviolet light.
MAKING THE PHOTOGRAPHS

It was necessary to make scales for both the wavelength of the fluorescent light and the exciting light, since the spectrograph used did not have a scale. The scale for the wavelength of the fluorescent light was made by taking a photograph of the spectrum of helium, mercury and argon directly through the spectrograph without changing its adjustments. The distance of each line in this photograph from the first prominent line in the violet end of the spectrum was measured with a traveling microscope. This distance was plotted against the wave lengths of the lines that could be recognized. The rest of the lines were fitted into the curve according to their approximate wave length as determined from the rough curve. The task was somewhat simplified by taking the photographs so that the spectra overlap. From this curve the distances of the various wave lengths from the fixed line could be read directly. A scale was made then by measuring over to the desired even wave lengths and making a mark. The scale was made twice as large as the photographs so that the lines would be sharp. Three scales were made side by side so that the whole plate could be printed at once, since each plate had three spectra on it.

The scale for the wave length of the ultraviolet light was made in the same way except that the wave lengths
of the principal lines of mercury were listed at the appropriate distances instead of marking the even numbered wave lengths.

After the scales were made, they were placed on a table under a piece of glass to keep them flat. They were evenly illuminated by three lamps placed at the proper positions. The uniformity of illumination was adjusted by the use of a photo cell which could be moved around over the surface. Next a camera was set up at the right height above the scales to reduce their size to exactly one-half. This was checked by seeing that all three mercury lines fell on the right wave length when one of the original negatives was put in the back of the camera. The ground glass had been removed from the camera and a piece of clear glass substituted.

It was thought desirable to present the final pictures as negatives and not as positives, so an intermediate negative had to be made. This was done by placing the original negative in the back of the camera, adjusting the scale so that it fitted the spectra, and placing directly over the negative a sensitive lantern slide plate. This was exposed by the light from the scale so that it contained the scale and spectrum as light areas on a black background. The prints were made from these intermediate negatives by merely exposing a piece of paper of the
right size to the scale and spectrum, then covering the central part and exposing again to give a border. For most investigations this copying procedure is unnecessary, since the original negatives furnish a more accurate measure of the intensities.
PREPARATION OF SAMPLES

In order to see the effect of the mole fraction of PbWO$_4$ on the fluorescence, it is necessary to have a series of samples starting with pure CaWO$_4$ and extending through pure PbWO$_4$.

The samples were prepared by the precipitation of the mixture of the two salts from solution. Solutions of 0.6 M Ca(NO$_3$)$_2$, 0.6 M Pb(NO$_3$)$_2$ and 0.6 M Na$_2$WO$_4$ were made up. To make the samples the Pb(NO$_3$)$_2$ and Ca(NO$_3$)$_2$ were mixed in the proportion desired. One hundred cc. of this solution was diluted with about 400 cc. of water and heated to boiling. The Na$_2$WO$_4$ was added to this solution slowly at first, then more rapidly until 100 cc. had been used. The solutions were boiled for five minutes and then filtered and dried. The best grade of C. P. chemicals was used, and as a precaution against impurities which might cause abnormal effects samples were made in different ways and from different materials. Some of the salts were recrystallized before making up the solutions, but no difference in the fluorescence could be observed. Other samples were made by digesting in water a mixture of PbO, CaO, and H$_2$WO$_4$. Another series of samples was made from solutions of Pb(C$_2$H$_2$O$_2$)$_2$, Ca(C$_2$H$_5$O$_2$)$_2$, and Na$_2$WO$_4$. These samples resembled the corresponding samples prepared from the nitrates as closely as two samples prepared from the nitrates resembled each other. The
samples seemed to be quite different depending on which side of the equivalence point they were precipitated. Samples digested in the presence of an excess of Pb\(^{++}\) and Ca\(^{++}\) seemed to show a stronger fluorescence than those digested in the presence of an excess of WO\(_4^-
\)

Some samples showed a fairly strong fluorescence before heating. Heating seemed to increase the fluorescence about four times on the average. Those samples with a very high CaWO\(_4\) content seemed to be affected the least as they exhibited a very strong fluorescence before heating. The samples with a fairly high PbWO\(_4\) content were erratic before heating. Sometimes they would exhibit a fairly strong fluorescence before heating but usually not. The optimum temperature of heating did not seem to be very critical for the samples with a high CaWO\(_4\) content, but for those with a high PbWO\(_4\) content it was fairly critical.

The series of samples made from the nitrates were all heated to between 500\(^\circ\) and 600\(^\circ\) C. Then half of each sample was taken and heated to about 1000\(^\circ\) C. The higher temperature improved the fluorescence up to a mole fraction of about 0.4 PbWO\(_4\).* Those of about 0.03 were very much improved, the blue fluorescence being excited

* In this paper mole fractions will always be expressed as moles of lead tungstate per mole of lead tungstate-calcium tungstate mixture. In the pictures pages 29 to 36 this is represented as \(\frac{\text{PbWO}_4}{\text{PbWO}_4 + \text{CaWO}_4}\).
by longer wave lengths of ultraviolet light. The higher temperature decreased the fluorescence of those samples with a mole fraction above 0.5. It may be that any excess lead should be left as the carbonate or nitrate and not be decomposed to the oxide.

When the heating changed the intensity of the fluorescence, the part of the sample showing the strongest fluorescence was taken for the picture. When there are two samples with the same mole fraction, the one made from the nitrate solutions is shown first. The sample made from nitrate solutions having a mole fraction of 0.8 PbWO$_4$ shows considerably more sensitivity to the longer wave lengths of ultraviolet than the sample made from a solution of the acetates. No explanation can be given for this. The samples of mole fraction 0.95 checked fairly well. The general distribution of light is about the same and any difference in general intensity can probably be attributed to differences in the plates used, since some of the plates were rather old.

Three pictures are shown of the sample with a mole fraction of 0.999. (See pages 35 and 36.) The first two were made at different times from nitrate solutions. The third was made from acetate solutions. In this picture the original plate was fogged from the edge, and the top had to be retouched. All three samples show good agreement both as to the general intensity and as to the
variation with wave length in both directions. In every case the pure PbWO₄ fluoresced much less than those samples containing a small amount of CaWO₄. Some of this difference may be because the best temperature for heating the samples may not have been found, but it seems more probable that a small amount of CaWO₄ really does very much improve the fluorescence of PbWO₄.
DISCUSSION OF PHOTOGRAPHS

The fluorescence of the various samples is shown in the photographs pages 29 to 36. At the left side of each picture the mole fraction of the sample is given. These mole fractions are expressed as the number of moles of lead tungstate divided by the number of moles of lead tungstate plus the number of moles of calcium tungstate. The scale at the bottom of the pictures gives the wave length of the fluorescent light expressed in millimicrons. The representative wave lengths of the various colors in a spectrum are: violet, 410 \( \mu \); blue, 470 \( \mu \); green, 520 \( \mu \); yellow, 580 \( \mu \); orange, 600 \( \mu \); and red, 650 \( \mu \). The numbers at the right are the wave lengths of the principal mercury lines exciting the fluorescence. The three vertical lines are not fluorescent lines, but are caused by reflection from the walls of the room and from the powder. They are the three most prominent mercury lines in the visible region. The one to the right is a yellow doublet (wave lengths, 577 and 579) but the slit was so wide that the two parts overlap. The one in the center is green (wave length, 546) and the one to the left is blue (wave length, 435.8). They are helpful for comparing with the wave length of the fluorescent light.

The first strong ultraviolet line producing fluorescence is 253.7 \( \mu \). In low pressure mercury discharge tubes this line is by far the strongest, but as the pressure is in-\[1\] Handbook of Chemistry and Physics, 22nd Edition, p. 1559.
creased the other lines get stronger until they are about as strong as it is. In the case of pure CaWO₄ this line produces a very strong fluorescence most of which is concentrated in the blue with a maximum at about 455 or 460 m\(\mu\). As PbWO₄ is added another maximum seems to develop at about 530 to 540 m\(\mu\). These two maxima blend together to give an almost uniform distribution from 425 to 600 m\(\mu\). The total amount of fluorescent light apparently passes through a broad maximum in the neighborhood of a mole fraction of 0.02 PbWO₄. For a mole fraction of 0.4 and greater the amount of blue light is less than the amount of light at the other end of the spectrum. The ultraviolet line 265.2 m\(\mu\) produces an effect very similar to that of 253.6 m\(\mu\). The ultraviolet line 280 m\(\mu\) hardly shows at all in the case of pure CaWO₄. As PbWO₄ is added it becomes more intense almost approaching the intensity of the two above. As still more PbWO₄ is added it becomes very weak again and almost disappears.

The lines 396 and 302 do not appear until a considerable amount of PbWO₄ has been added. It is interesting to note that their intensities are about the same when the mole fraction is about 0.03, but when it is 0.999 the second one is much more intense than the first. The fluorescence of the line at 312 m\(\mu\) does not become appreciable until the mole fraction of PbWO₄ is 0.6 and from a mole fraction of 0.9 on its intensity is the greatest of any of the lines.
SUGGESTIONS FOR FURTHER INVESTIGATION

Starting with a mole fraction of about 0.03 the samples were found to exhibit a strong phosphorescence. The luminescence lasted four or five seconds after the sample was removed from the exciting light and in some cases it would still show some luminescence after a minute.

It was noticed that some of the samples upon exposure to the ultraviolet spectrum would be darkened. In fact sometimes the complete image of the spectrum could be seen. This was especially true of those samples having a high PbWO₄ content and precipitated in the presence of excess Pb⁺⁺. The effect was presumably due to the deposition of free lead by a photochemical reaction.

One sample of CaWO₄ was prepared by precipitation in the presence of some LiCl. It was found that the blue fluorescence did not extend so far into the longer ultraviolet region—in fact almost half of the blue fluorescence was cut off.

A sample containing 0.01 moles of CaWO₄ and 0.99 moles of PbWO₄ was examined while hot. No fluorescence could be seen until the temperature had fallen to one or two hundred degrees. The line at 253.7 μm excited the first fluorescence, then other lines followed. This should be a good field of investigation, since substances which show a good fluorescence at high temperatures should be very valuable in high pressure mercury lamps.
It was noticed that in heating the samples in porcelain dishes the material fused into the glaze. The intensity of the fluorescence did not appear to be appreciably decreased— in fact sometimes it seemed to be increased. This should be further investigated, since highly fluorescent glazes and enamels should be very useful. Also the possibility of making other types of fluorescent glass should be investigated.

There is a vast number of other fluorescent substances both inorganic and organic that should be investigated, but it is only through a knowledge of the wave lengths of the exciting light and of the fluorescent light, as well as the intensity, that we can hope to make much progress in untangling the complicated relationships between chemical constitution and fluorescence. The problem of quenching of fluorescence should be investigated more from the standpoint of changes in wave lengths. This will furnish valuable information not only as to the nature of the fluorescent material but also as to the nature of the quenching agent.
SUGGESTIONS FOR IMPROVEMENT OF APPARATUS

Probably the most important limitation of the method as used is that the length of the ultraviolet spectrum is not great enough. Its length is limited by the length of the slit of the spectrograph. The height of the prism, diameter of the lenses, and height of the opening in the camera are also limiting factors. Ordinary spectrographs are not built with this use in mind so probably the best answer to the problem would be to buy the lenses and prism and build the rest of the instrument.

The second limitation of the method is the discontinuity of the light source. In some ways a discontinuous source such as the one used is superior to a continuous source. In a discontinuous source it is much easier to identify the wave lengths of the light. On the other hand sharp changes in the sensitivity of the substance with wave length might be missed if they come between the lines.

The third difficulty is the lack of perpendicularity between the spectrum and the direction of the beam of the monochromator. Quartz lenses are not made achromatic—that is the blue light comes to focus before the red light. Thus in a quartz spectrograph the photographic plate has to be tilted to make the light all come to focus on the plate. This tilting of the field does not work well with
an uneven powder that the light may diffuse into to a certain extent. This limitation could be overcome by using mirrors instead of lenses in the monochromator. There are several designs for such instruments.¹ This should eliminate the difficulty entirely, since the focal length of a mirror is independent of the wave length of the light.

¹ Wallace R. Brode, Chemical Spectroscopy, p. 35 and 218 (1939).
SUMMARY

A method of investigation was developed whereby the intensity of fluorescence was recorded as the density on a photographic plate; the wave length of the fluorescent light was recorded across the plate; and the wave length of the exciting light was recorded as the distance down on the plate. The method makes use of a monochromator and a spectrograph arranged so that the dispersion of one instrument is at right angles to the dispersion of the other. The visible part of the spectrum from the monochromator was not allowed to fall on the samples. The samples could easily and quickly be placed in position or removed. Thus before making the permanent photographic record they were accessible to convenient visual observation as to intensity of fluorescence and wave length of ultraviolet producing the fluorescence.

Samples were made and examined for the composition range extending from pure CaWO$_4$ to pure PbWO$_4$. Several interesting things were observed: The sum of the fluorescent light of all wave lengths excited by ultraviolet of all wave lengths passed through a broad maximum in the neighborhood of a mole fraction of 0.02 PbWO$_4$ as had been reported by other investigators. The sum of the fluorescent light was found to pass through a second maximum near pure PbWO$_4$. It was found that the distribution of fluorescent light in the visible spectrum changes with
mole fraction of PbWO₄ and also to a less extent with the wave length of exciting light. As the mole fraction of PbWO₄ is increased, the average wave length of the fluorescent light shifts toward the red—that is the color changes from blue to a color which is more nearly white. As the wave length of the exciting light is increased, the average wave length of the fluorescent again shifts toward the longer wave lengths.

The wave lengths of ultraviolet that excite fluorescence varies with the mole fraction. As the mole fraction of PbWO₄ in the samples is increased longer wave lengths of ultraviolet are able to excite fluorescence. Thus the maximum fluorescence excited by a single wave length is in general not at the same composition as the maximum of total fluorescence. For example, the ultraviolet line at 312 mμ does not show a maximum fluorescence at a mole fraction of 0.02 but shows a very strong maximum at a mole fraction of about 0.997 PbWO₄. The fluorescence exhibited by samples prepared with a mole fraction of about 0.999 was quite strong both by comparison with samples having a mole fraction of about 0.02 and with the fluorescent powders actually used in fluorescent lights.
BIBLIOGRAPHY


