FLUORESCENT LIGHT
and Its Applications

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and Its Applications

INCLUDING LOCATION AND PROPERTIES OF FLUORESCENT MATERIALS . . . A THEORETICAL AND PRACTICAL EXPOSITION OF FLUORESCENCE AND SIMILAR PHENOMENA.

By

H. C. Dake

Editor, *The Minerologist Magazine*
Co-Author, *Quartz Family Minerals*
Honorary President, *Northwest Federation of Mineral Societies*

and

Jack De Ment

Associate Editor *The Minerologist Magazine*
Research Chemist, *The Minerologist Laboratories*

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PREFACE

FLUORESCENT LIGHT AND ITS APPLICATIONS represents the work of many minds and many hands which have opened the fascinating mysteries of luminescence for over one century. Through investigations carried on over a period of years the present writers hope that these pages will reveal contributions to the work of their contemporaries. If nothing more than stimulation to comment were to result from this work the writers would feel satisfied, at least in part, that their aim would be fulfilled.

It was easy to write about the luminescence of minerals, gems, other substances, and the many uses of ultraviolet light. Fluorescence is a spectacular phenomenon, and even the casual observer can not help but stand in awe at the sight of a drab substance seemingly become living matter under the invisible radiations emitted by an ultraviolet light unit. So many new and valuable applications of fluorescence and ultraviolet light, have been discovered in recent years, the writers regret that the space available in this work does not enable them to present all available data.

We would like to emphasize one point in particular, to be remembered by all who turn these pages whether they are professional scientists or those without technical training. Our point is this: for every fact presented, for every experiment, for every detail, no matter its apparent unrelated nature, let every reader ask, "How can I combine this fact with the knowledge I now have to find a practical use?" We feel that in this manner developments will be forthcoming and profits on facts standing idle in the bank of knowledge will be used for betterment. Perhaps this is the salient feature to our many-sided purpose of writing this book.

Like numerous other phenomena, luminescence, was long looked upon as a laboratory curiosity and little thought was given to possible applications in the arts, industries, and sciences. It is significant that as early as 1912, W. S. Andrews, in conducting research on the fluorescence of various substances constructed an excellent working model of our present day fluorescent lighting tube. The commercial possibilities of the vacuum fluorescent tube of 1912 were not realized until nearly a quarter of a century later. This is only one of the innumerable instances wherein research work has later resulted in practical applications.

The hundreds of author references which appear in the text may prove monotonous and seemingly extraneous to some readers. One purpose of these is to give recognition to the previous work of both the scientist and the amateur. The reader seeking only material of a popular interest may object to the inclusion of subject matter which is solely of theoretical interest, and the searcher who scorns popular references may find portions of this book which are unorthodox. For the former a chapter on fundamentals is included while the latter may direct his attention to the more ponderable information. The aim of the writers has been to present chapters to cover a wide range of readers and applications. Since luminescence and uses of ultraviolet light are rapidly finding numerous practical applications, the chapters pertaining to theoretical considerations and types of ultraviolet units will be found useful in many fields. The inclusion of a voluminous bibliography was deemed desirable to enable the reader to obtain additional and detailed data in specific fields from original sources.

The writers are confident that the next decade will witness numerous new and valuable applications of luminescence and ultraviolet light. The field is scarcely scratched; the scientific plow will bring forth revelations with each furrow turned in the fertile field of study.

We have received aid from numerous sources. The Carnegie Institution of Washington was most generous in supplying valuable papers. Dr. V. L. Minehart of Portland, Oregon gave freely of his time to aid with studies requiring X-rays and radium. A number of original illustrations are the work of Virgil P. Barta of Portland, Oregon. Colonel Julian S. Hatcher of Aberdeen, Maryland supplied a number of excellent charts. Professor E. Mitchell Gunnell of Denver, Colorado and John D. Buddhue of Pasadena, California supplied data which has been included in our work.

Equipment manufacturers and supply houses proved most cooperative in supplying technical data and numerous illustrations which appear throughout the text. The California Isotope Company of San Fransisco generously loaned samples of heavy water for examination.

The Mineralogist Magazine of Portland, Oregon gave permission to make liberal use of numerous papers published during the past eight years. The writers feel that without the generous assistance from these sources much would be lacking in this volume.

In a work of this kind discrepancies occur in spite of careful proof reading. Our efforts have been to reduce errors to a minimum as well as to present information clearly and concisely. Constructive criticism, and corrections of errors will be welcomed by the writers, for a possible future second edition.

HENRY C. DAKE
JACK A. DEMENT

Couch Building,
Portland, Oregon.

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FLUORESCENT LIGHT
and Its Applications

CHAPTER ONE

HISTORICAL ASPECTS OF LUMINESCENCE

Luminescence has been known for centuries, according to old records. Phosphorescence was doubtless the first type of luminescence noted, but the exact date appears to be lost in the antiquity of history. The color change of certain solids and liquids in transmitted and reflected light, now known as fluorescence, was first termed *epipolic dispersion,* because the maximum strength of the color appeared to originate from the surface.

The fluorescence of fluorite from England was scientifically recorded as early as 1824, but was first intensively studied by Sir George Stokes in 1852. Stokes used the green fluorite from Alston Moor, Cumberland, England, for his experiments. He disliked the cumbersome phrase "true inner dispersion," then used, and because fluorite exhibited the phenomenon so markedly he suggested the term *fluorescence.* This suggestion met with immediate and permanent approval.

One of the earliest inorganic luminous substances to be generally marketed was calcined barium phosphate, known as *Bologna Phosphorus.* This material was first prepared by Vincenzio Casciarola, a cobbler in the City of Bologna, Italy, soon after the beginning of the 17th century. Casciarola appears to have been an alchemist when not engaged in cobbling, and in one of his many attempts to find the philosopher's stone he calcined powdered barite, found on the slopes of Monte Paterno near Bologna. The resultant preparation, an impure barium sulphide, glowed in the dark with a reddish color after exposure to sunlight· Alchemists welcomed this new addition to their stock of magical materials, and named it "lapis lunaris" or "moon stone", because like the moon it gave out in the dark, light it had received from the sun.

Medieval tomes on natural history not infrequently mention luminous stones. Even if a common source in ancient oriental literature is granted these legends, they can not all be explained by an assumption of an original mistaken idea. Granting this, four explanations — any one of which might be correct for a specific cause — may be advanced to account for luminous medieval stones.

(1) The ancients knew that certain minerals and gems were rendered strongly phosphorescent by exposure to sunlight. (2) The so-called luminous stones were actually rendered phosphorescent by external coatings of some organic oxidizable material, or an inorganic luminous substance. (3) Certain of these stones were perhaps rendered visible in the dark by a lantern placed cleverly in the background as to remain unobserved. (4) The "luminosity" of these stones was actually only the natural scintillating brilliancy typical of some facet cut gems like the diamond.

It appears probable that if the truth were known every luminous stone recorded by the ancients could be explained in any one of these ways. George Kunz held that the only naturally phosphorescent gem the ancients could have known was diamond. Luminous minerals were probably known to ancient peoples. An instance of this is the suggestion that the "chrysolampis" of Pliny the Elder was luminescent green fluorite. Berthelot, the great French chemist of the last century, believed that luminous stones of the ancients were really non-luminous minerals rendered temporarily phosphorescent by external applications of some such slowly oxidizing organic matter such as a paste of fish entrails. However, as materials of this kind would have produced only a relatively faint glow rather than the lamp-like brilliancy mentioned in many of the older legends, it would seem that this method was used only rarely if at all.

Certain of the early priesthoods, notably that of the Egyptians, are known to have been adept in chemistry, and it is within the bounds of reason to suppose they might have discovered certain luminous compounds, the secret of whose preparation was preserved down through the ages. Stones like the emerald, tourmaline, carbuncle, and others when used to ornament holy icons could have readily been made to appear self-luminous by means of cleverly concealed lamps or candles within the statues. Another means, by which the same impression could have been produced, is special arrangement of lamps within the temple or place of worship. The facet cut gems of holy relics could have refracted fleeting rays of these distant lamps and appeared, to the worshippers, as if glowing with their own fire.

That jewelled ornaments were actually used to produce this effect in the somber obscurity of medieval churches is affirmed by several contemporaneous travellers. It is to be emphasized that all of these explanations, except the first, admit the falsity of reports of luminous stones. It can hardly be doubted that some of these accounts were purely imaginary. Others, as already noted, mistakenly identified refractive brilliancy of certain gems with luminosity in the dark. Others admit deceptive practices to produce the effect of phosphorescence. But even if the great bulk of these accounts were false, a few of them, at least, were bonafide instances of phosphorescent gems and minerals.

EARLY VACUUM TUBE WITH FLUORESCENT SCREEN

Vacuum experimental fluorescent tube made by W. S. Andrews in 1912. The fluorescent material to be tested was reduced to a powder and coated upon a metal cylinder. The cylinder was sealed within the tube and the fluorescent color noted. This early tube is essentially the same as the modern familiar fluorescent lighting tube, except that in the latter the fluorescent powder is coated directly upon the inner walls of the glass tube. The tube illustrated here is probably one of the original fluorescent lighting tubes, but in 1912 its commercial possibilities were not realized.

The great difficulty rests in correctly determining what gems and minerals these might have been, since old terms for minerals, as well as descriptions of their properties differ so materially from our own as to be unrecognizable in many cases. Laufer has stated his disbelief in the idea that the ancients even knew fluorite, much less were acquainted with its luminescent properties. This would appear, on even a basis of circumstantial reasoning alone, to be an unwarranted assumption.

That ancient descriptions of luminous stones do not include mention of minerals at once recognizable as fluorite does not preclude the possibility of that mineral having been known. In view of the fact that ancient peoples, especially the Phoenicians and the Romans, were active in mining for metals and precious stones, and that fluorite occurs in quantity in certain deposits known to have been worked by them, e.g., the tin lodes of Cornwall, it would seem almost certain that they were acquainted with fluorite. The lead mines of Derbyshire, England, were worked by the Romans, and from the famous Blue-John mine, located near Castleton, they obtained the beautiful purple fluorescent fluorite. This fact is proved by vases carved from fluorite and found in the ruins of Pompeii. Some archeologists believe the famous murrhine vases of the Romans were fashioned from fluorite from England. While this, of course, does not prove that the Romans, or other ancient peoples were acquainted with the luminescent properties of fluorite, it does indicate that they knew certain of its physical properties to enable them to fashion works of art from this highly cleavable material.

E. Mitchell Gunnell is of the opinion that ancient man knew of the phosphorescence of fluorite; that the discovery was made purely by accident when some of the mineral along with lead ores was subjected to a crude smelting process. Gunnell also believes that at least certain of the ancient references to luminous stones refer to fluorite. These points are of course debatable and probably impossible to prove with certainty, but they do have the backing, at least, of strong circumstantial evidence.

Sir David Brewster, in 1833, passed a beam of sunlight, concentrated by a lens, through an alcoholic solution of chlorophyll contained in a transparent vessel. He was puzzled to note that the light, as it emerged, was the color of the solution while its path through the solution was a bright red. Supposing that this phenomenon was caused by solid particles held in suspension in the liquid, he called it "internal dispersion", a term later supplanted by "fluorescence" applied by Stokes. Brewster obtained similar results with fluorite and several other substances.

Sir John Herschel, in 1845, found that when a solution of quinine bisulfate was viewed by transmitted sunlight, the solution remained colorless except for the thin layer at the top which emitted a beautiful sky-blue light. Herschel named his phenomenon "epipolic dispersion" or surface dispersion, a term also supplanted later by fluorescence, coined by Stokes.

From the conclusions of Brewster and Herschel it is apparent that the true nature of the phenomenon was not recognized. In 1852 Stokes recapitulated the whole matter and concluded that the observations made by Brewster and Herschel could be referred to the same cause, there being a difference, however, in the effect produced by the medium through which the rays passed before acting on the specimen, and which brought about the different results noted. Stokes was convinced that such results could only be explained as due to polarization or a change in the refraction of light. The former alternative was soon eliminated as a possible cause. To test the second alternative supposition he produced a luminous spectrum, through the color bands of which, he moved a tube of quinine solution. No change in color could be observed in the solution until he reached about the middle of the violet region, when a bluish light began to appear as if the solution, at that point, became self--luminous. The blue color became more intense as the tube was moved farther into the violet region and continued to do so until the tube had been moved some distance into the dark space beyond the violet, i.e., the ultraviolet region. This experiment demonstrated that by passing light through particular media certain invisible rays, belonging to the violet regions, have their nature changed so as to be emitted as longer waves which appear in the visible spectrum.

Studies on the duration emission of luminescent substances began with E. Becquerel in about 1859. In the course of his investigations Becquerel devised the phosphoroscope which he immediately applied to the study of uranium compounds with results not otherwise obtainable since his unique approach used principles not entertained by methods of others of the time.

Kunz and Baskerville, in 1903, made the first modern and comprehensive examination of mineral species for fluorescence. They exposed to ultraviolet rays, X-rays, and radium radiations, over 13,000 specimens in the collections of the American Museum of Natural History in New York City.

The British Museum of Natural History, London, in 1903, made the first public exhibit of fluorescent minerals available. Radium radiations were used to excite a small number of specimens. Liebisch, in 1912, investigated the fluorescence of the minerals of the sodalite and willemite groups. The work of Liebisch, is of importance in calling attention to one of the few (sodalite) groups of minerals in which all members are fluorescent.

In 1912, E. Engelhardt, made a comprehensive survey of the distribution of fluorescence in minerals excited by ultraviolet radiations. He presented a list of over 400 specimens including 147 species, that fluoresced or phosphoresced, or both, when exposed to ultraviolet rays with a maxima at 3500 A. U. The compositional distribution of these fluorescent minerals (see table) is interesting.

Compositional Distribution of Fluorescent Minerals.

(*According to Engelhardt*)

Native elements	2
Sulfides and sulfo-salts	3
Oxides	13
Halides	12
Carbonates	18
Sulfates, chromates, etc.	23
Borates, aluminates, ferrates	4
Phosphates and arsenates	13
Silicates and titanates	17
Organic minerals	6

W. P. Headden, in 1906, started his important studies on the fluorescence and phosphorescence of calcite from Joplin, Missouri. Headden concluded that the phosphorescence was due to the presence of salts of the yttrium group of the rare earth metals. In 1927, J. L. Spencer of the British Museum, described the fluorescence of willemite and other zinc minerals. Spencer assented to the general belief that fluorescence ability was due to the presence of admixed impurities. Van Horn (1933) examined tungsten minerals under the iron arc.

Numerous investigations immediately related to mineral luminescence have been carried out in recent years. Although it is impossible to present resumés of all these studies, the important researches of Edward L. Nichols and Ernest Merritt, in 1912, in the physics laboratories of Cornell University are of historical significance. Investigations of this type laid the foundations for more objective research later.

Reference is made throughout the work of the present writers to researches by investigators who studied fields pertinent to luminescence. The Author Index indicates both an increasing interest in all types of luminescence, as well as numerous new applications of ultraviolet light in the sciences, arts, and industries.

CHAPTER TWO

RADIATION — COLOR — PERCEPTION

Radiation

It is rather apparent that energy is about the most important thing in the world. It may be regarded as primordial when in the form of radiant energy or energy of the sun as it is more commonly known. The transference of energy by emitted waves or particles is known as radiation. The kind of radiation considered herein is primarily radiant energy and is regarded as the basic form of all others provided, of course, conversion occurs with the aid of the devices of man as well as by nature.

Visible light is a form of radiant energy, as are the other kinds of radiation like X-rays, radio waves, and heat rays. Visible light, as well as the others, has certain well defined properties which delineate it as something individual and different from anything else in the universe. That is, it is set apart from all other things by the two important characteristics of rectilinear propagation and velocity. Since rectilinear propagation (travel in straight lines) is not characteristic of light alone we further depend on velocity to more specifically define light. This tremendous velocity, seemingly infinite but quite definitely finite, is approximately 186,300 miles per second.

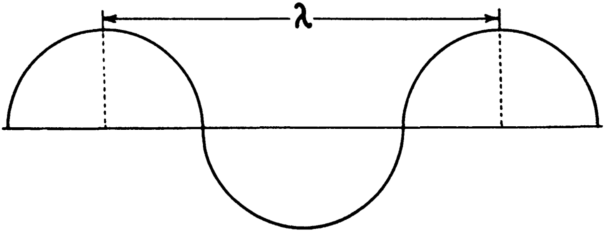
Light diffuses in all directions from its origin and appears to be emitted in minute quantities called quanta. These quanta may be compared to tiny bullets of energy, but quanta of radiant energy are only the units in which light is emitted or absorbed; it is transmitted in another form, one which is not fully understood although partially explained by a theory propounded by Huygens in 1678.

Huygens stated that a luminous body caused a disturbance in a hypothetical medium which he termed the *luminiferous ether,* but which has since been shortened to ether. This disturbance travels through the ether in the forms of waves and on reaching the eye produces the sensation known as vision.

Another theory, presented by Newton described the action only in terms of small bodies called corpuscles. These corpuscles may be regarded as similar to quanta. While the corpuscular theory is in disrepute among some physicists it has been recently revived and several fundamental points extracted from it and combined with Huygens' wave theory. Probably the combination of both theories explains the phenomenon more adequately than either theory used alone. Therefore, the wave motion should not be regarded as continuous, but imagined more as minute quanta or bundles of light.

Further refinements in theory were made by Maxwell when he termed the ether an elastic media which transmitted transverse waves called electromagnetic waves. These waves were postulated to have both electric and magnetic properties and were improved upon by Einstein in 1905. Einstein showed that the ether was not necessary for the propagation of electromagnetic waves but instead electromagnetic vibrations could be propagated through empty space.

A wave motion is a periodic disturbance transmitted continuously from one portion of the ether without motion of translation—sideward or lateral motion. The stereotyped example of wave motion produced in water by throwing a stone into a pool causing the up and down movement of a stick of floating wood aptly illustrates this.



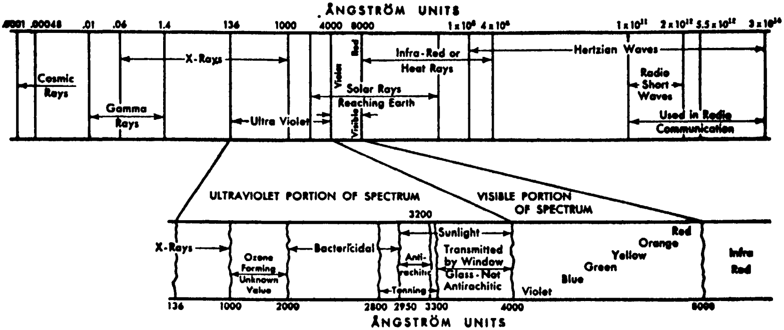
ILLUSTRATING WAVELENGTH

While the actual particles of the medium, those of the water, have no motion other than simple perpendicular oscillation the indicator, a stick of wood, merely moves up and down and is not carried along with the waves or ripples.

In the case of quanta, imagine a long trough being filled with water in one end and dripping out the other end. The drops represent quanta and it is rather obvious that while the drops enter and leave the trough as individuals, they lose their identity while passing through the trough. Light quanta behave in a similar way. The axis upon which a beam of light travels is called a ray, a purely mathematical concept useful in calculations on light. If we closely examine the actual path of a quantum of light we find that these oscillate on an axis in a series of waves. Upon the amplitude and frequency of these oscillations depends the intensity and color of the rays as we see them, provided they are in the range of our vision.

In comparing the two main theories which attempt to explain the nature of light, note that in Newton's corpuscular theory, light should travel faster in the denser medium, while in the wave theory, light should travel slower in the denser medium. Later, nevertheless, Foucalt and Fizeau found the velocity of light in a dense medium like water to be less than the velocity in a vacuum. The main reason for the popularity of the wave theory during the latter part of the nineteenth century was probably due to the re-enforcement obtained by the studies of Young, Fresnel, and Arago on the interference and diffraction of light. Since it is obvious that the theory accepted is the one which explains all the known phenomena of the time better than other theories it is apparent that the wave theory held superiority. Although the wave theory could explain the better part of the optical phenomena known then, its inadequate explanation of many optical phenomena at the present time makes its singular use unsatisfactory. It is important to note, however, that although radiation possesses dual characteristics it never exhibits both in one experiment. It exhibits either the properties of particles or the properties of waves.

Some consider the velocity of light one of the invariable constants of nature although others point out experimentally that the velocity of light does vary appreciably. The velocity of light is denoted by the symbol c. Furthermore, this constant, c, appears in the most unexpected physical calculations at the most unexpected times and, at least for the present, for no apparent reason.



THE ELECTROMAGNETIC SPECTRUM

Showing the position of ultraviolet radiations and the range of human vision as measured in Ångström Units. The exact nature and actions of the radiations between 1000 and 2000 A. U. is not known with certainty.

We speak of light waves as being long or short but these terms are meaningless without a tangible standard of comparison. Since it is known that the velocity of light from any region of the spectrum is the same it follows that the wavelength of light varies inversely as the frequency. More simply this means that for radiations or light of a high frequency a short wavelength will be had by the same wave. Correspondingly, with waves of a low frequency a long wavelength will be had.

Universally, and for practical purposes, the wavelength of light is expressed in fractions of a centimeter. The quantity used in most instances is that called the *Ångström Unit* after the noted Swedish physicist Angström. This, however, is not the only unit to express the distance between the crests or the troughs of a wave, i. e., wavelength. Others have been proposed and adopted as may be seen in the table.

Wavelength Units

Name	*Symbol*	*Value*
Micron	Å or A.U.	1 Å = 10^{-7} mm.
Ångström Unit	Mμ or mμ	1 mμ = 10^{-6} mm.
Millimicron	μ	1 μ = 0.001 mm.
X-Unit	X.U.	1 X.U. = 10^{-10} mm.

Formerly it was thought satisfactory to express wavelength in terms of microns, millionths of a meter. When this unit is used the wavelengths in the visible and ultraviolet regions are expressed in fractions. To avoid this, some investigators use the millimicron, one-thousandth of a micron, for expressing wavelength. By using this unit the wavelengths in the visible region may be expressed in whole numbers. For general work in radiation, wavelength expressed with three significant figures is usually adequate. Further complexity occurs in wavelength measurement when the Ångström Unit is used in so far as it has been difficult for workers to adopt a standard unit. In addition, the introduction of X-ray spectroscopy caused workers in that field to adopt the X-Unit, one X. U. = 0.001 A. U. So it is rather apparent that care must be used to express wavelength which of course, in any case, is in the centimetergram-second (C. G. S.) system of values. However, the most practical unit for ordinary purposes, and the one to be encouraged, is the Angstrom Unit.

The use of wavelength (λ) instead of frequency (ν) is generally to be preferred for expressing periodicity of radiation. As has been noted previously, wavelength is the distance between two crests or two troughs in a wave, or, according to J. W. T. Walsh, wavelength is the distance which separates consecutive points undergoing the same displacement.

Frequency denotes the number of oscillations per second while the amplitude of the wave is the extent of an oscillation. As the wavelength of light may be measured with considerable precision it follows that the frequency may be expressed by the simple relation.

$$\nu = \frac{c}{\lambda}$$

The reciprocal of wavelength is known as the wave number (N) and since it is directly proportional to frequency can therefore be used exactly as frequency would be used. Wave number denotes the number of waves per centimeter. The fundamental quantities may be further related by the simple relationship

$$c = \nu \lambda$$

COLOR

Only in a small portion of the spectrum are there radiations immediately visible to the eye. In all treatments of light and color one must not forget that there is no such thing as external and objective color but that color is merely the interpretation given by the brain to certain physical phenomena. In the process of seeing color an excitation of the retina, and subsequently the brain occurs. However, excitation of these may be also brought about by pressure on the eyeball, electrical discharges, by internal causes, and pre-eminently by that small band in the spectrum known as visible light. Color, however, originates in every instance by the impingement of visible radiations on the retina of the eye instead of by the other modes presented.

In spite of the fact that Alhazen in 1000 A. D. knew much about the properties of light he could only vaguely conjecture concerning vision and the way in which light reaches the eye from external objects. It was not until Huygens presented his wave theory that the first real approach was made.

Color is defined according to the conditions which specify it. Luckiesh, for example, regards color as psychologically, a sensation; physically, existent potentially in light or radiant energy; practically, produced by the selective emission of light in the case of the primary light source, or by selective absorption of light in the case of a reflecting or transmitting substance.

Of the considerations given by Luckiesh the physical explanation is of prime importance. In this is the visible region of the spectrum consisting of the familiar rainbow spread of blues, greens, yellows, oranges, and reds. The light above the red and below the blue in wavelength is, of course, invisible to the eye. White light consists of a mixture of all these colors. This is demonstrated by passing a ray of white light through a prism and noting the spectrum produced. This was performed in 1666 by Newton who projected a beam of sunlight on to a screen into a dark room, the beam had been previously passed through a glass prism. Newton, for the first time, demonstrated the true nature of light and at the same time laid the foundations for present day investigations into the properties and actions of light.

Imagine that a substance such as cinnabar, mercuric sulfide, is red by both transmitted and reflected light. Since the white light that falls on cinnabar is a mixture of all the colors in the spectrum, the part retained by absorption, either during transmission or while being reflected, is the remainder of the spectrum while the red is passed onto affect the eye. This is a simple illustration of the color mechanism although examination of the red light with a spectroscope may prove it to be other than pure red.

The nature of the surface of the object often has an influence on the color of an object. If the surface is rough or finely divided it may produce multiple reflections between the particles and appear to be of a slightly different color from that of the surface if the sample were smooth.

In essence it is rather apparent that the reason all objects, which we see, are visible is because the object is either luminous itself or is illuminated by other objects which in turn are either luminous or illuminated. In other words, the reason we see an object is because it emits its own light or passes light on, being reflected partially or in whole from another source.

When light strikes an object two actions may occur to determine color. The light may be absorbed partially or wholly, or the light may be reflected by the object either in part or in whole. In other cases a third action may occur; that when light falls on an object its color is determined by processes during transmission, provided, of course, observation is through the substance. Further complexity ensues by combinations of these or in rarer actions known to produce color in certain instances.

HUE AND WAVELENGTH
(*Abney*)

Hue	*Wavelength, A. U.*
Red	End to 6200
Orange	6200 to 5920
Yellow	5920 to 5780
Green	5780 to 5130
Blue-green	5130 to 5000
Blue	5000 to 4640
Ultramarine	4640 to 4460
Violet	4460 to End

According to Luckiesh, the three qualities of color are hue, saturation, and brightness, and these together with shade and tint are necessary to complete an effective description of color. He measures hue by wavelength, saturation by the presence of white, and brightness by a factor called the transmission coefficient which is used in the case of transparent materials and reflection coefficient in the case of opaque materials.

The primary consideration in hue is its relation to wavelength. Assuming that light of a certain wavelength affects human beings similarly, as it does for most persons, we may ascribe the phenomenon of hue to the wavelength of light. Since hue is color and hue is the predominating factor in a color mixture we may conveniently refer hue or color to wavelength for a more exact description.

The color that must be added to a hue to produce white or gray is known as a complementary color. It can best be described as a completing color, or, is often called the contrasting color. Therefore, a color and its complement complete the spectrum. However, considerations for this involve color addition in the correct intensity and quantity for the production of white. Complementary colors may be illustrated better on the familiar chromatic circle consisting of the placement of the three primary colors so that their complements are opposite and white originates in the center.

Brightness is also ascribed to the position between black and white; tint is the brightness term that covers colors mixed with white and shade is the brightness term that covers colors mixed with black. Likewise, the power of a color is called its strength since some colors appear stronger than others.

RELATION BETWEEN RADIATION, COLOR, AND LIGHT

(Rept. Jour. Opt. Soc. Amer. Prog. Comm. 1922-23)

Physical Phenomenon	*Objective Stimulus*	*Subjective Response*
Radiation	Light	Color
Intensity	Brightness	Brilliance
Wavelength	Dominant wavelength	Hue
Wavelength	Purity	Saturation

PERCEPTION

With the comparatively unimportant exceptions of certain methods of spectrophotometry and electrophotometry, all descriptions of fluorescence depend ultimately on the use of the human eye.

It is evident that the more fluorescent a body is, the more intense stimulation it produces in the apparatus of vision. The intensity of sensation, however, is not directly proportional to the intensity of the luminescence of the object. Also, a light stimulus must be of a certain strength before it can excite vision but the limit of excitability of the retina may not be fixed. The minimal amount of light stimuli required to produce a reaction on the retina is known as the *threshold*; this does not, however, depend on the absolute changes in intensity of the stimulus, but is proportional to the stimulus already acting according to Weber's Law.

In Weber's Law an increase in stimulus sufficient to call forth a conscious increase in sensation must always bear the same ratio to the original strength of stimulus to which it is added. Although the exactness of this law is sometimes disputed it seems to be generally accepted that for a median range of stimulation the law express an approximate relation between the two variables considered.

THE EYE

For ordinary purposes the eye may be regarded as a camera-like instrument, ellipsoidal and nearly globular being about 23 mm in diameter. The tough white outer coating on the eye which protects it from trauma by mechanical means, as well as radiation, is called the sclera. The sclera is opaque to light and extends over the surface of the eye except where light enters and in the rear portion of the organ. Where the light enters the eye the sclera is modified to a transparent cartilaginous membrane called the cornea which is more convex than the sclera. Of the accessory organs for protection of the eye the sclera is of importance but not necessarily of primary significance.

A second coat lies under the sclera. This, the choroid coat, is much more delicate and consists almost entirely of blood vessels and nerves. The colored choroid coat prevents entrance of stray light into the eye which might interfere with vision. On the front of the eye this coat is modified to form the iris which has the function of a shutter capable of regulating the amount of light which enters the eye. The aperture itself is known as the pupil. About the circumference of the cornea the choroid coat is considerably thicker and folded in the modification known as the ciliary apparatus. When a very bright object is examined the iris acts as a diaphragm to shutter down or reduce the size of the pupil and prevent injury to the inner eye.

The interior of the eye contains a light sensitive coating known as the retina. In use the light first passes from the space between the lens of the eye, situated behind the cornea and iris suspended by an arrangement of muscles, and the retina, into a layer of sensitive rods and cones. In the rods and cones, together with the several outer layers of the retina, the probably multiple actions which occur when light strikes the rods and cones are only partially known.

The nerve fibers of the retina originate in the optic nerve situated in the posterior central portion of the organ. The optic nerve, as is well known, terminates in the brain. Hence, we really see with our brain instead of our eyes.

The interior of the eyeball is filled with three transparent media, the first of which is contained in the space between the cornea and the crystalline lens. This media is nearly pure water and has a refractive index of 1.33 while just behind the iris is a lens formed of a material formed of a material like colorless soft gristle. The lens has a refractive index of 1.45 at the center and changes to 1.41 at the edge so that the effective refractive index is 1.43. Th crystalline lens, as it is called, is double convex and has greater convexity on the posterior surface than on the anteior surface. The third medium, enclosed between the crystalline lens and the retina is a thin jelly called the vitreous humour and it has a refractive index of 1.33.

The important structures, rods and cones, possess two distinct parts. One, the inner limb, is cylindrical and the other, the outer limb, is conical. Five million of these are connected to each other by a fine nerve fiber. The rod and cone layer rest on a layer of black pigment cells called the Pigmentum epithelium. When illumination of the retina occurs the cones shorten and become thicker and the tips recede from the normal unilluminated position. In addition, a fluid flows around the rods and cones, this fluid is extremely photosensitive and is ordinarily a deep red-purple color but on exposure to light is bleached. The rate at which this chemical is bleached by radiation of different frequences is proportional to the sensitivity of the eye to light of those frequencies.

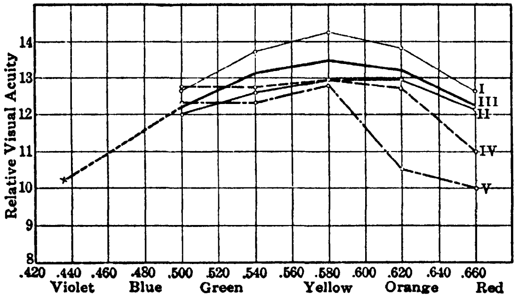
In the center of the retina is the macula lutea, the region where the rods and cones are numerous. Towards the center, however, the rods disappear entirely at a region called the fovea centralis which is the point of sharp or distinct vision. Over the other parts of the retina the proportion of rods to cones steadily increases with the distance from the macula lutea until at the periphery they preponderate in a ratio of about 10 to 1.

It is common knowledge among those who work with fluorescent screens in X-ray and radium research that to allow the eye to fully see any feeble luminescence of such a screen the observer must remain in the dark for a period of time. This is to allow the pupil to assume a condition of dilation or mydriasis. In such a state the pupil allows more light to enter the eye and while ordinary alterations in the size of the pupil normally occur when one passes from a light region into a dark region other things such as emotional states and drugs may cause mydriasis.

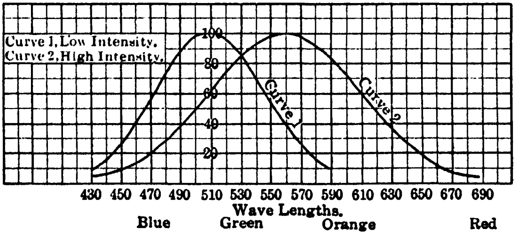
It has been pointed out by several investigators that before a fluorescence observation, especially in feebly excited specimens, that the observer remain in a dark room for a period of time which varies as to the case and to the observer. Guyot, Radley and Grant (1933) recommend periods of as long as five minutes. De Ment (1940) used periods of between 20 and 120 seconds depending on the type of specimen, intensity of fluorescence, and the source used. Farnau (1912) remained in a dark room for a half an hour before making observations in crystalloluminescence. Newcomer (1920) mentions the importance of allowing pupillary accommodation to occur before examining specimens for fluorescence in X-rays.

The disputation of Weber's Law resulted in a refinement called Fechner's Fraction. This relationship, enunciated in 1858, states for the sensation to increase by equal amounts, that is, by arithmetical progression, the stimulus must increase by geometrical progression. Related to Fechner's Fraction is the work of Steindler, Jones, and Nutting on the *limen*. A limen is the least difference of wavelength necessary to cause a perceptable change hue. The investigations of Konig and Brodhun demonstrate that Fechner's Fraction is fairly constant for over a fairly wide range but ceases to hold for lower values. In connection with this, for moderate intensities of light the results of the above two investigators agree with Weber's Law and the minimum value of the latter holds practically for most colors provided the intensity is moderate.

Even when a standard of comparison is available, the eye alone cannot give satisfactory quantitative measurements of brightness. Furthermore, the brightness of an object determines to some extent which details may be distinguished. Individuals vary widely in their visual acuity especially for red and green light, as has been demonstrated by Dow. The eye itself, as a receptor, is not equally sensitive to radiation of all wavelengths. That is, the amount of visual sensation produced by red light is not the same as the amount of visual sensation produced by yellow light. No objective form of equality may be obtained since radiations of different wavelengths produce different color effects on the visual apparatus, as well as different intensity sensations. The relative luminosity of the various regions of the spectrum depends on the eye, the region of the retina affected, the nature of the media interposing the source,



VARIATION OF VISUAL ACUITY WITH WAVE-LENGTH OF LIGHT. (*Barrows*)



LUMINOSITY CURVES FOR UNIFORM DISTRIBUTION OF ENERGY. (*Barrows*) the source, the type of dispersion, and, likely, on the psychological characteristics of the individual observer.

Newton regarded the spectrum as having seven primary colors when the means of resolving white light into its components was discovered. Later it was found by others that the number of different hues in the spectrum was from thirty to fifty for persons of normal vision. Recently, with refined means of technique and superior instruments, some 125 separate hues have been detected in the complete visible spectrum.

According to Charpentier, the sensation of color is lost before the sensation of light, especially for shorter wavelengths. Many investigators term the interval between the threshold of light sensation and the lower limit of color perception, the photochromatic interval. On the opposite end of the scale there is a tendency for all colors to become a yellowish-white provided their intensity is great enough.

The electromagnetic spectrum is large indeed and it is striking to note the amount of energy used by man in it. Melhase pointed out that all living organisms, including man, have developed and ascended the scale of evolution in proportion to the range of energy they have utilized. Man has utilized heat energy through his development of a nervous system; he has developed ears to rationalize waves of sound energy; the eyes intercept waves of light energy; and most important, he has developed brain cells with which to rationalize these stimuli and convert them into sensations of feeling, hearing, or seeing.

CHAPTER THREE

TYPES OF LUMINESCENCE

Luminescence is the emission of energy, as visible light, from a substance influenced by an exciting agent. It is the general term applied to light which is independent of incandescent heat; moreover, luminescence covers all forms of light radiation excepting those proper to a radiating body by virtue of its temperature. When a substance is luminescent by virtue of its temperature it is termed incandescent or candoluminescent.

Luminescence for practical consideration is of two kinds although theoretically these two kinds are identical in every respect except the lifetime of the excited state. *Fluorescence,* the transient phenomenon, is the emission of light only as long as the exciting agent is present. If the emission of light persists after the exciting agent has been removed the action is termed *phosphorescence.* In fluorescence the emission of light stops at almost the same instant as when the exciting agent is removed. In phosphorescence the emission of light continues for seconds, minutes, days, or even months after the exciting agent has been removed. Or, according to Hirschlaff, the distinction between fluorescence and phosphorescence is phenomenological and historical rather than scientific. It is arbitrary to discriminate since in each, luminescence is due to the transition of an electron caused by the absorption of a quantum of light.

Luminescence is classified according to the exciting agent causing either the fluorescence or the phosphorescence of a substance. Both occur, in some instances, in the same specimen although phosphorescence is less frequent than fluorescence. The discrimination between the two is sometimes limited by the visual acuity of the eye and on principles discussed elsewhere. However, luminescence in minerals is excited by practically all the agents listed excepting, of course, changes which involve tissues or require special agents unrelated or adaptable to this form of luminescence, e.g., bioluminescence in the firefly or in other light producing animals.

Excluding ultraviolet fluorescence, the most well known form, the others are usually less extensive and, in some cases, related since the agents which excite luminescence are often analogs, i.e., gamma rays from a radioactive source and X-rays differ only in wavelength; likewise, cathode rays and beta rays differ only in velocity being otherwise identical. Of the types of mineral luminescence other than that produced by ultraviolet light, thermoluminescence is of importance.

TYPES OF LUMINESCENCE

A—*Excited by the Electromagnetic Radiations*

1. Ultraviolet radiation (black light)
2. Infra-red radiation (heat)
3. Visible light
4. X-rays
5. Electrical waves
6. Gamma radiation
7. Hertzian waves (radio waves)
8. Infra-Roentgen rays (Grenz rays, long X-rays)
9. Schumann and Lyman radiation (short ultraviolet rays)

B—*Excited by Streams of Moving Particles*

1. Cathode rays
2. Beta rays
3. Alpha rays
4. Anode rays
5. Molecular beams
6. Neutron and Deuteron beams
7. Ions different than these.

C—*Excited by Changes in Physical Systems*

1. Friction with an unlike substance
2. Friction with a like substance

3. Crystallization
4. Cold
5. Pressure
6. Mechanical
7. Ultrasonic waves (sound waves)

D—*Excited by Changes in Chemical Systems*

1. Special types of oxidation
2. Other special changes in organic systems
3. Other special changes in inorganic systems
4. Flames
5. Electrolytic

E—*Excited by Miscellaneous Agents*

1. A combination of one or more of the above agents
2. Lesser known actions related or unrelated to these agents

THERMOLUMINESCENCE

This less common form of mineral luminescence is produced when substances are heated to temperatures below ordinary redness. Thermoluminescence does not imply that materials are heated so as to become incandescent. Moreover, it is known definitely that heat, as such, is not the cause of the luminosity but, instead, acts only as a mechanism to release energy previously stored in the mineral or other substance from exposure to light or by some other process.

In testing for thermoluminescence the common procedure is to heat a small fragment of the specimen on a small electric hot plate or over a non-luminous flame, in a metal dish. Tests are conducted in a dark room. As the temperature rises the luminescence appears and on approaching red heat the luminescence disappears. Northup and Lee (1940) found that with few exceptions the light emitted was of only one color and was usually preceded by a dim white glow at low temperatures when the thermoluminescence first became visible. At higher temperatures they found that in a few minerals a similar white glow could be seen but, more often, the principle thermoluminescent color was faintly visible up to extinction.

It is usually convenient to use samples several millimeters in diameter or slightly larger. Too large a specimen will not become uniformly heated and too small a specimen quickly becomes heated to incandescence and obscures thermoluminescent action. For minerals which decrepitate, such as fluorite and calcite, it is best to perform the examination in a test tube, otherwise a heated metal plate should suffice for the test. Testing a large number of specimens of the same mineral species will doubtless disclose that some are thermoluminescent while others are not. This indicates that the cause of the thermoluminescence, whether it is physical or chemical, is foreign to features which determine properties characteristic of mineral species.

Thermoluminescence has been investigated extensively. Probably one of the earliest such studies was by Du Fay who in 1726 mentioned green fluorite, quartz, and calcite as brilliantly luminescing when gently warmed. Other substances that begin to emit light at temperatures of well below 525°C. are certain varieties of fluorite, diamond, marble, hackmanite, wernerite, calcium-larsenite, calcite, and fluorapatite. Investigation on the thermoluminescence of several thousand specimens was performed by Leon. He endeavored to establish a relationship between the color of the thermoluminescent light and the composition of the mineral. It was found that minerals rich in calcium carbonate showed an orange to yellow luminosity, phosphates a green color, and sulfates a blue glow. Few instances of red luminosity were observed and no relationship to chemical composition could be drawn. Calcite has also been examined by other investigators. In 1906 Headden observed that of the various colors exhibited by calcite from Joplin, Missouri areas, the deep yellow variety gave the most brilliant thermoluminescence. Analysis indicated that this variety contained a greater amount of the rare earth oxides of the yttrium group of metals than did the colored, less phosphorescent kinds. Headden attributed thermoluminescence in this calcite to activation by yttria or some other oxide of the same group. Some years later Pisani confirmed Headden's observations on the distribution of brilliant thermoluminescent properties in Joplin calcite but disagreed with the latter's conclusion that yttria was the activating agent. He analyzed various highly luminescent calcites from French, German, and English localities and found that none contained rare earth elements. In 1923 Headden published further papers on the subject and advanced the opinion that the luminescence ability of Joplin calcite was due to atomic structure rather than chemical composition. The fundamental observation as well as the basis for this was the behavior of the calcite after exposure to radium. Heating the thermoluminescent sections to about 400°C. destroyed both color and ability to luminesce when heated again. The exposure of such deactivated specimens to radium radiations restored both color and ability to luminesce. Similar treatment of originally·weakly thermoluminescent varieties developed the yellow color and high phosphorescent properties characteristic of most thermoluminescent sections. Wick noted that previous exposure of the specimen to radium emanation intensifies the thremoluminescence of many minerals. Przibram and his associates obtained similar results.

In 1909 Urbain examined specimens of fluorite spectroscopically, and found traces of certain rare elements. He inclined to the belief that one or more of these elements activated luminescence. Several years before Humphreys examined specimens of fluorite from more than a hundred different localities in order to determine the distribution of yttrium and ytterbium in this mineral. He observed that the three richest specimens in both elements were all highly thermoluminescent. This seemed to indicate that these elements were responsible for the luminescence.

Thermoluminescence appears to be most common in non-metallic, anhydrous, and crystalline minerals and these characteristics, along with a good cleavage, also seem favorable for the production of triboluminescence.

CATHODOLUMINESCENCE

The impingement of streams of electrons or cathode rays on certain minerals produces luminescence. The fluorescence of willemite and kunzite while subjected to cathode rays is an example of cathodoluminescence. In the production of luminescence by cathode rays, certain apparatus is used and on this apparatus often depends the success of the study.

In testing, a V-shaped glass tube is used with metal electrodes sealed in either arm. The mineral sample is placed in the apex of the tube which has a side arm provided so that a vacuum pump may be attached and the entire system evacuated. On the application of an electric current, at high potential, a stream of cathode rays or electrons is produced and these impinge on the specimen. Under the bombardment of the rays the sample, if excitable, will luminesce. The potential difference applied between the electrodes in such a tube is of the magnitude of several thousand volts, usually more and not often less. In the apparatus used by T. Tanaka, cathode rays were produced in a special vacuum tube carrying a 0.4 milliampere current at a potential of 4000 volts. An exhaust pump was used to reduce the pressure inside of the tube. For observing cathodoluminescence the greatest care is used to exclude stray light and in some instances special auxiliary apparatus is used for determinations of luminosity.

Cadmium sulfate has an intense cathodoluminescence, somewhat less brilliant than that of willemite. Aragonite from Arizona luminesces a green color while other samples of the same mineral luminesce a brilliant orange color. The chief activating agent in the luminescence of calcites, crystalline limestones, and dolomites is usually manganese and generally their luminescent color is orange-red or orange. In these minerals luminescence is generally faint since oftentimes manganese does not show a prominent luminescence power. Fluorites cathodoluminesce violet, blue, and green. When heated and re-examined they luminesce an orange color in some cases. Fluorite from Castleton, Derbyshire, England luminesces a yellow color while samples obtained near Rosiclare, Illinois fluoresce a bright blue color of medium intensity. Pure alumina is non-luminescent but the addition of chromium causes the varieties, spinel or corundum, to luminesce red. Corundum from Craigmont, Ontario gives a faint green luminescence while samples of artificial ruby often luminesce a beautiful green color. Heating a sample of spinel to red heat for a half an hour changed a previously non-luminescent specimen to one with a beautiful greenish luminescence.

According to Lecoq most spinels show a red cathodoluminescence although others show green. If artificial spinels are prepared with traces of either manganese or chromium, green and red luminescence is produced respectively. He attributed the luminescence of spinels to those metals which caused the color in artificial specimens. One of the most strongly cathodoluminescent minerals is willemite. The investigations of J. J. Thompson on positive rays (canal rays, anodoluminescent agents; the rays opposite in charge to cathode rays) owe their success partly to the existence of this highly luminescent material. The origin, according to Nichols, of the luminescence in willemite has been investigated by relatively few. Its luminescence color is always yellowish-green although its natural color varies widely.

SOME CATHODOLUMINESCENT MINERALS

(*Nichols*)

CALCITES	
Westchester Co., N. Y.	Medium intense orange
Mahopac Mines, Putnam Co., N. Y.	Faint orange
Tomkin's Cove, N. Y.	Medium intense orange
Long Hill, Conn.	Faint orange
Mahopac Mines, Putnam Co., N. Y.	Bright orange
Rockland Co., N. Y.	Medium intense orange
Cumberland, England	Bright red-orange
Colorado	Faint orange
Franklin, N. J.	Intense red-orange
Lowville, N. Y.	Very bright orange
CRYSTALLINE LIMESTONES	
Amawalk, N. Y.	Medium intense orange
Verplanck's Point, N. Y.	Faint orange
Aragonite, Arizona	Green then white

Dolomite, Manchuria, China	Faint orange
Dolomite, Manchuria, Chian	Medium intense orange
Magnesite, Manchuria, China	Medium intense red
FLUORITE	
Derbyshire, England	Yellow
Vassar College	Violet
Vassar College	Bright indigo
Rosiclare, Ill.	Medium intense blue
Cumberland, England	Blue
New Hampshire	Violet-blue
Unknown	Light yellow
CORUNDUM	
Craigmont, Ontario	Faint green
Franklin, North Carolina	Faint greenish
KUNZITE	
Pala, Cal.	Bright orange
Unknown	Bright orange

TRIBOLUMINESCENCE

Triboluminescence is the emission of light accompanying a frictional action such as rubbing, scratching, breaking, or crushing. It has also been called piezoluminescence. Early workers thought the cause of this luminescence due to minute particles in the mineral becoming raised to a glow by heat of friction. That this was not the case, however, was proven as early as 1792. Since the beginning of the present century much work has been done on the subject, many substances studied, and several theories advanced to explain the phenomenon. In 1908 Karl studied certain synthetic triboluminescent substances and concluded that the property was peculiar to solid solutions of a certain degree of dilution containing an activating material known as a triboluminogen.

Fused calcium chloride, Romberg's "Phosphorus", if rubbed on the sleeve will glow with a greenish light. Pope found in 1899 that the bluish light emitted during the shaking of crystals of saccharin was intense enough to be seen in daylight. Luminescence appeared, however, only in impure specimens and freshly crystallized samples. Cane sugar, milk sugar, mannite, vanillin, cocaine, benzoic acid, atropine, asparagin, r-tartaric acid, l-malic acid, hippuric acid, and others of a similar nature are triboluminescent. The color of the triboluminescent light from different santonin derivatives varies from yellow to green. Harvey (1917) noted that certain animals are triboluminescent but adds that this has no connection with the nature of animal light.

In a study of over a hundred triboluminescent minerals, Lindener observed that triboluminescence has no connection with chemical composition since it occurs in all chemical classes. He also found that it seems to occur most frequently in crystals having no center of symmetry and that it has no connection with hardness. Triboluminescent minerals are generally brittle and have well defined cleavage. In 1910 Trautz explained this property as due to the discharge of minute electric sparks induced primarily by differences in potential; these differences he attributed to the presence of foreign substances. Further, in 1926 Nelson succeeded in photographing the spectra of triboluminescent minerals. He used fluorite, sphalerite and other minerals. The triboluminescent color of both these specimens was orange. Nelson also photographed the triboluminescence spectrum of an artificial phosphorescent zinc sulfide. He observed that the color of phosphorescence, fluorescence, and triboluminescence exhibited by the same substance appear to be similar.

Sphalerite is one of the most interesting, as well as important, luminescent materials known. It has triboluminescent properties, the first study of which was probably in 1750 by Hofmann who observed that this mineral gave out light when crushed or fractured. His specimens of sphalerite were from Scharfenberg, Germany. The light yellow, granular crystalline sphalerite from Beaver County, Utah also has an exceedingly brilliant orange-yellow triboluminescence. Levison found, in 1904, that this mineral had a triboluminescent spectrum which embraced red, orange, yellow, yellow-green, and green lines. The duration of emission was about 0.02

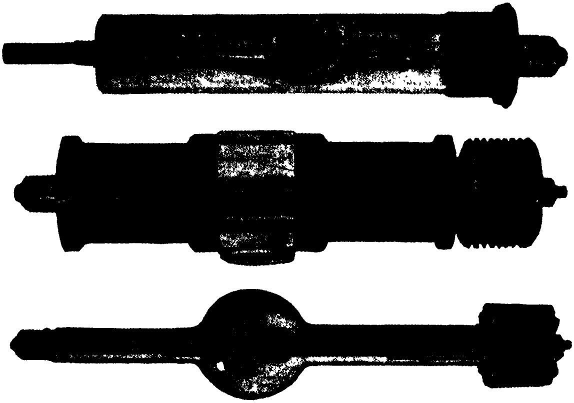
second. Kunz found that the same mineral exhibited radioluminescence when exposed to beta and gamma rays from radium. Spencer in 1927 described a discovery of the now well known granular sphalerite from Tsumeb, Southwest Africa. This exhibited a remarkably brilliant orange-yellow triboluminescence and also fluoresced a strong orange color in ultraviolet light.

Wick found in 1937 that the emission of triboluminescent light closely resembled phosphorescence and low temperature thermoluminescence. This is stated to come from unstable excited centers which may be activated by exposure to radium, X-rays, and cathode rays. The emission is characteristic of the mineral itself and is not dependent upon excitation other than mechanical breaking or crushing. Materials which show marked triboluminescence contain small amounts of impurities which serve as activators as in the case of most other luminescent substances. Certain impurities dominate and others are supressed. The intensity of triboluminescence is affected by heat treatment.

X-RAY LUMINESCENCE

Of historical importance is the luminescence of materials under X-rays. Without this type of luminescence the early discovery of X-rays themselves would not have taken place nor would there be, at the present time, certain methods of fluoroscopy and X-ray photography. When X-rays strike certain substances they may cause fluorescence or phosphorescence, depending on the case. However, the luminescence in either case is not exactly the same as the luminescence caused by other exciting agents. The emitted light caused by X-rays is often ultraviolet light of medium wavelength instead of visible light. However, visible light is also emitted when certain substances fluoresce under X-rays. Gases, solids, and many liquids are affected. A crystal of rock salt will phosphoresce for a half an hour or more after exposure to these rays. The fluorescent differences between diamond and glass have been used to discriminate between imitations and natural specimens.

It was found in 1920 by Newcomer that within a considerable range the fluorescence produced by X-rays is independent of the quality of the X-rays used and is proportional only to the energy alone provided maximum emission occurs as X-ray energy. One of the first investigations into the luminescence of minerals under X-rays was performed in 1915 by Schuhknecht although as early as 1896 Edison found that calcium tungstate fluoresced more intensely than did the platinocyanides under X-rays. Edison examined 1800 substances and obtain 72 with a good luminescence. It was, of course, due to the fluorescence of barium platinocyanide under X-rays that the discovery of these penetrating radiations is due. Had not this significant fact been observed previous to 1895, for other radiations, Roentgen's significant discovery might have been delayed for several years longer. It rather apparent that the role of fluorescent minerals in the history of science has been large and of tremendous significance.



X-RAY TUBES SUITABLE FOR PRODUCING FLUORESCENCE.
(Courtesy of Eureka X-Ray Tube Corp.)

In an extensive study of the X-ray luminescence of organic chemicals Newcomer found that sodium bromide fluoresces not in the visible region but in the ultraviolet regions. He found that many organic chemicals do fluoresce in the visible region but that a moderate number also fluoresce in the ultraviolet regions. MacDonald and his associates (1932) applied this to practical use in medical work. They found that the living cancerous cells which are comparatively resistent to the direct action of X-rays may be treated with solutions of organic compounds which fluoresce in the ultraviolet regions by X-ray excitation. Under the action of these ultraviolet rays, 2000 to 2500 A. U. in wavelength, the cells become violently agitated and die in a short time.

X-RAY LUMINESCENCE

(*Schuhknecht*)

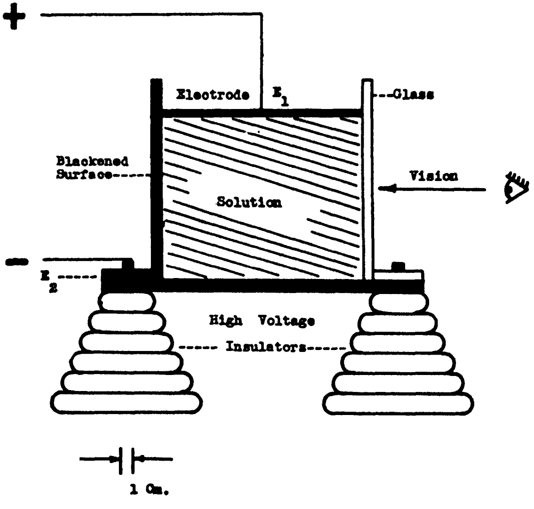
Substance	*Maxima, A. U.*
Fluorite	2840 (ultraviolet)
Fluorite and siderite	2800 (ultraviolet)
Scheelite	4330
Zinc Sulfide	4500
Potassium platinocyanide	4500
Barium platinocyanide	4800
Calcium platinocyanide	4800
Uranium ammonium fluoride	4100

St. John and Isenberger (1934) directed attention to an effect of X-rays with, perhaps, some unsuspected possibilities. They found that a few materials phosphoresced for months after exposure to X-rays had ceased. A photographic record was made three months after subjecting chemicals to continuous direct exposure to X-rays at about 200 Kv. for several hours. Calcium tungstate was used since the reactions were first noted in intensifying screens coated with this material.

It is interesting to note that when X-rays strike the eyes there ensues a sensation of luminescence which continues for several seconds after the rays have been removed. W. J. Morton, in 1905, described a fluorescent substance contained in the organs of animals, including humans, which he called animal quinodin and to which he attributed the fluorescence of tissues under X-rays.

ELECTROLUMINESCENCE

The application of electrical discharges at high potential to certain substances produces luminescence. Samples may be tested in a partial vacuum or in the atmosphere. In more practical atmospheric tests the specimen is unusually placed in a transparent container constructed of a material with suitable dielectric properties. This vessel has electrodes placed at a distance to permit sparkover to just occur. Interposed between the tips of the electrode is the specimen. The discharge disseminates over the specimen, which may be in its normal form or may be powdered, and excites luminescence. The facility of application of high frequency currents or of high potential direct currents such as those used in X-ray energization for the production of this type of luminescence is apparent.



Arrangement for Studies on the Electroluminescence of Liquids (*De Ment*, 1939).

Potential differences of between 10 and 150 Kv. usually suffice for most studies. With a 300 Kv./0.2 to 0.8 ma. current more effective results are sometimes obtained.

Materials particularly electroluminescent are the secondary uraninites such as schroeckingerite and hyaline opal containing autunite. Calcium sulfide, barium sulfide, and zinc sulfide are markedly electroluminescent. These phosphoresce strongly after excitation with currents of low heating value. De Ment (1939) investigated several hundred substances for electroluminescent properties. He found that the application of 100 Kv. to a quantity of specimen, just sufficient to prevent sparkover, produced light in many materials. Fluorescein, in alkaline solution, acridine picrate, quinine in sulfuric acid solution, β—methyl umbelliferone, esculin, and eosin fluoresced.

Absorption measurements were made upon the electroluminescence spectrum of benzene vapor in 1907 by Henri. The spectrum of benzene vapor excited by a Tesla discharge was found resonant by Hartley in 1908.

In 1923, McVicker, Marsh, and Stewart observed that benzene vapor at ordinary pressure and boiling point luminesced green when excited by an electrical discharge. The green spectrum contained a fragmentary carbon spectrum together with some metallic and air lines. On reducing the pressure to 65 mm the vapor, at ordinary temperatures, luminesces. This spectrum can be photographed and consists of a number of fine bands which fall into seven groups, of which the seventh is represented by only one member; namely, the band at $\frac{1}{\lambda} = 3765$ A. U. Another group of four strong bands follows with a narrow band accompanying each and then two less strong and broader bands in which a primary and secondary band might have been fused together. This arrangement is repeated in five more groups with the difference that the secondary bands become too weak to measure towards the more refrangible end of the spectrum. The wave numbers of all bands seem to be expressed by the general formula,

$$\frac{1}{\lambda} = 98.712n - 98.712m/6$$

where $n = 33, 34, 35, 36, 37$, or 38 and $m = 0, 1, 2, 3 \ldots\ldots$

The cell used for these studies consisted of a glass tube 4.4 cm. in diameter and closed at one end with a quartz window. On the other end a mercury electrode passed through a stopper. Two side tubes served as inlet and outlet for the vapor under examination. The exterior of the cell was covered with metal foil which constituted the second electrode. A double-walled steel jacket surrounded the glass cell. This jacket contained three tubes, one of which was for the insertion of a thermometer and the other two for the inlet and outlet of the vapor of liquid with constant boiling point. In some instances heated mercury flowed through these tubes. An 18 inch spark coil was used to energize the inner electrode while the jacket or metal foil covering was grounded.

CRYSTALLOLUMINESCENCE

Crystalloluminescence may occur when solutions crystallize. It was probably first described by Bandrowski in 1894 when he observed the blue sparkling light given off during the crystallization of arsenious oxide, sodium fluoride, or when hydrochloric acid or alcohol was added to hot saturated sodium chloride solution. In further investigations on crystalloluminescence Farnau allowed pupillary accommodation to occur in order to note more carefully the experiments performed by Bandrowski. After a half hour's wait in a dark room, until the eyes become sufficiently sensitive for fine observation, 50 grams of sodium and potassium chloride, bromide, and iodide were shaken with 50 cubic centimeters of alcohol and the glow appearing during the precipitation was observed. In a similar manner concentrated hydrochloride acid was used as a precipitant for the chlorides of sodium and potassium.

Trautz, in 1905, studied crystalloluminescence and arrived at the conclusion that the light is really a special case of triboluminescence in which the growth of crystals causes them to rub together. The light becomes much more intense on stirring a mass of crystals which exhibit crystalloluminescence. In some cases the crystalloluminescence is unquestionably due to triboluminescence from crystals rubbing together although this is not true in every case, as Weiser demonstrated in 1918. His studies were

COLOR OF CRYSTALLOLUMINESCENCE
(*Farnau*)

Salt	*Reaction*	*Precipitation*
Sodium chloride	Blue	Bluish-white
Sodium bromide	Blue-white	Bluish-white
Sodium iodide	White	Greenish-white
Potassium chloride	Blue	Bluish-white
Potassium bromide	Blue	Blue
Potassium iodide	Greenish-white	Green

also on the luminescence produced when saturated aqueous alkali halide solutions were added to alcohol or hydrochloric acid. The salt crystallizes out under these conditions and Weiser found the light brightest when the concentration of alcohol or acid is such as to cause a "heaping up" of sodium and chloride ions. He inclined to the opinion that the bluish light was due to the combination of ions produced by rapid dissociation. Only if this proceeds rapidly does luminescence occur.

Weiser studied the crystalloluminescence and triboluminescence of arsenious chloride and potassium sulfate. By photographing the luminescence through color screens of different absorptive powers a spectrum could be obtained and this was found to be identical for both the triboluminescence light and crystallouminescence light. In the arsenious chloride a band appeared in the green-blue, blue, and violet regions. Weiser concluded that the light in this case was also due to a recombination of dissociated ions. He also concluded that crystalloluminescence in general was due to the rapid formation of molecules from dissociation occurring during the violent disruption of the crystal. Bigelow remarks that it is probable that the cause of crystalloluminescence is the same as the cause of triboluminescence. In quantitative studies Weiser included the effect on the intensity of the crystalloluminescence of sodium chloride produced by (1) varying the nature and concentration of the precipitant, (2) stirring the precipitating solution, (3) adding a colloid, (4) increasing the viscosity of the solution by adding a non-electrolyte and, (5) by varying the temperature. From these he concluded that the maximum intensity of crystalloluminescence results under conditions which favor the accumulation throughout the solution of the largest possible concentration of ions in excess of the equilibrium concentration so that the luminescent reaction, once started, may rapidly go to completion.

Baly regards the crushing of the crystal as a means of liberating the energy of the chemical reaction which has proceeded at some previous time and stored in the precipitate. According to A. D. Garrison (1927) the fact that the color of the triboluminescence is the same as crystalloluminescence for the same salt may be explained by either theory although as yet there is no experimental evidence in favor of either idea. If the Baly suggestion is correct freshly prepared crystals capable of triboluminescence should have a different chemical nature from aged crystals not capable of triboluminescence owing to the molecular phases involving a high energy level. Garrison adds that they should also have different absorption bands and possibly a greater solubility.

Dake (1940) suggested that the phosphorescence appearing on the surface of quiet tropical waters might be due in some cases to crystalloluminescence. The phenomenon is often ascribed to bioluminescence in micro-organisms. It is known that a dynamic equilibrium exists at the surface of the sea and the supposition of Dake is futher qualified by the fact that every salt, alkali halide, examined by Farnau (see table) and others are found extensively in the ocean.

PYROLUMINESCENCE

Nichols and Howes (1938) stated that luminescence may be commonly regarded as an action of instability generally occurring where matter is dissociating and entering into new combinations. The conditions within a flame are peculiarly favorable for the production of luminescence and the light from flames, containing salts, is ordinarily ascribed by chemists to flame reactions rather than to the direct effect of temperature. This was pointed out in 1915 by Bancroft and Weiser as the true nature of flame reactions and it has been emphasized many times since then.

Investigation of luminescence by flames was initiated in 1923 by Nichols and Howes who were led to look for luminescence excited by visible light from discrepancies in attempted measurements on the opacity of a hydrogen flame rendered luminous by additions of calcium chloride. They found that the brightness of the flame plus the light transmitted by the flame from a nitrogen-filled tungsten lamp placed behind it should normaly be slightly less than the sum of the two intensities taken separately. Instead of a loss occurring by absorption the combined brightness was greater. It followed, therefore, that the flame was actually somewhat brighter when exposed to light from the neighboring source.

For advanced study on the luminescence of flames, excited by visible light, Nichols and Howes constructed a special burner. They used an ordinary acetylene burner supplied with compressed hydrogen. Air containing finely divided spray of the salt to be studied was carried from the aspirator into the immediate proximity of the air ducts of the burner through the tubes and drawn into the flame. A further supply of impregnated air from the same aspiratory was delivered to the outer face of the flame, which was flat, through narrow longitudinal slits in the side tubes mounted horizontally and parallel to the faces of the flame near its base. In this way the salt reached the flame with better results than when introduced into the hydrogen gas before the latter enters the burner.

In flames there are certain regions of photoluminescent sensitivity and the luminescence itself depends on the conditions of combustion. The sensitiveness to excitation is chiefly confined to certain narrow layers of the flame, and particularly to the boundary between the oxidizing and reducing regions. That is, the sheath surrounding the main body of the flame, which is most active in producing luminescence when brought in contact with various oxides, is also the chief seat of photoluminescence of the flame itself. Turbulence of a flame destroys this boundary while quiet flames enhance it and therefore are found peculiarly sensitive.

A flame impregnated with spray containing thallium chloride showed a 50% increase in intensity. It seems that these results are closely related to those on the excitation of sodium vapor D lines and the 3030 line described by Strutt. The first observation of the fluorescence of D lines in a sodium flame was in 1910 by R. W. Wood. He placed the vapor in a special tube having flat windows on the front and the side adjoining each other with a side tube for filling. A beam of exciting radiation was sent into the vessel by means of a lens so that it came very near the side window. This was to avoid reabsorption of fluorescent light by unexcited molecules which might obscure the result.

CHEMILUMINESCENCE

Chemiluminescence is the production of light during a chemical reaction proceeding at relatively low temperatures. Bancroft in 1913 suggested the theory that luminescence of all kinds are really forms of chemiluminescence. Garrison (1927) regarded this as somewhat of a stretch of the meaning of the term chemical change to include all types of luminescence under the heading of chemiluminescence. He added that a complete discussion and classification of types of chemiluminescence must include its connection or possible connection with each of the other types. Irrespective of this, there appears to be evidence that many cases of luminescence, occurring under widely differing circumstances, are really chemiluminescent processes.

Chemiluminescent reactions are of two kinds, namely, *indirect* and *direct*. In indirect chemiluminescent reactions the chemical reaction is not the direct source of the energy radiated but occurs as an intermediate process in the transformation of some other form of energy into light. In direct chemiluminescent reactions the radiant energy appears at the expense of chemical energy.

The most well known type of direct chemiluminescent reaction is probably that of the action of substances in solution at ordinary temperatures although flames and metals heated to high temperatures in sealed tubes belong to this type.

The reaction of calcium oxide, barium oxide, or potassium oxide with concentrated sulfuric acid produces light. The decomposition of hydrogen peroxide by various substances also produces light. E. N. Harvey (1917) considered chemiluminescence as oxidation reactions involving the absorption of gaseous or dissolved oxygen and may be distinguished from other forms of luminescence by this. The term oxyluminescence seems more proper for this action. In 1877 Radziszewski noted that a large number of substances like aldehydes and ammonia derivatives of aldehydes emit light on oxidation in alkaline solution. Delepine found that many sulfur compounds emit light when oxidized in solution. Dufford, and his associates found that Grignard compounds in certain solvents glow when oxidized. These investigators found that the nature of the solvent influences the intensity of the emitted light but apparently not the color. One Grignard compound, para-chlorophenylmagnesium bromide is thought to produce the most intense light yet found in chemiluminescent reactions, when oxidized.

The first observation of the glow of phosphorus when exposed to air was probably made by Brandt, its discoverer. The glow of phosphorescence was formerly regarded as a peculiarly persistent type of phosphorescence akin to the glow of the impure alkaline earth sulfides. Freshly cut surfaces of metallic sodium and potassium produce a glow, if warmed to temperatures of from 60°C. to 70°C.

The slow oxidation of certain substances, such as essential oils, causes chemiluminescence to occur. Radziszewski (1877) gave a long list of such materials, which when oxidized slowly in alcoholic alkaline solution would emit light. Certain waxes, paraldehyde, metaldehyde, acrolein, disacryl, aldehyde amonia, anisidin, glucose, lecithin, cholesterin, cholic, taurocholic, and glycocholic acids, and cerebrin are a few of these substances which glow. In 1905 Guinchant described the chemiluminescence of uric acid and asparagin. Pyrogallol glows intensely, as well as phenol derivatives, and rarer aldehydes. Stevenson (1911) found that visible light is emitted when quinine sulfate dehydrates rapidly. E. N. Harvey (1920) stated that pyrogallol can be oxidized in a number of ways and some of these closely imitate the mechanism of light production by animals.

Harvey classifies oxyluminescent reactions into fourteen kinds. In one, light is emitted by oxidation of a substance in air spontaneously. Instances of this at ordinary temperatures are: phosphorus, freshly cut surfaces of active metals, thiothers, and thiophosgene. At melting or vaporizing points fats, terpenes, sugars, resins, gums, and ethers are prone to luminesce. On oxidation, in aqueous or alcoholic alkaline solution, many substances emit light, including the fresh extracts of plants and fresh fruit and vegetable juices. Also, many organic materials luminesce when oxidized in hypoiodite, hypobromite, or hypochlorite solution. Likewise, the oxidation of organic substances by peroxides produces an intense glow in a number of cases. Ozone and permanganate solutions have been used extensively for this.

Probably the best known demonstration of light production during a chemical reaction is that of luminol or 3-aminophthalhydrazide. In the oxidation of luminol by hydrogen peroxide, in the presence of other chemicals, an intense light is emitted. The light producing reaction occurs only in alkaline solution and its intensity and duration vary with the alkalinity. Up to a certain point the amount of light evolved increases with increased alkali concentration. The mode of light emission appears to vary considerably with the nature of the oxidant seemingly most satisfactory with mild oxidizing agents.

Plotnikov and Kubal (1938) described colored chemiluminescence. This may be produced by adding fluorescent dyes to the reagents in the 3-aminophthalhydrazide reaction before mixing. The addition of fluorescein produces a yellow-green color while opal-blue-rose is produced by the addition of rhodamine. Numerous other colors are readily obtainable where various mixtures of compounds are used.

BIOLUMINESCENCE

Bioluminescence is the production of light by living organisms. The light may be produced by microscopic sized organisms or it may be from larger animals, the latter of which have more specialized structures designed for light production. The microscopic sized organisms often feed on dead meat, eggs, or other organic matter, often causing luminescence. The light seen on the surface of the ocean is often due to immense aggregations of luminous bacteria. Harvey (1917) considered bioluminescence a case of direct chemiluminescence occurring in solution or at liquid interfaces. Animal light, physically, is identical with any other light since it consists only of visible radiations. No ultraviolet light or other penetrating radiation has been substantially proven to exist, although Muraoka believed that a penetrating radiation was given off by the firefly. That bioluminescence is not a vital process dependent on living cells has been proven by desiccation experiments. Luminous cells, when dried, become dark, but if dried quickly and properly they again luminesce when placed in water. There have been reports that light is given off by organisms, as high in the scale as the sheep, when brain cells function.

The light given out by animals during life processes is never dependent on previous illumination by other agents, that is, never dependent on excitation by an outside agent. It is not connected with crystallization, friction or related actions seen in mineral luminescence but depends on oxidation of a definite substance contained in the luminous apparatus of the luminous organism. The light giving substance is called a *photogen* and may be found in many organisms as granules. When it undergoes oxidation inside of the organism it is known as intercellular luminescence and, if excreted as a luminous exudation, it is known as extracellular luminescence.

OTHER FORMS OF LUMINESCENCE

Lyoluminescence was described in 1895 by Wiedemann and Smith as the light accompanying the solution of crystals of lithium, sodium, or potassium chlorides which had been colored by exposure to cathode rays. They ascribed this form of light production to the triboluminescence from stirring crystals during solution. Nyswander and Cohn described a mechanical method for exciting material to thermoluminescence for a number of substances including glass and colorless fluorite. These materials were heated to redness and then ground in a mortar. The powdered material showed a dim thermoluminescence when heated to a temperature of about 350°C. This action was termed *tribothermoluminescence.* According to Wick (1937) fluorite from Franklin, New Jersey; Montrose, California; New South Wales; Deming, New Mexico; Weardale, England; Obira, Japan, and others show this type of luminescence. Tribothermoluminescence is not due to exposure of heated crystals as it was proven by heating some crystals of fluorite exposing part of them to light for four days, keeping the other part in the dark, and noting that no difference could be observed in the emission.

Many substances fluoresce brilliantly during exposure to an intense source of visible light. The masking action of the visible light usually obscures the fluorescence although the light of quinine sulfate in acid, eosin, esculin, fluorescein, petrolatum, and others may be seen. Harvey states that 10^{-8}gm of eosin per cc will fluoresce appreciably in daylight. Wawilow states that one part of esculin in 10^{-10} parts water may be seen in ultraviolet light but that excitation with visible radiation occurs to a lesser extent. Other substances of a similar nature fluoresce strongly in visible light, provided of course, that fluorescence is not masked largely by the visible light itself.

The sulfides of alkaline earths, however, may be excited to phosphorescence by visible light. W. S. Andrews pointed out that five of the metallic elements, remarkable for their luminescent properties as shown by their compounds, are found in consecutive order in the second group of the periodic table: calcium, zinc, strontium, cadmium, and barium. This is apparent in all forms of luminescence and will be noted elsewhere. The sulfides of these elements, with the possible exception of cadmium, are more or less luminescent and in order to bring out this quality they require, in solid solution, a definite but exceedingly small trace of another element. For studying luminescence Andrews devised a vacuum tube, the real forerunner of our modern fluorescent lighting unit. In the tube he placed samples spread on metal plates, exhausted the tube to about one mm of mercury pressure and applied a potential difference of 10 Kv. to the electrodes. This apparatus may be regarded as somewhat of a modified form of cathode ray tube and is practically the same as tubes used for investigations into the electroluminescence of materials at pressures less than atmospheric.

Reduction of the temperature of fluorescein and gelatine to 202° K. caused phosphorescence to occur for some 30 seconds, according to Ochai. This is one of the few instances of the rare type of luminescence caused by extreme cold. The effect of radio waves of a wavelength of 1.97 Mc. on normally luminescent minerals causes no effect other than to raise the temperature. With radio waves of a very high frequency, however, luminescent effects are sometimes produced in minerals susceptible to excitation by other agents.

In 1919 J. Lavaux described a case of luminescence appearing during *electrolysis*. He found that certain metals which produce, along with the anion, insoluble adherent salts also excite luminescence during the state of intense anodic polarization. Iron, copper, cadmium, and lead are negative to both luminescence and anodic polarization, while aluminum magnesium, zinc, and bismuth are susceptible to both. Aluminum is best for study purposes. Aluminum, magnesium, and zinc demonstrate both phosphorescence and polarization while bismuth shows only sparking.

Mechanical luminescence was observed in 1925 by J. W. French. He observed that unrolling tape luminesces. He also found this independent of any charge imparted during the initial winding of the roll. It seemed that mechanical luminescence was the result of a sudden extension and rupture of the tenacious, viscious threads into which the adhesive material is drawn. French further compares this form of luminescence to that of bioluminescence and suggests a relationship with an explanation for bioluminescence by actions found in mechanical luminescence.

Radiophotoluminescence, described by Przibram, is the property possessed by certain substances of glowing longer and more intensely when exposed to ordinary light after an initial exposure to radium radiations. This is shown in kunzite, fluorite, apatite, orthoclase, adularia, wollastonite, scheelite, and in many tourmalines. An extensive study of kunzite disclosed that the intensity of the exposure to beta and gamma rays increases with time up to a flat maxima and then decreases. With increasing time of exposure the total light emitted approaches a saturation value. Przibram found that colorless spodumene phosphoresces only a fraction of a second while kunzite phosphoresces many minutes. Both kunzite and fluorite, after exposure to radium rays, show increased susceptibility to triboluminescence. A specimen of kunzite was found to exhibit radiophotoluminescence 15 years after exposure to radium rays!

The impact of *alpha rays* from a radioactive source such as radiothorium also produces luminescence. Willemite and zinc sulfide phosphor, artificially prepared, scintillate when bombarded by alpha rays. The principle of the spinthariscope and the radioscope depend on the luminescence produced on a screen of zinc sulfide phosphor by alpha rays emitted from a radioactive substance.

The action of *gamma rays* on matter is sometimes accompanied with light. Cherenkov found that liquids in a very pure state emit a faint blue fluorescence when subjected to the action of gamma rays. Sulfuric acid, water, paraffin, acetone, organic liquids and others fluoresce in this way. The fluorescence excited by gamma rays is not influenced by a change in concentration or by the addition of quenching agents although this occurs in fluorescence excited by visible light.

The action of *beta rays* for fluorenscence excitation is similar to that of cathode rays since beta rays, being electrons, are analogs of cathode rays. The primary difference between the two is in their relative velocities. R. B. Taft (1939) suggested that preliminary searches for lost radium salts could be made with willemite or fluorescent screens. This, however, seems applicable only to large quantities of radioactive material such as that used for therapeutic work.

Luminescence is excited in some materials by *neutrons*. In observations by Wick and Vincent (1940) it was found that excitation was more effectively produced by slow neutrons than fast neutrons. In a material for neutron excitation it is desirable that an element highly reactive to neutrons be present. The material should also contain a heavy element capable of absorbing radiation such as X-rays. As is to be expected, materials excited by neutrons are also usually excited by X-rays, cathode rays, and the radiations from radioactive substances. The intensity of luminescence can be increased by mixing with a small quantity of some material containing an element highly reactive to neutrons.

The explanation for excitation of luminescence by neutrons is that neutrons react with the nuclei of certain atoms which form a component part of the luminescent substance or with the nuclei of atoms of some other substance highly reactive to neutrons which may be mixed with it or near it. As a result of this reaction radiations are emitted which excite luminescence.

Gamma rays appear to be a factor in the excitation and secondary radiation as well as internal conversions may also play a part in the mechanism.

CHAPTER FOUR

THEORY OF LUMINESCENCE

One of the most striking things about luminescence is the small amount of material required to cause a visible emission of light. To take an extreme case, consider the flash of light which results from impingement of a single alpha particle on zinc sulfide phosphor. If a sheet of paper is covered with a layer of finely divided pure mercuric chloride and a globule of mercury is rolled across the powder, a fluorescent path is left from the formation of traces of mercurous chloride by the contact of the mercury with the mercuric salt (Radley and Grant, 1933). A solution containing one part of luciferase in 1,700,000,000 parts of water emits light when luciferin is added and vice versa (E. N. Harvey, 1917).

Pyrogallol in water, one in five million parts, can be oxidized, with light emission, by potassium ferrocyanide and hydrogen peroxide (E. N. Harvey, 1917). Visible light is produced when M/100 pyrogallol and hydrogen peroxide are oxidized with a solution containing one part in 250,000 of colloidal platinum (Gross, 1917). Bromides in amounts as small as 10^{-6} gram may be detected by the conversion of fluorescein at pH 5.5 to eosin provided examination in ultraviolet light is used (Ganassini, 1904 and F. Hahn, 1933). One part in 500,000 of uranium in kidney ash may be detected by fluorescence (Eitel, 1928).

The addition of concentrated sulfuric acid and meta-hydroxybenzoic acid to over 5 gamma of glycerol produces a green color if examined under ultraviolet light (Eegriwe, 1935). A difference in the age or erasure of typewritten pages may be detected in ultraviolet light (Mitchell, 1935). The trace of the path of a bullet by the scorch produced on passing through cloth was demonstrated by A. Bruning in 1931 with ultraviolet light. Blood present to the extent of 0.0002 cubic centimeter in 5 cubic centimeters of water may be detected by the method of Heller (1916) and others. Species of *Bacillus tuberculosis* appear differently in ultraviolet light (Pulvertaft, 1934).

The fluorescence of one part zinc in 10,000 is detectable by the use of δ-hydroxyquinoline (M. Haitinger, 1932). One-hundredth gram-mole of lead tungstate will activate barium tungstate to luminescence (Beutel and Kutzelnigg, 1931). One part of sodium salicylate in 50,000 parts milk may be detected by fluorescence (J. Grant, 1933). Preserved eggs appear differently in ultraviolet light than do fresh eggs due to the fluorescence produced by chemical products in the shell which develop only with time.

The same results may be obtained with fresh milk and milk after standing a short time. In the latter a lactochrome develops and causes a blue fluorescence. Honey may be separated by capillary action into two products not otherwise detectable provided they are examined in ultraviolet light (Orban and Stitz, 1928). One gamma of arsenic may be dedected by the Gutzeit tests if the mercuric chloride paper is examined under ultraviolet light (A. King, 1928). Gadolinium to the extent of 10^{-6} gram in 50 grams of flux may be detected by the yellow fluorescence produced in the borax or phosphate bead (M. Haitinger, 1933). One part of cerium oxalate in 10^{-4} of flux, one part of terbium in 5000 of flux; one part of samarium in 1000 of flux and one part of europium in 500 of flux may be determined by the blue, yellow-green, orange, and red colors developed respectively. The morin test in conjunction with ultraviolet light will detect 0.3 gamma of aluminum in 0.05 cubic centimeter of solution. The fluorescence produced by small quantities of organic substances is often much greater than the fluorescence produced by small quantities of inorganic substances. These are but a few examples of the sensitivity of fluorescence analysis and the small amounts of material required to cause a visible emission of light.

PHOSPHORS

Luminescent minerals and several other kinds of substances generally come under the classifiction of solid solutions. They often consist of compounds in which a small amount of an active material is intimately associated. The trace or impurity in a luminescent substance is called an *activator* (or a phosphorogen) and the large amount of inert substance acts as a flux or constitutes a solvent. Artificial compounds of this nature are termed ***phosphors*** and consist of a basic material, such as an alkaline earth sulfide, activated by a trace of heavy metal. This mixture is melted together with the flux. Phosphors may be represented as

$$\mathrm{AB}+\mathrm{M}+\mathit{flux} \xrightarrow{\Delta} \mathrm{PHOSPHOR} \qquad (1)$$

where A may be Ca, Ba, Sr, Mg, Be, Na, K, Rb, Cs, Cd, Li, or Zn. B indicates that one of the following compounds of the above element is formed: sulfide, oxide, selenide, telluride, tungstate, silicate, carbonate, cyanide, hydride, thiocarbonate, thiosulfate, or thiocyanide. M, the trace element may be one or more of the following: Mn, Pt, Ni, Cu, Zn, Fe, Co, Ag, Sn, Au, Sb, Tl, Pd, Bi, Pb, U, Nd, Cb, Ga, Dy, Pr, Sm, Y; Yb; La, Ho, Sc, Gd, Er, Eu, Tm, Tb, some of the radioactive elements, Ra, Po, Ac, or others. The flux may be the sulfate, borate, thiosulfate, mono or diphosphate, chloride, fluoride, or others used either singularly or mixed of the following: Na, K, NH_4, Ba, Li, Be, Mg, or Ca.

Phosphors activated by more than one element are known as polymetallic phosphors. Monometallic phosphors are those activated by only one element. Minerals are usually polymetallic phosphors although some varieties are monometallic. The notation for a typical phosphor (CaBiS) is self-evident.

SOME SIMPLE MONOMETALLIC PHOSPHORS

(*Lenard and Klatt*)

Activator	*Solvent*	*Flux*	*Luminescence Color*
Cu	SrS	CaF_2	Bright green
Cu	BaS	NaF	Greenish-white
Cu	BaS	NaCl	Yellow
Cu	BaS	$Na_2B_4O_7$	Orange-yellow
Cu	CaS	$Li_2SO_4 . CaF_2$	Bright blue
Pb	SrS	$Na_2SO_4 . NaF$	Yellowish-green
Pb	SrS	NaF	Green

Activator	*Solvent*	*Flux*	*Luminescence Color*
Pb	BaS	Na_2SO_4	Yellow
Pb	CaS	$Na_2SO_4 . NaF$	Bluish-green
Bi	SrS	Na_2SO_4	Green
Bi	BaS	$Na_2B_4O_7$	Yellow with orange
Bi	BaS	$K_2B_6O_{10}$	Yellowish-orange
Mn	SrS	Na_2SO_4	Yellowish-green
Mn	CaS	$Na_2SO_4 . CaF_2$	Yellow-orange
Ag	SrS	$Li_2SO_4 . Li_2CO_3$	Purple
Sb	CaS	$Na_2SO_4 . NaF$	Blue
Zn	SrS	CaF_2	Green

CATHODOLUMINESCENCE PRODUCED WITH RARE ELEMENT ACTIVATORS

(C. James, and Nichols, Howes, and Wilber)

Phosphor	*Color*
NaFTm	Red
CaOTm	Blue
Al_2O_3Tm	Blue
NaFEu	Red
NaFDy	Orange
CaF_2Tb	Yellow-green
CaOTb	Yellow-green
NaFY	White
CaOY	Blue
CaF_2Pr	Orange-red
$Na_2B_4O_7Eu$	Reddish
NaFSm	Red
CaOSm	Red, very bright
NaFNd	Red
$Na_2B_4O_7Tm$	Violet
CaOEu(1:333)	Reddish

MECHANISM OF LUMINESCENCE

Luminescence occurs when an electron transition results from the absorption of a quantum of light. The light causes the atom to be raised from its ground level to an excited state from which it returns to a lower level. The period required for the return to the lower level qualifies the case as either fluorescence or phosphorescence depending entirely of course on the duration of this period (lifetime of the excited state). When the lifetime of the excited state is of the magnitude of 10^{-8} second the phenomenon is usually regarded as *fluorescence.* If the lifetime of the excited state is greater, of the magnitude of 0.01 second, the action is usually regarded as *phosphorescence.* Obviously, however, the differentiation between the two in time values given is based on determinations by instrumental means rather than by visual means. If discrimination is performed on the basis of visual acuity the value for phosphorescence would be greater than the time value given and would vary considerably from observer to observer.

The emission of light accompanies the return to the lower level and it has been found that the rate at which displaced electrons return to their normal orbits is proportional to the luminescence of the excited radiator and for sufficiently large values of t, $L \propto t—^{2}$. This is in agreement with the experimental results on phosphorescence and is of importance since it demonstrates that an exponential decay of phosphorescence occurs only if the electron returns to its parent, i.e., its original center:

$$L = \frac{\sigma n}{\sigma t} \qquad (2)$$

F. Perrin delineates phosphorescence and fluorescence according to the intermediate metastable level reached between absorption and re-emission. In phosphorescence an intermediate level is reached between absorption and re-emission and emission occurs only if the energy is taken up from the surrounding medium. In fluorescence the intermediate action does not occur to such an extent as only "spontaneous" transitions occur. The properties of the medium, in the case of phosphorescence, delay the return of the electron to its lower level. A loose binding of the electron results with an action such as that in thermoluminescence or triboluminescence where the loose bond is broken and the electron proceeds to return to its ground level. The binding of the displaced electron, being dependent on the properties of the medium, is increased with an increase in viscosity of the radiator. In gases, at least under normal conditions, binding does not occur; for liquids of greater viscosity binding increases and in solids it is manifested by long lifetime phosphorescence which may last for months. The case cited for the phosphorescence of calcium tungstate after intense exposure to short wavelength X-rays illustrate this.

When a phosphor or other luminescent substance emits light, it gives, in most cases, an emission according to a fundamental law known as *Stokes' Law.* This law states that the wavelength of the fluorescent light is always greater than the wave length of the exciting radiation. It was first described in 1852 in the memoir "On the Change of Refrangibility of Light" by Sir G. G. Stokes. In terms of energy the relationship states

$$\epsilon \text{ em} < \epsilon \text{ ab}$$

While Stokes' Law holds true for the majority of cases it does not follow in certain instances. In some cases the wavelength is the same for both the absorbed and emitted radiation. That is, the efficiency appears to be perfect. This is known as *resonance radiation.* In the other case Stokes' Law does not hold where the energy emitted is greater than the energy absorbed. This is known as *Anti-Stokes' Emission.* In 1935 Prileshajewa showed that there is an energy difference as much as 1.1ν between the exciting light and the fluorescence of aniline vapor. This added energy is attributed to additions from the internal energy of the molecule. Nevertheless, for short periods of emission in minerals and other complex phosphors, Stokes' Law is rigidly obeyed

This means that the efficiency of phosphorescence for minerals and other phosphors will be near unity. The efficiency of a phosphor is the ratio of the energy of emitted light to the energy of the absorbed light.

This efficiency is in close agreement with the view that one quantum of emitted light is associated with one quantum of absorbed light

$$p = \frac{h\nu_e}{h\nu_a} \doteq \frac{\lambda_a}{\lambda_e} \tag{3}$$

EFFICIENCY OF PHOSPHORS

(*Schmieder*)

Phosphor	Mean λ of Emitted Light	λ of Exciting Light	p observed	p calculated
CaSBi	4400 A.U.	4350 A.U.	0.97	0.99
		3650 A.U.	0.82	0.83
ZnSCu	5150 A.U.	4350 A.U.	0.84	0.85
		3650 A.U.	0.73	0.71
CaSCu	5250 A.U.	4350 A.U.	0.76	0.85
		3650 A.U.	0.64	0.70

Since the fundamental difference between fluorescence and phosphorescence is in the duration of the afterglow, it follows that a relationship expressing the life of an excited state might depend on the time required for the electron to remain in the higher state before returning to its lower state with the emission ot light. The mean life for both cases of luminescence was defined by Hirschlaff

$$\tau = \frac{I}{\sum_{m} A_{mn}} \tag{4}$$

where A_{mn} is the transition probability from the state *n* to any lower state *m*. The quantities are further related with the intensity of the luminescence and the frequency of the line in the spectrum with its frequency ν_{mn}.

DECAY OF PHOSPHORESCENCE

The emission of fluorescent light of brief duration has only been recently investigated. Only for phosphorescence of comparatively long duration were more detailed studies made by early workers. The decay was originally assumed to follow the law of diminution of brightness .

$$I = \frac{1}{(a_1+b_1t)^2} + \frac{1}{(a_2+b_2t)^2} \tag{5}$$

Nichols, Howes and Wilber (1928) stated that measurements of Waggoner in 1908 and Zeller in 1910 on the lifetime of afterglows of brief duration tended to confirm this. In 1912 Ives and Luckiesh, and Trowbridge in 1911 performed experiments which indicated that this relationship was not absolute in every instance and required modification according to the case.

More recent studies indicate that the rate of decay of phosphorescence follows an *exponential law* in most cases provided the system is homogenous. In emission the intensity decreases with time according to the relationship

$$I = I_{0}e^{-\alpha t} \tag{6}$$

However, in his studies on the decay of phosphorescence E. Becquerel (1860) regarded the law of decay as probable in the form of $I=I_{0}e^{-\alpha t}$. He found that observations could be fairly well represented by an exponential expression. Becquerel assumed that no appreciable time was required for the exciting rays to produce their full effect. That this assumption is not qualified was shown by later studies.

For phosphorescence of long lifetime Becquerel proposed the relationship

$$I^{m}(c+t) = cI_0^{m} \tag{7}$$

This expression held fairly well for seven specimens examined. It was used later by Darwin in 1881 and by C. Henry in 1892. Darwin found the expression adequate for his investigations while Henry modified it to

$$i^{0.5936}(t+27.18) = 1647.5$$

In 1891 H. Becquerel studied phosphorescence from a theoretical standpoint. He assumed that phosphorescent light was due to molecular vibrations caused by the exciting radiation. The approach was from the aspect of determining the law of decay by the nature of the dampening forces. It was shown that an exponential law of decay would result if the vibrations met with an opposing force proportional to the velocity. If the resistance is proportional to the square of the velocity the law of decay is

$$I = \frac{1}{(a+bt)^2} \tag{8}$$

For phosphorescent spectra H. Becquerel assumed that the following relationship could be used

$$I = \sum \frac{1}{(a+bt)^2} \tag{9}$$

with one term for the summation of each band. Both terms were found to express the experimental results obtained by E. Becquerel on the blue phosphorescence of calcium sulfide with great accuracy.

In the derivation of his laws for the decay of phosphorescence H. Becquerel assumed that the vibrations produced by the exciting agent would continue for minutes or even hours. Nichols and Merritt (1912) regarded the suppositions as somewhat untenable. It was implied by Becquerel that the vibrating molecules or atoms exist during radiation without collision with other atoms or molecules. Or, that if such collisions did occur they were without effect on the radiating molecules or atoms and their vibrations. However, the law of Becquerel appeared to be of very general application and this was shown later when Nichols and Merritt derived the same expression from entirely different theoretical considerations.

For heterogenous systems, where a series of absorption and emission processes occur independently and simultaneously, the total intensity is usually given by the sum of the exponential functions each with different constants representing a different rate of decay for the various bands. Nevertheless, the sum total of the light decays in the same way according to an exponential function. Probably the best fitted mathematical relationship to represent the decay of phosphorescence is

$$I = \sum_{k} OKe^{-aKt} \tag{10}$$

It is reasonable to assume that this relationship fits an experimental curve when there are a number of centers whose excited states have different lives. This function, however, represents the velocity of a mono-molecular reaction.

In 1917 Nichols and Howes recognized a new type of phosphorescence of short lifetime and high brilliance. Two distinct types of phosphorescence were found. One, *persistent phosphorescence,* was sharply distinguished from the other, *vanishing phosphorescence.* Moreover, it was later found that both types could occur in a single substance. Calcites from Franklin, New Jersey for instance, showed vanishing phosphorescence under excitation by visible light (*photoexcitation*) and persistent phosphorescence under cathode rays. Both types were obtainable with this calcite at any temperature between — 180°C. and + 300°C.

In persistent phosphorescence the curve of decay is composed of a succession of linear processes of diminishing slope proceeding from the origin of time. For vanishing phosphorescence the curve of decay is composed of a succession of linear processes of increasing slope proceeding from the of time. The curve in this case is plotted with the time from the close of excitation as abscissae and the reciprocal of the square root of the intensity ($I^{-1/2}$) as ordinate. Nichols and Howes state that the distinguishing criterion between the two kinds is in the sign of the intercepts of the various processes at the origin of time. In persistent phosphorescence all intercepts are positive. In vanishing phosphorescence some intercepts are negative.

The observation of a *delayed phosphorescence* was reported by A. Keith and J. L. Jones (1939). These investigators noted the appearance of a white phosphorescence after a small but appreciable delay in rare earth pegmatites from Llano County, Texas.

CONCENTRATION EFFECTS

Broadly speaking, the behavior of fluorescent solids is identical with the behavior of fluorescent liquids. In each a luminosity of considerable intensity may be produced by minute traces of substances called activators. If the concentration of the activator, in both cases, passes a certain optimum, the intensity of the luminosity is reduced considerably. Maximum brightness in some instances is often reached with one part of active material in ten thousand parts of solvent although the optimum concentration is rarely as great as one part in a hundred.

The relation between the intensity of fluorescence and the concentration was investigated by Brüninghaus in 1909. He explained the existence of an optimum concentration as a result of absorption. It was assumed that the active material in the outer layers of the substance lost its ability to radiate, but retained its absorbing power for fluorescent light emitted from the interior of the mass. It was further assumed that an increase in concentration caused an increase in the fluorescence excited in the interior, presumably in proportion to the number of molecules excited in the interior; and also produced an increased absorption of this light by the surface layer. The intensity of the light that escapes is therefore given by the following relationship with x the concentation of active material

$$I = Kxe^{-kx} \tag{11}$$

Brüninghaus found this relationship held with some exactness for cathodoluminescence in manganiferous calcium phosphate but doubt was thrown on the theory when the relationship failed to hold for liquids or did not receive experimental verification for solids.

A relationship similar to that of Brüninghaus was used by Perrin for fluorescent solutions

$$\phi = \phi_0 e^{-kc} \tag{12}$$

where ϕ_0 and ϕ are the initial and observed intensities of fluorescence respectively, and c the corresponding change in concentration, k being a constant of the latter. For small concentrations there is lack of agreement although for solutions the conclusions of Perrin have been confirmed by experimental results.

An advanced theory as to the most effective proportion of an activator was presented by Merritt in 1926. The observations included both theories cited and the use of experimental data obtained with uranium as an activator in various solvents (Nichols and Slattery, 1926).

F. Perrin investigated, in 1924, the relation betwen concentration and intensity of fluorescence and suggested two alternative reasons for the decrease in luminescence at higher concentrations:

(I) The exciting light, in the form of a quantum of small cross section, strikes two active molecules which are so close together that the energy is divided between them and is less likely to cause excitation, or,

(II) When two active molecules are sufficiently close together their fields overlap and they couple in such a way so as to diminish their power of responding to excitation.

POLARIZED FLUORESCENCE

The light emitted by fluorescing objects may be *polarized.* This was observed in 1857 by Grailich and has since been studied extensively.

Polarization of fluorescent light may be affected by a number of factors. L. Grisebach (1936) pointed out that elliptically polarized light does not result in eliptically polarized fluorescence. However, the temperature, wavelength of the exciting light, solvent, concentration or the presence of foreign substances may influence the polarization of fluorescence bands.

Jablonski (1934) found the degree of polarization to decrease with a decrease in wave length of exciting light, the latter being from 3500 to 5500 A.U. In studies by Merritt and Morey (1930) results indicated that fluorescent light is polarized to the same extent throughout any one fluorescence band.

S. M. Mitra (1934) found the polarization of fluorescent light from fluorescein and rhodamine B, on addition of potassium iodide, to increase steadily although in glycerol solutions this increased to a maximum. Mitra also studied the effects of viscosity, solution, and wavelength of exciting light. It was observed that polarization decreased rapidly with an increase in concentration.

Polarization of resonance radiation has also been studied. In investigations on the polarization of Hg resonance radiation Hanle found that magnetic fields affected polarization only slightly although the plane of polarization was altered. Since the rotation of a plane is

$$\alpha = \tfrac{1}{2} \text{ arc tg} 2\, \tau \omega \tag{13}$$

where, $\omega = \dfrac{eH}{mc}$, or the precession velocity;

the application of *degree of polarization,*

$$P = \frac{P_0}{\sqrt{1+4\pi\,\tau^2\,\omega^2}} \tag{14}$$

where P_0 is the degree for $H = O$, has been to measure a number of lives of different atomic states. For example, $\tau \cdot = 1.1 \times 10^{-7}$ sec $= 2537$ A.U. (Hg).

According to Hirschlaff (1939), P depends on the concentration and has been found to decrease with an increase in c. An increase in temperature, due to increased Brownian Movement, tends to diminish P. This has been studied by F. Perrin.

Perrin arrived at the following expression for the degree of polarization,

$$\frac{1}{P} = \frac{1}{P_0} + \left(\frac{1}{P_0} - \frac{1}{3}\right)\tau\,\frac{V\eta}{RT} \tag{15}$$

P is then zero for natural light and 1 for complete polarization while P_0 is the extrapolated value for the maximum degree of polarization in the absence of rotation, and is a constant for a particular substance; V is the molecular volume of the dye molecule.

The degree of polarization may also be defined by,

$$P = \frac{I_x - I_y}{I_x + I_y} \tag{16}$$

where the x-axis is given by the direction of the exciting electric vector and the z-axis by the direction of observation.

According to Hirschlaff, it is obvious that the life of the excited molecule changes with the yield of fluorescence. If quenching molecules are added to a dye solution, for example, thus decreasing the fluorescence, the excited molecules are deactivated before they have time to emit according to their natural life τ_0. It follows that quenching will usually result in a shorter life τ for the excited molecules; therefore, the yield of fluorescence, the ratio of emitted light intensity in the absence of quenching molecules to that with them is proportional to $\frac{\tau_0}{\tau}$. According to Wawilow, $\frac{\tau_0}{\tau}$ should be a linear function of $\frac{c}{\eta}$ or $\frac{T}{\eta}$ and which has been found to hold within a limited range.

Protracted studies were made by Nichols and Howes (1919) on the polarized spectra of the double chlorides and the double nitrates of uranyl salts. It was found that the four double chorides, uranyl ammonium chloride, uranyl potassium chloride, uranyl rubidium chloride, and uranyl cesium chloride, crystallize in the triclinic system. The crystals are pleochroic and their fluorescence spectra and absorption spectra are polarized although these differ from many of the other uranyl compounds examined. The difference being that both in the fluorescence and absorption regions each band is resolved at + 20°C. into a group of five bands forming homologous series of constant frequency interval. Each of the five bands which constitute a group is a doublet, the two components of which are polarized at right angles to one another.

OTHER INFLUENCES ON LUMINESCENCE

Many correlations have been obtained between the lives and characteristics of fluorescence and phosphorescence, and chemical and physical properties. For example, lowering the temperatue of a fluorescent solution usually increases the duration and the intensity of the fluorescence. And, as has ben stated, the duration of the afterglow in phosphorescence bears a relationship to the viscosity of the medium. The duration of the phosphorescence increases with the viscosity of the medium. This explains why some substances will not glow in liquid solution but if put in the form of solid solution with sugars, for example, they phosphoresce.

It has ben found that there is no correlation between the efficiency of fluorescence and the conductivity of a fluorescent solution. However, Pincussen (1920) found that the wavelength of the emitted light increased with an increase in dielectric constant for a series of solvents in which dimethylnaphtheurhodine was dissolved. De Ment (1940) extended the results of Pincussen to include both heat of combustion and formula weight for the solvents used. Greater accuracy was obtained for correlations in the latter cases.

In 1939 Hirschlaff pointed out that there is no simple relationship between the degree of dissociation and the fluorescence intensity. Quinine hydrochloride exhibits similar changes in intensity with concentration in chloroform as in water where the dissociation constants differ considerably. The fluorescence of certain dyes has been investigated extensively and the intensity and color of emitted light depends on the pH of the medium in many cases. The practical use of this has been in titrimetry with chemicals which change fluorescence color at a certain pH. Results have been superior, in some instances, e.g., dark colored liquids such as wines, to those obtained with color in white light.

In certain phosphors and luminescent solutions the addition of a trace of some substance will inhibit or *quench* fluorescence. An effect of this is acids on fluorescein which quench the fluorescence entirely at low pH values. However, the addition of OH^- or similar ions tends to neutralize this quenching action. In certain instances the absence of water, especially in pure inorganic substances, tends to quench fluorescence. In luminescent screens for television and electronic work a lag prevents adequate results, it has been found that the addition of 0.5 to 2 parts per million of Ni to ZnS prevents this lag.

The vapors of selenium, sulfur, and tellurium fluoresce. A magnetic field will quench the fluorescence in these elements. The intensity of fluorescence has been found to increase wih pressure because the association between the molecules is increased and increases the number of absorbing atoms or molecules. However, when the pressure reaches a certain optimum the fluorescence decreases. The resonance radiation of mercury is quenched by the addition of small amounts of other gases such as argon and helium. Similarly, resonance radiation, as well as fluorescence in some cases is reduced in intensity by the addition of foreign gases. Oxygen acts as a quencher on certain materials. Benzoflavin, for example, is quenched with the increase in oxygen pressure. This gas acts very srtongly as a quencher in most instances varying, however, in degree of efficiency for different substances.

When the concentration exceeds the optimum, quenching usually occurs. There are two cases to consider (cf. Perrin). In one, the excited molecules encounter an unexcited molecule by collision and part of the energy is transferred to the unexcited molecule. In higher concentrations the well known action of polymerization may occur. Polymerized molecules being huge complex clusters of simpler units, do not fluoresce. In connection with this the increase in viscosity prevents association between molecules and thus inhibits quenching.

Inhibition of the fluorescence of uranium salts by compounds of an antioxygenic nature was investigated by F. Perrin in 1928. The work was extended by Achard and his co-workers in 1933. They found that S^-, CNS^-, I^-, NO_2^-, $S_2O_3^=$, $S_2O_4^=$, $HAsO_3^=$, some of the alkaloids, phenol, cresol and aniline were inhibitors. Muller, West and Jette (1928) found the quenching of uranyl salts a function of the deformability of the anion of the quenching solution. With some variance they found that the ions were quenchers in efficiency according to their order: $I^- > CNS^- > Br^- > Cl^- > SO_4^= > NO_3^- > F^-$. Banov (1934) found that the quenching of solutions of fluorescein and similar substances corresponds approximately with the salting out activity of the ions: $Br^- > Cl^- > NO_3^-$ and, $Na^+ > K^+ > Li^+ > NH_4^+$.

Many materials originally inactive are made luminescent by exposure to X-rays. Calcium sulfate shows this effect strongly provided that it contains a small amount of manganese as an activator. Wick and Slattery (1928) found exposure to X-rays produces two kinds of change in this material. One of these results in a thermoluminescence, which appears quickly upon heating and lasts for a very short time, while the other is shown by a luminescence which appears more slowly and lasts longer. If the material is allowed to stand at room temperature after exposure the first effect disappears in a few hours while the second may last for months. Both of these effects may be preserved indefinitely by keeping the specimen in liquid air after exposure. In the studies of Wick and Slattery the decay of thermoluminescence was observed at different temperatures and after to exposure to X-rays of various wavelengths. Exposure to ultraviolet light of a definite wavelength was found to suppress the effect produced by exposure to X-rays. Results obtained by Wiedemann and Schmidt (1896) from exposure to cathode rays are similar to these.

Lenard found that phosphorescent materials are greatly changed by pressure. Nichols and Wick (1930) found that excitation, whether by corpuscular bombardment or the action of radiation of short wavelength, sets oxygen free. They regard the resulting glow as due to the return of the oxygen to a state of combination. Excitation, then, may be regarded as a reducing process. It follows that the glow may be prevented by the removal of the oxygen as rapidly as it is formed, as in certain cases of cathodo-bombardment or by the presence of a reducing agent such as hydroquinone, as has been found in solutions of fluorescent dyestuffs. Excitation may be omitted altogether where reduction has previously taken place by ordinary chemical processes, if free oxygen is povided from without as in the glow of phosphorus or of the other chemical reactions which emit light. An activator is necessary for the production of luminescence in so many cases

THERMOLUMINESCENCE AFTER X-RAY EXPOSURE
(45 Kv./2 ma.)
(*Wick and Slattery*)

Phosphor	*Thermoluminescence,* 250° *C.*	
	Unexposed Color	*After ½ Hr. Exposure*
CaO	None	None
$CaCO_3$	None	None
CaOEr	None	Violet and blue
CaOSm	None	Orange
CaODy	None	Yellowish-white
CaONd	None	Faint blue
$CaSO_4$	None	None
$CaSO_4Mn$	None	Bright green

that it is reasonable to assume that it is an essential factor. The activator may be regarded as the source of free oxygen and the solvent may be regarded as having no part in the dual reduction-oxidation process to which the glow is due.

Oxygen set free at low temperatures is in part in active form since ozone is always associated with the reducing action of ultraviolet radiation, etc. Since ozone is the agent by means of which the luminescent glow may be produced in the absence of excitation, and since it or an equivalent form of active oxygen occurs when the glow is due to excitation, it is reasonable to assume that ozone is a necessary agent in luminescence, upon which the presence or the absence of glow depends.

MINERAL ACTIVATORS

The variability of fluorescent effects is familiar to all workers in the field and it is believed by some that this variability is due to the influence of those factors, known and unknown, which cause fluorescence. The principle source of knowledge concerning the causes of fluorescence in minerals, as has been previously indicated, is by studies on artificially prepared phosphors and spectroscopic and chemical analysis of fluorescent minerals themselves. The study of the synthetic phosphors has revealed certain facts concerning the influence of varying amounts of an impurity present in a phosphor on luminescence and which can be included in an explanation of mineral luminescence. The examination of minerals has, in a number of cases, actually shown us what impurity or impurities are present and those which can be held accountable for the luminescence behavior.

In the preparation of certain phosphors both the nature and amounts of impurities as well as the physical treatment given them is reflected in the luminescence behavior of the finished product. Zinc sulfide, which is not fluorescent or phosphorescent when pure, although before preparation of the artificially impure form must be prepared with some degree of purity and then contaminated and treated specifically.

The presence of manganese as an impurity in zinc sulfide produces a brilliant yellow luminescence while the addition of bismuth produces the phosphor ZnSBi which has a green luminescence. In the iron phosphor

ZnSFe all luminescence is quenched. In the preparation of the copper phosphor ZnSCu the impurified (fluxed) mixture is heated to a temperature of about 600°C. producing a blue luminosity. At temperatures of 900°C. the phosphor produced exhibits a green or yellow luminosity. Other such variations with impurification and heat treatment indicate that the color and intensity of the luminescence of alkaline earth sulfide phosphors can be changed almost at will depending on the nature of the product desired. Polymetallic impurification can also be used with success to produce phosphors with hues midway between the primary colors. This has been done on a commercial scale in Germany as exemplified by the philosophical "toy", the phosphoroscope comprised of several tubes containing variously colored sulfide phosphors mounted in a case.

Much work on the alkaline earth sulfide phosphors has been performed both in this country and abroad. Among the most exhaustive studies were those of Lenard and Klatt. While even a fairly complete resumé of this series of papers cannot be given a few of their important findings, important because they should also apply to mineral phosphors are presented. Lenard and Klatt found that these phosphors consisted of a sulfide acting as a solvent for a minute trace of an activating ingredient. The active ingredient, a metal, produced maximum phosphorescence only when pesent in small quantities and larger quantities or smaller quantities lessened the intensity of the phosphorescence. The phosphors could only be produced by bringing the mixture to a red heat and all attempts to prepare them by precipitation from solution failed. According to Nichols this indicated that the crystalline state was necessary for the occurrence of phosphorescence in certain substances. Maximum phosphorescence was produced by the activator whose quantity was governed by the law of optimum concentration. The intense heat required for the production of these phosphors has a definite but somewhat contradictory application to the problem of causation of luminescence in minerals. Many minerals which fluoresce or phosphoresce are definitely of low temperature origin, calcite, strontianite, and witherite, for example. If the explanation of Nichols is correct, that the necessity of heat treatment is to produce a crystalline state then this apparent contradiction is incorrect since mineral phosphors are certainly crystalline. The case of fluorescent opal, which still maintains its original rank as an amorphous mineral, must then be considered as an exception to the assumption of Nichols.

SOME MINERAL ACTIVATORS

Calcite	Mn, Dy, Y, Tl, Sm.
Aragonite	Mn, Tl, Dy, Sr, Cu.
Dolomite	Mn, Tl, Dy, Sr, Cu.
Fluorite	Sm, Y, La, Ce, Mn, Yb, Er.
Spinel	Cr, Sm, Cu, Mn.
Willemite	Mn, Tl.
Kunzite	Mn, Sm, Yb, Tl.

Like artificial phosphors luminescence in minerals is most likely due to the admixture of traces of elements so minute as to usually escape detection by ordinary analytical means. Regarding this, Pringsheim stated that the luminescence of minerals also appears to depend on the accidental introduction of minute quantities of atoms foreign to the characteristic crystal lattice. These are also held responsible for the characteristic color of minerals in transmitted light, although their exact nature in most cases is still not known with certainty. It is apparent, however, that such admixtures do not always cause visible coloration in the mineral, an example of this being the diamond, some water clear specimens of which give a pale blue, orange, or reddish luminescence.

Of the many minerals studied to determine the nature of foreign atoms fluorite has probably received most attention with calcite and willemite also subject to extensive investigation. In specimens of fluorite examined in 1906 by Urbain, luminescence was produced by cathode rays. He examined luminescence spectra with the spectroscope and demonstrated traces of several rare earth elements as the activating impurities. Two specimens with a green luminescence were activated by ytterbium, one with praeseodymium, and another having a rosy-white cathodoluminescence was apparently activated by samarium and dysprosium. In 1924 Tanaka published the results of a spectroscopic research on the causation of cathodoluminescence of fluorite similar to the earlier work of Urbain. He found that rare earth elements were responsible in all cases for the luminescence observed. In the specimens, the chief activating agent was samarium while other activating elements present were yttrium, lanthanum, thallium, cerium, and ytterbium. Further, the luminescence colors of violet, blue, or green often changed to orange after heating the mineral. This, however, was regarded as a poor criterion by which to identify the activating element in the mineral.

In fluorite, as well as in other minerals it has been the practice to consider the elements responsible for the color in white light as also responsible for the luminescence properties. Hydrocarbons, for instance, have long been held to be the cause of the various colors fluorite exhibits and in earlier studies into the cause of fluorescence these organic substances were regarded as activating agents. It is true that the yellow fluorescence of certain specimens of fluorite is due to the presence of myiads of minute bubbles of free petroleum. In 1933 E. M. Gunnell reported such a specimen from the Hardin County, Illinois area. In these rare cases the fluorescence noted is that of the included hydrocarbon while the fluorite may be negative. In 1906 Morse investigated the relationship of color to the optical properties of fluorite and concluded that organic substances, which at least in part cause color, have nothing to do with the fluorescence of this mineral. According to E. M. Gunnell, who is supported by the evidence of many investigations, rare earths are activators in all specimens of fluorite examined so far.

Calcite is another commonly fluorescent mineral to which the luminescence is due to impurities. Headden's investigations have been cited elsewhere on the highly thermoluminescent sections of golden calcite from Joplin, Missouri. Tanaka's investigations in 1924 with the spectroscope indicated that manganese is the activating agent in calcites. Yttrium, samarium, and other rare earths appear less frequently as activators. The specimens examined were from Putnam and Westchester Counties in New York; Long Hill, Connecticut; Franklin, New Jersey, and Cumberland, England. No relation between the intensity of luminescence and amount of activating metal present could be established in any but one of these specimens.

The sample from Franklin, New Jersey contained the greatest number of bands due to manganese and exhibited the most intense fluorescence of any. A specimen from Long Hill, Connecticut exhibited a weaker fluorescence than other calcites with less manganese. According to Bruninghaus, the luminescence ability of $CaCO_3Mn$ phosphor is not destroyed until the concentration of manganese exceeds 10%. Since it did not appear reasonable to explain the weak fluorescence of the Connecticut calcite on the basis of too much manganese, Tanaka suggested that it might be due to the presence of unfavorable elements, or the absence of favorable elements, or the failure to obtain some unknown natural treatment essential for production of a bight fluorescence.

Tanaka also examined certain specimens of aragonite and dolomite with the spectroscope. His conclusions regarding these carbonates were that the chief activating agent in the luminescence of calcite, crystalline limestone, and dolomite is usually manganese. Sometimes, it was found, that manganese does not produce a strong luminescence, the reasons for which are unknown. In some cases strontium was the chief activating agent, especially in aragonite, producing a greenish and comparatively faint luminescence. Other activating agents found were dysprosium, yttrium, thallium, and samarium.

Scheelite was subjected to a spectroscopic examination by De Rohden in 1914 and rare earth elements were found in all seven specimens excited by cathode rays. Didymium, samarium, and terbium were found to be the chief activating elements judged on the basis of affording the most intense bands in the spectra. The widespread presence of rare earths in scheelites has been noted by other investigators also.

Manganese generally appears in association with fluorescent minerals and while it can hardly be said that fluorescence is due in every instance to manganese, as several prominently fluorescent species apparently do not contain this element, there are indications that some connection with manganese can usually be traced. Many minerals showing the phenomenon do have manganese as an essential constituent as an impurity, or in very minute quantities often associated as a pigment. Those which contain none often occur associated with manganiferous species such as those at Franklin, New Jersey.

Manganese-free calcite does not fluoresce but manganiferous calcites and dolomite from Franklin, New Jersey fluoresce in colors which range fom a weak pink to a bright red. T. W. Ward (1939) pointed out that pectolite from Franklin, New Jersey gives a pure yellow luminescence which is ascribed directly to its slight manganese content. The 0.11% of MnO in kunzite has also been suggested as an explanation of the strong phosphorescence of this mineral which lasts for several minutes after exposure to the iron arc.

Margarosanite is a rare calcium-lead-manganese silicate which fluoresces a pale violet color. It is noteworthy that this color is often given by the zinc-lead-silicate-larsenite, which also contains calcium and manganese; and by hardystonite which contains 1.5% MnO with one-third being CaO. Calcium-larsenite, being similar to larsenite, but with some lead replaced by calcium might be expected to show the violet fluorescence similar to that in the last described varieties. Nevertheless, this is not the case as the color is a vivid lemon-yellow. Manganese is present in this mineral, analysis showing up to 0.57% MnO. Hedyphane fluoresces with an indistinct bluish-gray color. Apparently it contains no manganese but it occurs with tephroite which is a highly manganiferous silicate containing up to 69.59% MnO.

Ward points out also that some of the mineals which apparently contain no manganese may not be as free as believed. The apparently pure calcite which fluoresces with a violet color is an example, and while the fluorescence cannot be traced directly to a manganese content it is interesting to note that this calcite originates in a locality where calcite is commonly impregnated with manganese. Clinohedrite with 0.50% MnO gives a slightly orange-yellow tint, difficult to distinguish from, but weaker than that of pectolite.

CHAPTER FIVE

METHODS OF EXAMINATION AND TECHNIC

General Considerations

In ordinary studies of mineral luminescence subjective methods ot examination as well as subjective methods of noting results are most often used. The reasons for this are numerous and varied. Perhaps the main reason is that words consist of a simple and easy means of describing the action which results from placing a mineral in ultra-violet light. Other reasons are probably as apparent. Words are favored because of the inaccessability of the non-technical student of fluorescence to objective means of analysis which require instruments and training in their use. The difficulty in obtaining radiation standard in spectral characteristics contributes to variation and prohibits more objective studies. Such studies usually include theoretical and laboratory research on both exciting light and emitted light.

Although instrumental means of anlysis are sometimes beyond the reach of the student it is well to keep the statement of Luckiesh in mind when word descriptions carry important conclusions or much gravity in important conclusions. Words at their best are mere approximations, they are unwieldly and indefinite in comparison with the conciseness and accuracy of mathematical media. Their inadequacies are particularly emphasized in descriptions of color, color of fluorescing minerals for example. Scientific progress in color, as well as in fluorescence, depends on the standardization of methods and terminology, the latter of which implies more than the singular use of words. Esthetic appreciation is little concerned with exactness. The esthetic sensibility feels or wants to feel; the scientific sense knows or wants to know.

Since instruments like the spectrograph are not ordinarily available to the general observer words are depended upon to describe fluorescence actions. When words are used extensively certain considerations should be kept in mind as to their application, use, and subjective nature. Primarily to be remembered is that the simplest terms possible should be employed in descriptions. Terms which do not confuse—terms familiar to all and which may be used with the least amount of ambiguity should be chosen. Likewise, terms for describing intensity of fluorescence should be handled with care. Probably a minimum amount of incorrectness and ambiguity would result from the singular use of comparison with well known mineral specimens. For example, description of a fluorescing specimen in terms of a well known fluorescent specimen such as wilemite or scheelite. In this case the quality of color, response, as well as relative intensity might tend to clarity interpretation of fluorescence being observed by several persons.

The variability of luminescence actions depends on the observer in many instances. For some persons the differentiation between true fluorescence, color in white light, and reflected, transmitted, and the additive effects of color is apparently difficult. The reasons for this are probably complex and variable. Persons vary widely in conception of what pure fluorescent emission actually consists of. Others fail to respond normally to light of various wavelengths. Reception to radiation of different wavelengths varies for persons of different ages. Radiations at about 3800 A.U. are stated to be visible to persons, some between the ages of 15 and 30 years, while many older persons can see only down to about 3950 A.U. This is important in the observation of fluorescence and in it is a field for investigation. In a few cases inability to discriminate is the result of fatigue, inexperience, or carelessness. The person who studies fluorescent actions objectively appears to be rare; the persons who regard the action subjectively and esthetically are frequent.

The extent and size of discrepancies either in interpretation or in reception of fluorescent light was demonstrated by Van den Akker, P. Nolan, Dreshfield, and H. F. Heller in 1939. In research on the size test for paper by fluorescence it was hoped that the subjective method for interpretation could be used, i.e., simple visual observation, should the personal error be small. It was assumed that the method would not be of greatest value unless different operators could obtain sensibly the same results using only written instructions.

The method was tested for this requirement by using six men, only one of whom knew anything about the test. They were told the purpose and the nature of the method and received only a word description of the end point and what it would be like. No personal instruction was given as to the equipment or its mode of operation and use. These men were given test specimens cut from a sample in such a manner that their data should have agreed. In addition, each received a few specimens to experiment with before the test was begun. These operators, therefore, were regarded as inexperienced, without the advantages of personal instruction. The results obtained are shown in the table. The results obtained by two of the operators agreed fairly well with the result obtained by number VI, the regular observer, but othe deviations were regarded as intolerably large. It later became apparent that operator number IV judged the end-point soon after the appearance of spots (stars) and did not wait until half the treated area fluoresced uniformly. The other two observers waited until more than half the treated area fluoresced uniformly.

JUDGING FLUORESCENCE END-POINT WITH VERBAL INSTRUCTIONS ONLY,

Uranine B Size Times, (*Van den Akker,* 1939)

Observer	I	II	III	IV	V	VI
Seconds	55	90	72	54	60	63
	274*	94	82	55	67	70
	54	96	90	52	70	70
	66	108	87	65	75	74
	68	100	88	57	66	67
	65	91	80	56	61	69
	64	102	85	57	70	65
	66	97	84	57	66	71
	66	94	92	56	..	67
	69	106	90	61	70	75
Averages	64	98	85	57	67	69

*Excluding 274 seconds.

While this is only an instance of the "intolerably large" deviations in interpretation of fluorescence by different persons it illustrates the extent to which word descriptions are reliable. Not only in fluorescence but also in the observation of color under white light do discrepancies occur. G. Marcher (1939) pointed out that a colorful array of gems might cause one observer to be startled by their beauty while another observer might be somewhat apathetic towards the same display which evoked a relatively dissimilar reaction in a third observer. Instances of this kind are common in both fluorescence and color in white light and should emphasize that words, at present the pactical and universal method for describing fluorescence, are in themselves subjective and should be used carefully.

FACTORS INFLUENCING FLUORESCENCE APPEARANCE

I—THE SPECIMEN
1. Physical nature, multiple
2. Chemical nature, multiple

II—THE EXCITING AGENT (*Ultraviolet radiation*)
1. Spectral character of the ray
    a. Wavelength
    b. Distribution; maxima and minima
    c. Residual visible radiation
        1. Spectral character
2. Intensity of the beam
    a. Shape

III—SPECIMEN-RAY RELATIONS
1. Distance from the source
2. Angle specimen placed in ray
3. Angle observed

IV—OBSERVER
1. Previous experience
2. Conception of the action
3. Visual acuity
4. Response

5. Color discrimination
6. Relation to
    a. Specimen
    b. Ray
7. Fatigue
8. Psychological make-up
    a. Objectiveness of observation

V—THE RESULT

1. Lifetime of the excited state
    a. Fluorescence
    b. Phosphorescence
    c. Both
2. Color
    a. One
    b. Several
3. Intensity
4. Dependence on wavelength of ultraviolet light
    a. Independent
    b. Dependent
5. Purity of the phenomenon

EXPOSURE OF THE SPECIMEN

Ordinarily specimens of minerals are placed in ultraviolet light in a more or less random fashion. Haphazard procedure suffices for general observation although in liquids or solutions of fluorescent chemicals this does not always produce adequate results. Also, specimens, unless highly excitable, such as acid-quinine sulfate solution or alkaline-fluorescein solution, are sometimes restricted in excitation by the vessel in which contained and exposed. In some instances exposure to ultraviolet light is made without regard to the transmission characteristics of the container which may be opaque to wavelengths that would excite fluorescence.

While fused quartz or other similar vessels are often not available a fair substitution may be made with Pyrex vessels or small cells constructed with fluorite, mica, or quartz microscope slides as windows. In most cases observing the sample in a non-fluorescent tray gives good results. Other tests may be made in the manner suggested by Radley and Grant (1933) by placing a drop of liquid between two quartz microscope slides and examining in reflected or transmitted ultraviolet light. In some liquids it is well to progressively dilute the specimen and examine at different stages of dilution since fluorescence often appears according to an optimum concentration.

Regarding the observation of liquids it is interesting to note the more objective approach by Hirschlaff (1939). He states that the reason why the fluorescence color of pure and undiluted liquids is often missed is twofold: In one the observations are made in a way that the emitted light is viewed at right angles to the exciting beam of ultraviolet light. Since every ion or molecule in a pure liquid can absorb incident radiation to a varying degree the light is completely absorbed in the first layer of the liquid itself and therefore cannot penetrate farther into it. In this case surface fluorescence of alcohols, some oils, and other materials appears. This will be observed only in the same direction as the incident light.

In the second case the fluorescence of liquids is found to be quite strongly quenched by unexcited homologous molecules, i.e., molecules of the same kind and of the same liquid. This is due to the obviously close association found in liquids and on account of the neighboring resonance in their energy levels. This, *concentration quenching,* handicaps the observation of fluorescence of undiluted homogenous liquids. For these reasons the fluorescence of liquids can best be studied in solution form provided they are irradiated with wavelengths they can absorb.

In the examination of minerals such care need not be taken since solids, if markedly fluorescent, usually respond irrespective of position in the incident beam of ultraviolet light. In cases where the specimens may be broken an examination of a freshly exposed surface should be made. For minerals, pulverization and examination at different stages of pulverization often reveals differences in luminosity. Sifting through screens of different meshes and the use of other mechanical methods for separating constituents often presents luminosity studies not obtainable with the simple and more qualitative procedure generally used.

Semi-quantitative investigation into fluorescence characteristics of mineral specimens may be made either for study purposes or for purposes of identification and comparison. Spotting the surface with dilute acid and dilute alkali often modifies fluorescence color and intensity so as to allow discrimination of specimens otherwise identical in ultraviolet light. This technique is used with moderate success for differentiating samples of the same mineral but from different localities with impurities of a different nature as evidenced by the modification in fluorescence.

For ordinary examination specimens are cleaned thoroughly, as is to be expected, and examined when dry. Dake (1939) used a technique of etching to separate the constituents of a heterogenous specimen. He subjected an ore of willemite, calcite, and franklinite to the action of 15% hydrochloric acid for several minutes. The chemical action resulted in the etching out of the calcite, leaving the strongly fluorescent willemite in high relief. This technique may be used further to isolate pure quantities of sparsely distributed fluorescent particles from a matrix of any carbonate.

It is important to regard variations in fluorescence as arising in the source of the ultraviolet light as well as in the specimen and observer. The source of ultraviolet light, and its emission characteristics frequently modifies fluorescence and less frequently phosphorescence of minerals. For example, many specimens under a cold quartz tube lamp appear quite differently than the same specimen under a black bulb type lamp. This is due to several reasons. The wavelength emission of the various types of lamps varies considerably. In addition, the wavelength emission of lamps of the same type may vary appreciably. De Ment (1940) pointed out that residual components of the visible spectrum, that is, blue, green, violet, red, etc., are likely present in most sources of radiation available. In some instances the emission of violet and red is so large as to completely overshadow the delicate blue and lavender fluorescence known to exist in many minerals and certain rare chemicals. These residual wavelengths not only overshadow the delicate colors but produce additive effects that mask the true appearance of other fluorescent colors. These give rise, together with the actual color of the mineral, to qualities of color and intensity not otherwise obtained with monochromatic or more selected wavelengths of ultraviolet light. Instances of these color effects are numerous in the literature on fluorescence and are so great in some studies as not only to be faulty but to render them valueless.

There is good reason to believe that the explanation of De Ment accounts, at least in part, with varying effects obtained with lamps of the same type but of different manufacture. This applies also to filters which may vary from batch to batch both in type and efficiency of transmission. Of further importance is that the human eye itself fluoresces. Grunsteidl (1933) suggested that fluorescence be observed through cells of potassium nitrite solution to cut out any reflected ultraviolet light which might cause the eye to fluoresce and give the specimen a false color value. Moreover, the spacial relationships (specimen-ray-observer) often affect the luminescence *appearance* of mineals to a varying degree. Some specimens placed several centimeters from the lamp appear slightly different when examined at a distance of half a meter. This is due not only to a reduction in intensity of certain wavelengths absorbed by air, but also to differences in interpretation of color effects by the individual at the greater distance. Actions such as this are evident more in hot filament sources where wavelengths often include violet and red.

COLOR

Of the more quantitative methods used in fluorescence studies the colored filters employed by Stokes were the forerunners of the more refined means used at present. With colored filters Stokes found that if a substance were visible through a red window the fluorescent light was assumed to have the red component of the spectrum present; if visible through the blue window it had a blue component and so on. In this was a rough, but superior to word description, analysis of fluorescence color could be made. In the same way Lunden (1928) used a frame of colored glasses for the examination of fluorescence in sugars. Radley and Grant (1933) pointed out that a set of accurately graded color glasses allowing only rays of a specific color or wavelength range to pass would be useful if produced at a low cost. The use of solutions of aniline dyes suggests itself for grading fluorescent minerals.

A rather well known technique, but apparently not extensively applied to the problem of objective determinations of fluorescence colors, is a method related to the color glasses used by Stokes. It has been known that by mixing red, green, and blue light of a suitable character in special apparatus light of practically any color, including white light, could be synthesized. This principle provided a basis for systems of color classification and color specification. That is, by specifying the amounts of each of the three hues required to match the color being observed a more exact determination is made. The *Ives Colorimeter* is an instrument of this sort, designed by H. E. Ives in 1909 for the measurement of all colors in terms of three primary colors. By means of this colorimeter it is possible to describe a color accurately in terms of the red, green, and blue components of a standard white light. In white light, red is assumed to have a value of 100, green 100, and blue 100. For example, pink is designated with red = 100, green = 50, and blue = 80.6. This means that by mixing red, green, and blue in the proportion given the sensation produced on the brain is that of pink. Two colors alike to the eye measure alike in the colorimeter. The method provides a more objective approach to color determination and while it presents a means of numerically comparing the visual effect of fluorescence from different specimens it differs considerably from the *spectrophotometer*. The spectrophotometer gives the intensity at every point in the spectrum but only an approximate indication of how the eye will compare the color in question with another.

Since red, green, and blue suggest psychological components rather than physical constituents the terms were changed to red = x; green = y; and blue = z. Thus the color regarded as a primary stimulus, may be denoted in terms of relative amounts of x, y, and z components required to match a certain wavelength instead of in psychological terms to match light of another color. For example, light of wavelength 5000 A.U. is described in terms of the three distribution coefficients x, y, and z. In this case $x = 0.0049$; $y = 0.323$; and $z = 0.2720$.

The Ives Colorimeter consists essentially of an oblong box, at one end of which are four slits; one clear, the three others equipped with the red, green, and blue screens. By means of levers the openings of the three colored slits can be altered to read by scales from zero to one-hundred, or in other values should the determination be in x, y, and z terms. Within the instrument a wheel of lenses is rotated rapidly by a small motor. This causes the three colors to pass across the field of vision and mixes them by persistence of vision. The optical system is such that one observes a divided field, one part consisting of the mixture of the three primary colors and the other the color to be matched as viewed through the clear slit, in this instance, a fluorescing specimen.

The *Guild Colorimeter* used by Morgan and MacLennan in 1928 on the fluorescence of butters and margarines is based on this principle.

The *Zeiss step-photometer* is another instrument which gives a quantitative expression of both color and intensity of fluorescence. This instrument, used by M. Haitinger (1931) matches the light from the sample and the standard as seen through blue, red, and green filters. The numerical values obtained being plotted as percentages of the total light emitted in a Helmholtz-König triangular color diagram. In this the tone, degree of saturation and intensity of fluorescence is evaluated quantitatively since color is given in terms of two rectangular co-ordinates.

As is well known, the instrument used to break up light is called the spectroscope. Basically, all designs of spectroscopes consist of four parts (1) the slit, (2) the lenses, (3) the dispersing system, and (4) the observing or recording system. Various optical and mechanical devices and arrangements are also used with this instrument depending on the purpose for which it is designed.

Studies on the spectrum of a luminescing substance often provides significant information as to the mechanism occurring. A fluorescence spectrum consists of one or more bright bands usually varying greatly in width and oftentimes extending throughout the entire visible region. The spectrum of a fluorescent substance is either a homogenous complex of systematically related components or a heterogenous complex of unrelated components. In either case the components frequently overlap giving the appearance of a single band which is called a mixed band or a homogenous band. When the components overlap completely or not at all the appearance is that of a group of bands.

The *principle of essential identity* was demonstrated experimentally by Nichols, Howes, and Wilber in 1928. It is concerned with the spectra of luminescing substances and may be summed as follows: (I) Two spectra are essentially identical when all their components are members of the same set or sets. (II) A set is an aggregate of equi-distant bands or components, where distance is measured in frequency units. (III) A full set is a set in which all the members between the two outer limits of the spectrum are present. (IV) An incomplete set is one with missing members, but in which distances between existing members are always exact multiples of the frequency interval. Sets in the spectra of solid solutions are generally incomplete, or, perhaps seemingly so since inadequate methods used pick up the weaker members of the set or those which are most completely submerged. (V) The spectra to which this definition applies are spectra comprised of bands either separate or overlapping. The structure in question has been found to occur even when overlapping is so complete that the components are entirely submerged and the spectrum appears to be continuous. So far as is known, all luminescence spectra are of the above types. (VI) The luminescence spectra of solids containing a given activator are essentially identical, i.e., they are made up of components belonging to the same set or sets. Although the relative intensities of the components may vary the sets of components present in the spectrum depend only upon the activator.

The ideal and practical mode of describing fluorescence is obviously by *photography*. By the use of modern *color film* it is possible to obtain superb photographs of fluorescing minerals. These can be used as lantern slides for lectures or may be examined photometrically or by the other procedures possible. Heretofore, technical data on the photography of fluorescent minerals has been lacking. The exact time for exposure was not known with certainty. In 1939 C. W. Jarrett used Kodachrome film for obtaining accurate photographs of fluorescent minerals. He found it necessary to remove all of the wavelengths below 4000 A.U. since Kodachrome film is sensitive to light not included in the visual range of the human eye. In order to correctly photograph fluorescent minerals in their exact fluorescent colors Jarrett placed two 2-A filters over the camera lens to cut off wavelengths at about 4000 A.U. These transmit practically all of the light between 4000 and 7000 A.U., i.e., the visible range. The intense blue of scheelite and fluorite and the green of willemite required less exposure than the red of calcite. Five minutes exposure obtained exact colors in the blue regions and fifteen minutes exposure obtained exact colors in the red regions. The time of exposure, of course, varies with the stop used. Kodachrome registers fluorescent colors as they appear to the human eye provided the proper filters and exposure are used.

INTENSITY

For the measurement of intensity of fluorescent light word descriptions are used extensively. The varied and highly subjective use of terms such as strong, bright, intense, weak, pale, medium, showy, and so on, denote the degree with which intensity may actually be described with words. As words are the favored media for intensity descriptions, reference can only be made to the cautions stated previously unless, of course, instrumental means are used for determining the character of the exciting light or fluorescent light. Data on the exact nature of fluorescent light is often useless without data on the exact nature of the exciting ultraviolet light. The latter includes not only specific wavelengths but the percentages from the various types of ultraviolet light units.

Light *intensity* is expressed in candles; *flux* or the amount of light is expressed in lumens; *illumination* in lux (meter-candles), photos (cm-candles), or, foot-candles; and *brightness* in lamberts (surface emitting of reflecting one lumen per cm^2), or candles per cm^2 (candles per $cm^2 \times \pi =$ lamberts). A uniform point source of 1 candle emits 4π lumens. In luminescence measurements, according to Pfund, one deals not so much with light intensity as with brightness of a surface or of a known depth of liquid or gas from which the amount of light emitted in lumens can be calculated.

The illumination of a surface is given by

$$\text{Phot} = \frac{I \cos \theta}{d^2} \qquad (1)$$

where I is the intensity of the light source in candles, *d* the distance from the light source in cm, an θ the angle between the light sources and a line normal to the surface.

The emission of light from a perfectly diffusing surface or the luminous intensity is also proportional to the cosine of the angle of emission. This is *Lambert's Cosine Law Of Emission,* the practical effect of which is to make the apparent brightness of a surface independent of the angle of view. If the illuminator of the surface is given in phots, the value is multiplied by a reflection factor for the surface to obtain brightness in lamberts in any direction. This is important in measuring by use of illuminometers, the brightness of surfaces calculated in illumination and not in brightness units. Lambert's Cosine Law does not hold for layers emitting light or transparent to the light emitted. The apparent brightness increases as the grazing-incidence is approached. This may be useful in measuring the brightness of fluorescent solutions. The amount of light emitted from gases or liquids can be determined from measurements of the brightness of a given thickness and the absorption (1 — T, where T is the transmission). Pfund states that if light passing through a solution is absorbed

$$T_1 = \sqrt[n]{T_n} \qquad (2)$$

whereas if scattered

$$T_n = \frac{1}{1 - n + \frac{n}{T_1}} \qquad (3)$$

where T_n is the transmission of n thickness and T_1 the transmission of unit thickness. Usually both absorption and scattering occur in a solution so the first expression is sufficiently accurate. Having measured the brightness in lamberts, B_n of a given thickness n of luminescent fluid, the brightness of a one centimeter thick layer of perfectly transparent fluid —B_1 is given by

$$B_n = \frac{B_1(T_n - 1)}{\log_e T_1} \tag{4}$$

It follows that a centimeter cube of absolutely transparent fluid whose brightness is given in lamberts will emit four times this value in lumens in every direction. Such measurements have been made by several investigators. Adams (1924) applied these relationships to the chemiluminescence of phosphorus and Harvey (1925) applied them to the bioluminescence of bacteria.

Instruments utilizing the principles of light absorption may be used for studies on intensiy of fluorescent light. For the measurements of emitted light two main methods other than word description have been used. The most simple procedure and the one on which screens of different density depend is the photometric method. In this the eye is the final judge although with the aid of instruments accuracy within 1% is often obtained. In other methods, the photoelectric phenomenon is used and the eye does nothing other than read the scale on instruments. In some cases this is not necessary since the result may be recorded on a moving drum.

For examination of a large number of fluorescent minerals the *photometer* is particularly useful although it gives results in terms of relative intensity unless calibrated or used with auxiliary equipment. Essentially, a photometer consists of a screen illuminated by the two sources to be compared. For example, a fluorescing mineral with an incandescent lamp of the same hue and of known intensity.

A partition between the two sources prevents mixing of the two beams. In use the distance of the two sources from the screen is varied until the illumination on the screen appears to be the same for both. In more refined apparatus each source appears as half the field, making comparison much more simple. For comparison with incandescent sources colored filters are used to match the specimen in the approximate wavelength region emitted to prevent discrepancies which occur from differences in interpretation of different hues.

Ultraviolet Monochromator for producing pure emission of light of wavelengths as low as 2000 A.U. Two quartz prisms and construction for high light gathering power produce an intense beam of monochromatic light. (*Courtesy of Bausch and Lomb Co.*).

Since illumination by a source of light is inversely proportional to the square of the distance the values of the two intensities in terms of each other may be computed where d_1 and d_2 are the distances of the two sources of illumination from the screen of the photometer respectively, and A_1 and A_2 the illumination of the screen due to the source measured and the standard source respectively. I_1 and I_2 are the intensities appearing on the screen. Since $A_1 = A_2$.

$$A_1 = K \frac{I_1}{d_1^2} \qquad (5)$$

$$A_2 = K \frac{I_2}{d_2^2}$$

Photoelectric cells and other equipment not dependent on the human eye for comparison are used to a limited extent for measuring the intensity of fluorescent light. With the increase of application of fluorescence to the arts and sciences the adoption of such apparatus for measuring the intensity of luminosity has increased. A promising form, and an exact instrument for physical photometry is the photoelectric cell. Its applications to the field probably will increase the number of objective studies as well as re-enforce fluorescence analysis to the extent of placing it on a basis with the present forms of chemical and physical analysis.

The response curve of some photoelectric cells does not resemble the visibility curve for the normal eye. It is apparent that two illuminations of the same visual brightness might excite quite different currents in a given photoelectric apparatus. Nevertheless, the numerous advantages of the photoelectric cell over visual methods of photometry make the former desirable since objective methods are to be substituted wherever possible for subjective methods. The act of reading a scale on a meter is capable of far greater precision and is much simpler than the matching of two illuminated fields by the eye.

There are three essential types of photoelectric photometers, any of which may be used for the measurement of the intensity of either fluorescence or phosphorescence. The method used, however, depends somewhat upon the type of photometric measurements to be made, the precision required, the type of sample, its luminosity and wavelengths emitted, and perhaps on the type of excitation. Requirements to be incorporated in the apparatus are simplicity of operation, ruggedness, reliability, and reproductibility of results.

In *direct photoelectric photometry* the intensities are compared in terms of photoelectric currents produced in a cell. For adequate results the cell should respond equally to radiations of all wavelengths or should respond exactly as the eye would under the same conditions. The sensitivity of the cell should not change appreciably with time or use and for control readings monochromatic light should be available. The direct method is the simplest and most adaptable to work in mineral fluorescence.

In the *balanced cell method* two photoelectric cells are used, one illuminated by the fluorescing mineral and the other by the standard source of illumination. This method is more complicated than the direct method and may be depended on whereas unreliable or inadequate information is obtained with other methods.

The *equal deflection method* uses a single cell illuminated alternately by a standard source of light and by a fluorescing mineral. With this method studies which involve rates of decay may be performed. In the equal deflection method extremely high precision is obtained by coupling the system with a high-gain vacuum tube amplifier.

For methods of photoelectric comparison which depend on the final reading in photoelectric current values a variety of instruments may be used. These obviously depend on the nature of the investigation and on the intensity of the light being measured. Galvanometers, electrometers, vacuum tube amplifiers, or others suitable for experimental work may be used in some instances while special procedures will have to be devised for others.

The *fluorophotometer* is an instrument particularly designed for measuring the fluorescence of liquids and solutions. The assay of materials or substances which can be converted into fluorescent materials is exceptionally accurate and reproducible. Because of the high sensitivity of the instrument, accurate fluorescence analysis in the magnitude of fractions of micrograms is readily accomplished. The fluorophotometer may be applied to fields other than fluorometry. It extends to include colorimetry, nephelometry and turbidimetry.

In use, the exciting beam of ultraviolet light passes into a solution and causes it to become fluorescent. The fluorescent light strikes a photocell, which transforms the light into electrical energy; this photoelectric current is then registered on a galvanometer. Since the intensity of fluorescence depends upon the intensity of the exciting light and upon the concentration of the fluorescent material, this concentration can be determined by using a fixed exciting intensity. The galvanometer deflection is generally in linear relationship to the concentration of the fluorescent substance within the limits used.

The "fluorometer" is especially adapted for determinations of vitamins A, B_1, B_2, B_6, and nicotinic acid. For procedure see the chapter on applications.

DURATION OF PHOSPHORESCENCE

The difference between fluorescence and phosphorescence on the basis of duration of an excited state has been mentioned previously. Since there is no instantaneous return of a displaced electron to its shell, it follows that measurement of the period required for this return, provides a means for investigation into the nature of luminescent phenomena.

The first measurement of the phosphorescence of a few thousandths second duration was by E. Becquerel in 1859. In first considerations of a contemplated measurement of this kind Becquerel was confronted with several apparent facts before construction of such an instrument could be accomplished. Among the considerations which presented themselves were, the quantity of the phosphorescent material available, the total period of decay, the temperature at which the specimen was examined, the nature of the exciting agent, the ease with which saturation of the specimen occurred, and the initial brightness of luminescence.

Instruments for the determination of the period of emission as well as the nature of emission are called *phosphoroscopes.* They may be of the type which allow observation of the specimen periodically excited and periodically viewed at a later phase. They may facilitate continuous observation of a specimen continuously excited. Or, phosphoroscopes may allow observation of a specimen excited for a measured interval and intensity of emission measured at a later time. The latter are applicable to the slow types of decay.

In one of the phosphoroscopes devised by Becquerel the intermittently excited type was constructed. In this the specimen was mounted between two parallel disks and alternately illuminated and observed through properly adjusted openings in the disks. These disks each had four open sectors mounted on the same axis but in different phase. In use, the exciting light passed into the translucent crystal specimen through the rear disk while the opaque sector prevented light from coming through, to affect the eye. As the disk was revolving at a high velocity, the light was quickly stopped from passing to the crystal by interposition of an opaque sector of the rear disk. A fraction of a second later the continued rotation brought an open sector of the front disk in line with the crystal and allowed the light to be viewed on a dark field. In Becquerel's instrument the rotating parts were mounted in a brass drum driven by a crank through a system of gears. The afterglow of platinocyanides of 0.003 second was detected with this instrument.

For opaque specimens another type of instrument was constructed. A rotating disk with three openings 120° apart revolved on a fixed vertical axis between two fixed disks with two openings 180° apart. The specimen was mounted below these and excitation from light passing through one set of openings in phase allowed observation of emitted light a fraction of a second later in the other set of openings in phase.

E. Wiedemann (1888) constructed a phosphoroscope with a hollow drum fitted with a collimator, lens, and revolving disk for the admission of light. The light passed intermittently through the openings in a sectored disk and intermittently excited the specimen mounted inside the drum. This instrument was constructed so as to exclude stray light since it is evident that undispersed phosphorescence with an intensity of 10^{-2} to 10^{-6} that of the exciting light would be disturbed by stray light.

In 1861 E. Becquerel designed a phosphoroscope using the specimen continuously excited and constantly viewed at a later time. This consisted of a drum whose periphery was covered with a phosphorescent specimen. At one portion of the drum the exciting agent impinged on the specimen and 90° from it a viewing collimator or photometer was placed. Such an instrument was used in 1882 by Tyndall for lectures.

In studies on the phosphorescence of calcite Nichols and Howes (1916) used an 8 cm drum which was coated on the periphery with the powdered specimen. The exciting agent was a spark gap placed 180° from the eye-piece. Although this angle remained constant the time of decay could be varied between 0.01 second and 3 or 4 seconds by changing the motor field or adding a worm gear drive.

In the study of cathodophosphorescence Nichols and Howes (1919) used a vacuum phosphoroscope which allowed cathode rays to impinge on the periphery of a drum coated with calcite. Intensities of phosphorescence were measured with the aid of a lamp, photometer bar, and Lummer-Brodhun cube.

The third type of phosphoroscope, in which the specimen is excited for a definite time and viewed at varying but definite periods after excitation, was used by Nichols and Merritt (1912) for the study of sphalerite. In this instrument the specimen was mounted diagonally in a box with two openings having shutters, one to admit exciting light and the other to allow the luminescence to be viewed after excitation. This arrangement excluded light appearing during excitation but allowed observation of the phosphorescence with no fatigue when the shutter of the luminescence window was opened. The instrument was suitable for studies on phosphorescence of several minutes duration. The time when the phosphorescence intensity became equal to the comparison field presented points for plotting a decay curve.

There is probably no single phosphoroscope well adapted for the study of all mineral specimens. In studies on phosphorescence, in the past, the investigator has often devised one or more instruments for the observation of the vaious types of phosphorescence. In the future the instrument must be adapted to variable behavior in the specimen. Also, the precision with which the time of observation is to be obtained makes it necessary that the modern phosphoroscope be equipped with an accurate tachometer. The plotting of decay curves has indicated that both times and excitations be known. The lack of constancy of excitation has been recognized and many observations corrected in this respect.

The importance of obtaining the same degree of saturation as decay begins is obvious if the results are to be considered comparable. In the continuously excited phosphoroscope the importance of this factor becomes evident. The use of the interrupted excitation type for eclipses of sixteen or less a second should be entirely avoided because of the behavior of the eye when flicker occurs. The human eye should not be fatigued beyond instant recovery during the process of observing decay, neither should it be dark-adapted before beginning a set of observations. The necessity of adequate screening is of importance when it is considered that luminescence radiation is several thousand times less intense than the visible light required to excite it in photoluminescence. Stray luminescence may add to the selected portion of the luminescence beam and produce errors. These factors are fundamental considerations for the future student of phosphorescence.

CHAPTER SIX

SOURCES OF ULTRAVIOLET RADIATIONS

There are numerous sources of ultraviolet light which may be utilized for the demonstration of fluorescence in minerals, and a host of other substances. Ultraviolet radiations are generated by (1) very hot bodies and by (2) ionized gases. For laboratory purposes or for other required generation of ultaviolet radiations either of the above sources may be utilized.

(1) VERY HOT BODIES. Any incandescent flame or solid is usually rich in ultraviolet output, and sources of this type were used by research workers many years ago. One of the earliest sources of ultraviolet, used in the laboratory, was a gas-lamp burning carbon disulfide vapor in an atmosphere of oxygen. Long ago it was learned that sunlight was rich in ultraviolet, and early investigators in the field of fluorescence often utilized this convenient source With the recent development of the modern and efficient ultraviolet light sources, practically all investigations and demonstrations are made in this manner.

Included under the "hot" sources of ultraviolet radiations are the sun, iron arc, carbon arc, spark gap, mercury arc (in fused quartz tubes), high intensity mercury vapor lamps, and incandescent electric light globes.

(2) IONIZED GASES. Various gases and vapors ionized by an electrical discharge emit ultraviolet radiations. The substances generally used for generating short wave radiations are argon and neon gas, and mercury, sealed within an evacuated quartz tube. The mercury and gases are ionized by the passage of current via the electrodes sealed at each end of the tube. Lamps of this type are generally referred to as "cold quartz tubes" — the tube may be either fused quartz or one of the recently developed cast forms. Quartz tubes have the advantage over the hot types of lamps in that the former generate little heat, consume little electrical energy, offer a wide range of ultraviolet output, and give long life.

There are numerous ultraviolet units available on the market, intended for many purposes, including home use, illuminating large collections of fluorescent minerals, research laboratories, mining operations, and various industrial applications. These ultraviolet light units range in price from fifty cents upwards. Recently a number of low priced bulbs and lamps have been made available, hence no one need forego the delights of fluorescence, for lack of a suitable source of ultraviolet radiations.

Let it be understood that there is no type of lamp which will prove effective for every purpose. All units have their advantages and disadvantages. For some purposes a unit which emits a large percentage of long rays will prove most effective, while for other uses a lamp rich in short rays is indicated. In the electromagnetic spectrum, ultraviolet radiations as generally from about 136 to 4000 A.U., but the ultraviolet sources under discussion do not give usable wavelengths shorter than about 1800 A.U.

INCANDESCENT SOURCES OF ULTRAVIOLET

ARGON BULB. In recent years there has been developed a small two watt glow lamp operating on either alternating or direct current at 110 volts, and generally referred to as the argon bulb. Due to the fact that the lamp consumes only two watts of energy very little heat is generated. The argon bulb, filled with argon gas, emits no radiations shorter than about 3900 A.U. However, a number of minerals and substances having fluorescent properties react in a satisfactory manner.

The low current consumption of the argon bulb, makes possible the use of radio "B" batteries as a source of power. Three 45 volt batteries connected in series, giving 135 volts, or two 45 volt and one 22½ volt batteries connected in series, giving 112½ volts may be used. The use of batteries gives a portable lamp which may be used in the field for night prospecting.

SUNLIGHT. A view box fitter with a filter and using sunlight or a strong electric light as a source of ultraviolet, will prove satisfactory for some puposes. The glass filter is fitted in the top of the view box, the substance to be tested is placed inside the box, and observation is made by placing the eyes at the viewing aperture. For best results the direct rays from the sun or electric light should fall directly upon the filter. Owing to the filtering effect of the atmosphere, no ultraviolet radiations shorter than about 2900 A.U. reach the earth from the sun. The incandescent electric globe gives only a small percentage of radiations shorter than about 3700 A. U.

Corning glass filter number 587 or 986 may be used with the sunlight viewing box; the three millimeter (polished) filter number 986 will give the best results with sunlight.

ELECTRIC LIGHTS. All incandescent electric lights, including powerful spotlights and flood lights give off ultraviolet radiations, but due to the filtering effect of the surrounding glass bulb the wavelengths are only in the near ultraviolet. Considerable visible light is present hence a filter must be used. The heat resisting filters are indicated.

BLACK BULB. Photoflood lamps have been recently adapted as sources of ultraviolet; these are available from large lamp manufacturing firms, and are marketed under various trade names including *Black Bulb, Black Light, Purple X, and Wonderlite.* These are generally referred to as the "black bulb", and are a convenient source of long wavelength radiations.

Aluminum reflector (right) with screw bulb base "black bulb" high intensity mercury vapor lamp. Heat-resisting glass filter is built around the lamp filaments. At left is transformer used to operate ultraviolet light source. (*Photo courtesy Keese Engineering Company, Hollywood, Calif.*).

The black bulb differs from the high intensity mercury vapor lamp in that no transformer is required to operate the former. The black bulb is constructed with a heat resisting filter surrounding the lamp filaments. This type of lamp generates considerable heat and is intended only for intermittent service. The rated life varies from about 50 to 200 hours, with a current consumption of from 100 to 350 watts.

The photoflood lamp operates on 110 volts, but the filaments are rated at only 55 volts, hence the filaments generate considerable light and heat with accompanying short life. The ultraviolet rating of these lamps is approximately the same as that given for Corning heat-resisting filter number 587. Being inexpensive, easily portable, light in weight, operating on standard 110 volt A.C. socket, the black bulb has numerous applications in both the arts and industries. In operating this type of lamp, the bulb should not touch any cold object, which may cause breakage, and should be used enclosed in a reflecting shade. The radiations are entirely harmless and will not "sunburn" the skin. Where continuous service is required for a long period, two bulbs may be utilized with intermittent service.

HIGH INTENSITY BLACK BULBS. Several electrical equipment manufacturers produce a filament type of mercury vapor lamp as a source of ultraviolet radiations, which require an auxiliary transformer to provide suitable starting and operating voltages. In some types a heat-resisting filter directly surrounds the lamp filaments, while in others the filter is a separate unit. Lamps of this kind can be operated in any position and have an average rated life of from 500 to 1000 hours. The heat-resisting filter used is essentially the same as that employed on the black bulb (photoflood light), hence both types of units provide approximately the same range of radiations and give essentially the same fluorescence.. However, the high intensity type units operating from a transformer can be burned continuously and give much longer life.

According to the manufacture of the Sperti lamp, the unit, operates in conjunction with a reactor that develops 105 watts, producing 95 watts in the mercury tube. The Sperti lamp reactor operates from 110 volts A.C., and is fitted with a removable heat-resisting filter. The Sperti tube will develop wavelengths as low as 2200 A.U., but the intense visible radiations require the use of a filter.

The Keese Engineering Company of Hollywood, California, manufactures a variety of ultraviolet light units of both the long and short wave types, suitable for numerous applications. The tubular type of lamp sold under the trade name of NiCo, is of the mercury vapor type, and operates from a controlled voltage auxiliary unit. The envelope of the NiCo tube is composed of heat-resisting, nickel cobalt, filter glass, and according to the manufacturer the output rating starts at about 3200 A. U., with the maximum rating at 3650 A. U.

MERCURY ARC LAMPS. For many years the mercury arc lamp found wide favor as a source of ultraviolet radiations for therapeutic purposes. The radiations from this type of lamp are said to extend from 1800 to 14,000 A.U., but relatively small percentages of the total radiations are within the range suitable for the demonstration of fluorescence. Considerable visible wavelengths plus heat are emitted by the mercury arc. The radiations are mainly in the region of 3600 A.U. wtih scattered bands in the shorter region.

For the demonstration of fluorescence, a filter must be used with the mercury arc, and since considerable heat is generated it is not feasible to use non-heat resisting filter. The mercury arc lamp is essentially a fused quartz tube partly filled with metallic mercury, and electrodes sealed at each end. The passage of current causes some of the mercury to vaporize, and become ionized with the emission of ultraviolet radiations. Mercury arc lamps suffer loss of efficiency after about 500 hours of use.

For specific purposes the mercury arc lamp has its usefulness. As a source of monochromatic light in polarimetry, spectroscopy, and interferometry, the mercury arc is valuable. For the demonstration of fluorescence of minerals and various other substances, the more modern types of ultraviolet light equipment are more convenient and practical.

SPARK DISCHARGE. The high tension disruptive spark discharge between metal electrodes of iron, nickel, or tungsten provides a source of radiations rich in short wavelengths. The iron spark is particularly rich in ultraviolet, and the spectral lines are quite uniformly distributed.

The iron spark is operated from auxiliary equipment. Visible light is also generated, hence best results will be noted when a filter is employed with this unit.

CARBON ARC. The carbon arc is another source of ultraviolet rich in short wave radiations. The carbon electrodes used for the generation of ultraviolet generally contain an iron core, or are impregnated with various substances to increase the output of short radiations. The carbon arc gives radiations ranging from approximately 1800 A.U. into the visible. Considerable heat, fumes, and visible light are emitted from the carbon arc, and this is a disadvantage for some uses.

A heat-resisting filter must be used with the carbon arc, if a non-heat resisting filter is used, a copper sulfate solution cell or some similar means must be used to protect the filter. The carbon arc finds wide use for theatrical purposes, where it is necessary to project a beam of ultraviolet a considerable distance and to cover a large area. For projection purposes the standard five millimeter heat-resisting filter number 587 is indicated. The carbon arc operates on direct current from a special transformer and requires considerable amperage.

IONIZED GASES AS ULLTRAVIOLET SOURCES

Within recent years there has been developed numerous types of ultraviolet light sources which employ the principal of ionization of gases for the generation of short wavelength radiations. These lamps have many advantages over the hot types, including simplicity of construction and operation, little heat, small current consumption, and continuous operation.

The ultraviolet light sources dependent upon the ionization of gases are often referred to under the name of "cold quartz tubes". The most efficient type is that made from pure fused quartz tubing, generally about nine millimeters in diameter.

The quartz tubing may be bent to any desired shape, the tube exhausted, "pumped" with neon or argon gas, and mercury added. An electrode is sealed at each end of the tube, and connected to a small high tension direct current transformer. Short tubes will operate on about 3000 volts; long tubes require additional voltage. The passage of current through the tubes causes the mercury and gases to become ionized with the emission of considerable ultraviolet radiations of short wavelengths. Fused quartz or high silica content glass is used for the tubing to permit the emission of the short radiations otherwise filtered out by ordinary gases, or the glass used in the familiar neon tubes.

Since the cold quartz tube units consume little energy, they may be operated successfully from ordinary dry cell batteries, for an efficient portable source of ultraviolet. A "Hot Shot" battery will operate a ten inch cold, quartz tube for forty hours or more, while the familiar storage battery, used in the automobile, with its greater storage capacity will operate the tube much longer. The non-heat resisting filter with its greater efficiency can be used with the cold quartz tube type of units.

EFFICIENCY. For energy output the cold quartz tube yields a greater ultraviolet output than any other source of radiations, suitable for practical purposes. Photometer tests indicate that the average efficiency of the cold quartz tube is appoximately as follows: Of the total energy emitted from the tube, 73% is in bands ranging from 2536 to 2540 A.U., 18% in radiations shorter than 2536 A.U., and from 2900 to 3660 A.U., 3% of the total energy input is absorbed by the quartz tube, and 6% is dissipated in heat and visible bands. It will be noted that at least 90% of the radiations are of wavelengths suitable for the production of fluorescence in minerals and other substances.

The cold quartz tube operates from a small transformer unit, connected to the standard 110 volt, A.C. outlet. The tube consumes no more energy than an ordinary size electric light globe. Despite the low current consumption the lamp has large output—about 10,000 ergs per square centimeter at 2537 A.U. The low output of visible light makes it possible to fluoresce many substances without the use of a filter, but the fluorescent colors will be of a deeper shade with the use of the filter. Cold quartz tubes have a long life; after several thousands of hours use the efficiency may be reduced slightly, but this loss can be restored by "repumping" the tube with a fresh supply of mercury and gases. The cold quartz tubes are also widely used for therapeutic purposes.

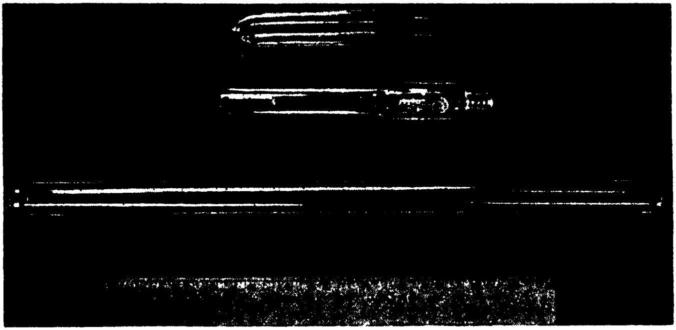
Attention is called to the fact that polished aluminum is a far better reflector of ultraviolet light than other metals. By tests it has been shown that polished aluminum is 25% more efficient than polished tin or chromium. For this reason most ultraviolet units are fitted with aluminum reflectors.

Cold quartz tube type of ultraviolet units are available from a number of manufacturers, and are marketed under various trade names, including the following. The Mineralight of the Ultraviolet Light Products Company of Los Angeles, California, is available in numerous types suitable for a diversity of applications, and includes portable units. Ultray, by H. N. Retherford Company of Los Angeles is also available in standard and portable types. The Chesbert units, manufactured by the Chesbert Company of San Francisco, California, employ large diameter ionizing tubes of the "cast" type of quartz glass. All give off short wavelength radiations, operate practically cold, can be burned continuously, can be used with non-heat resisting filter number 986, and are available in both portable and standard lighting circuit types.

The thickness of the wall of the quartz tube causes a slight variation in the output, as the thicker walled tubing absorbs more ultraviolet. But this variation is generally not discernible in most practical applications. The cold quartz tube lamps fluoresce a greater variety of minerals than any other single ultraviolet light source, and are considered the most efficient of all.

Some so-called quartz tube lamps are made with a high silica content glass tubing known to the trade as "French Glass". This glass does not permit the passage of the same range of short wavelengths as does pure fused or cast quartz, despite the fact that ionized gases are used within the tube. "French Glass" has a lower fusing point, can be worked more freely, and is less costly than pure quartz. Used without a filter this type of tubing is considerably less effective than quartz, although with a filter "French Glass" tubing is suitable for some purposes.

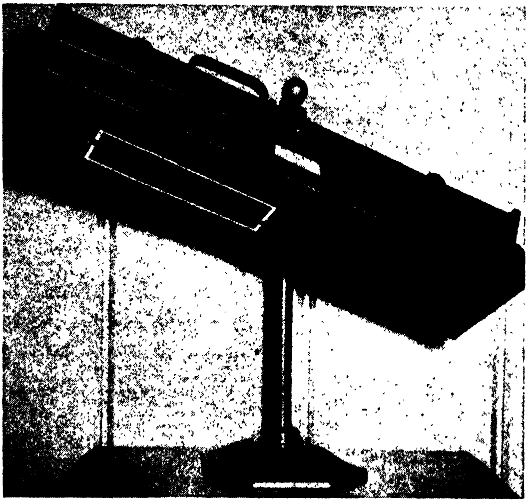
GERMICIDAL TUBES. Recently developed are a number of ultraviolet light units intended primarily for the destruction of bacteria, and marketed under trade names of Germicidal Tubes and Sterilamps. The new tubes operate on the principal of the ionization of gases, since mercury and other gases are contained within the tubes. The bactericidal lamps operate from a small self regulating transformer, consume only a small amount of energy, give off little heat, and have a long life. One type of germicidal tube is stated to have a life of approximately 4000 hours, but in actual practice it has been shown that this type of tube gives longer service.



Short wavelength ultraviolet light units, for bactericidal purposes, and for the demonstration of fluorescence. Screw socket base (middle) unit is self-contained. Lower tube consumes only 15 watts, and is operated from small transformer. (*Photo General Electric Company*).

The seventeen inch Germicidal Tube operates from a special reflector unit, fitted with sockets for the tube, and the proper type of reactor or transformer. The unit operates from any standard 110-125 volt, A.C. electric outlet. After some 1000 hours of use the tube may lose from 15% to 20% of its original efficiency, but continued use appears to bring about no additional deterioration. The seventeen inch tube gives off a small amount of radiations between 1850 and 2000 A.U. which is in the ozone poducing range. While the production of ozone is important for bactericidal purposes, it is of no value for the demonstration of fluorescence. The largest percentage of radiations are between 2000 and 2800 A.U., with a heavy concentration of bands at and near 2537 A.U., making the Germicidal Tube type of lamp suitable for any fluorescence requiring short wave radiations.

Germicidal Tubes are not constructed of fused quartz, but are made of a special quartz glass of recent development—a product of the Corning Glass Works. Detail regarding the manufacture of this newly developed glass is lacking, but it is apparently 98% or more (quartz) silicon dioxide. Short waves of approximately 1700 A.U. pass through a one millimeter thickness of fused quartz, and one type of bactericidal tube is stated to give of radiations starting at 1850 A.U., hence for the production of short wavelengths the newly developed glass is at a high point of efficiency.



Stand type of ultraviolet light unit, giving short wavelength radiations. One or two 2 x 6 inch filters may be used with this unit. (*Courtesy Chesbert Company, San Francisco, Calif.*).

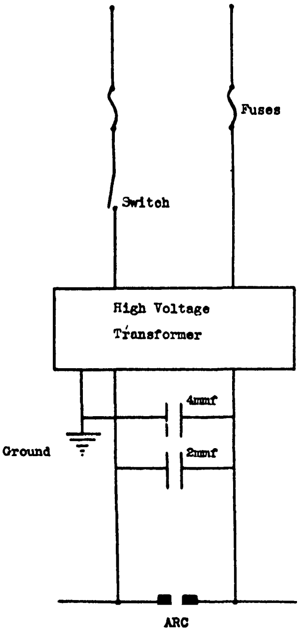
The Germicidal Tubes appear to give off slightly more visible light than the cold quartz tubes. This can be readily demonstrated when the two units are used without filters. Under the open germicidal tubes, substances like red fluorescing calcite appear a paler shade of red compared to the reaction under the open fused quartz tube. The non-heat resisting filter, Corning number 986, is best suited for both the fused quartz tubes and the germicidal tubes, and since the radiations of both types of lamps is concentrated in the range of from 2500 to 2600 A.U., the fluorescing effects of both lamps will be approximately equal. The fifteen watt germicidal tube is one inch in diameter, gives off a large volume of ultraviolet and is well adapted for a diversity of purposes where it is desired to illuminate a large area.

CONSTRUCTION OF AN IRON ARC

An iron arc suitable for the fluorescence of minerals and other substances may be constructed at a small cost, as outlined below. This type of unit has been described by Robert Heineman of the Arizona Bureau of Mines, in the January 1935 issue of The Mineralogist Magazine.

The apparatus described by Heineman is compact and easily portable. All operating units can be placed in a carrying case, 9 x 10 x 13 inches, and weigh approximately 25 pounds. The unit operates on 110 to 120 volt, A.C. The basic circuit is shown below. A ¼ kilowatt Thordason transformer rated to deliver 8000 volts from the secondary, with an input of 110 volts to the primary is used as the power unit. The iron core of the transformer. and one secondary terminal are wired to both a binding post and a pin jack, either of which may be used for connecting a ground wire, which should be grounded to a radiator, or water pipe for safety. Voltage above 4000 is generally suitable for an iron arc apparatus, but the high voltage condenser must be designed to fit the circuit.

The condenser can be constructed by coating old photographic glass plates, four by five inches in size, on each side with lead foil. The plates are first carefully cleaned, the lead foil attached with shellac, and all air bubbles pressed out. A ¾ inch margin is left on the plates to prevent the current jumping around the plates. About twenty-four plates have proper capacity for the unit described. The coated plates are placed in a stack, with a strip of copper foil between each plate for electrical connection. An uncoated plate is placed over and below the stack of coated plates, to hold the outside strip, and the whole is tightly bound together with black friction tape. The assembled plates are placed in a suitable size metal can with copper stips protruding from the top, and melted paraffin poured around the plates until the can is filled within a half-inch from the top. When the paraffin has cooled the filling may be completed with molten sealing wax.



Wiring diagram for transformer used in construction of iron arc. (*Drawing by Virgil P. Barta.*)

The arc can be constructed in a small Bakelite box, $1\frac{1}{2}$ x $1\frac{1}{2}$ x 5 inches in size, with bottom open. The arc itself consists of two iron nails, held in position by two brass binding posts. An iron bolt is also fastened between the two nails so there are actually two arcs. Two brass rods form the support for the arc box and also to make electrical connection. The brass rods slide through two telephone jacks in the main panel so that the arc box may be pulled foward over the specimen under examination. Each jack is connected to a binding post in the main panel, so that if the arc box is completely removed from case, these binding posts give a source of high voltage oscillating current for operating high frequency electric apparatus, Crookes tubes, and similar equipment.

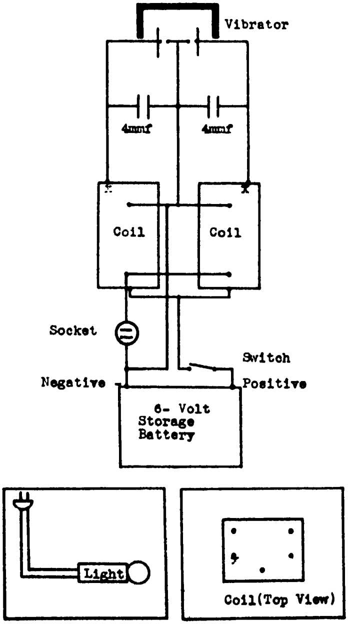
Two brass strips are attached to the arc box to hold a glass filter, which may best be 1½ x 5 inches in size. Corning filter number 587 is indicated for use with the iron arc. Two standard ten ampere fuses should be wired into the circuit to protect the supply line. The iron arc gives excellent fluorescent effects with a number of substances.

Light weight, compact, cold quartz tube, ultraviolet light unit operated from a dry battery for portability. (*Photo Ultraviolet Light Products Co., Los Angeles, Calif.*).

PORTABLE UNITS

For field prospecting for various minerals, cold quartz tube sources of ultraviolet, can be adapted to operate from dry cell batteries. Portable cold quartz tubes find wide use in prospecting for the tungsten mineral scheelite. Prospecting for outcrops of the mineral is done at night, while underground the ore deposits may also be traced by the use of ultraviolet radiations. In the milling of scheelite the heads and tailings are frequently observed under the cold quartz tube to note the approximate recovery.

Adapting a cold quartz tube for field use is a simple matter, as will be seen in the wiring diagram shown next. There are a number of ways in which the tube may be operated from a "Hot Shot" dry battery or a six volt automobile battery. The positive and the negative wires from the battery are properly connected with an auto coil. The outlets from the high tension side of the coil are attached to the electrodes on each end of the quartz tube. A switch should be placed in the circuit. The number of dry cell batteries required will be dependent upon the length and diameter of the tube.



Typical wiring diagram for cold quartz tube portable source of ultraviolet light. (*Diagram by Virgil P. Barta.*)

A number of excellent ready-to-use portable cold quartz tubes are available from equipment manufacturers. These units are compact, light in weight, and can be carried in a pack on the back. By the aid of portable sources of ultraviolet radiations, numerous deposits of valuable tungsten ore have been located. In collecting various fluorescent minerals in the field, portable units are widely used for night work.

Flashlights may also be adapted as a portable source of ultraviolet light, giving long wave radiations. The ordinary glass covering the small incandescent globe of the flashlight is removed, and a circular piece of thin polished filter glass number 597 is installed. While the flashlight affords only a feeble source of ultraviolet radiations, tests can be made by holding the specimen close to the light source and using a five cell flashlight.

PROTECTION AGAINST RADIATIONS

Ultraviolet radiations above 3200 A.U. are not harmful and require no special protection for the eyes and skin. In working with the black bulb types of ultraviolet light sources where the greater percentage of the radiations are concentrated at 3650 A.U. no protection need be given to exposed parts of the body.

Ultraviolet radiations below 3200 A.U. can be very harmful to the human organism, if the unprotected eyes or skin are exposed for longer than a few minutes. The open carbon arc, the mercury arc, cold quartz tubes, Germicidal Tubes, and all others where short wavelengths are developed should not be directed toward the eyes or skin, unless protection is provided. Where these types of lamps are used for protracted periods, the eyes should be protected by suitable glass goggles, and gloves worn to protect the skin on the hands. Ordinary glass or colored glass goggles filter out the short radiations, which may otherwise bring about a painful "sunburn" of the eye ball.

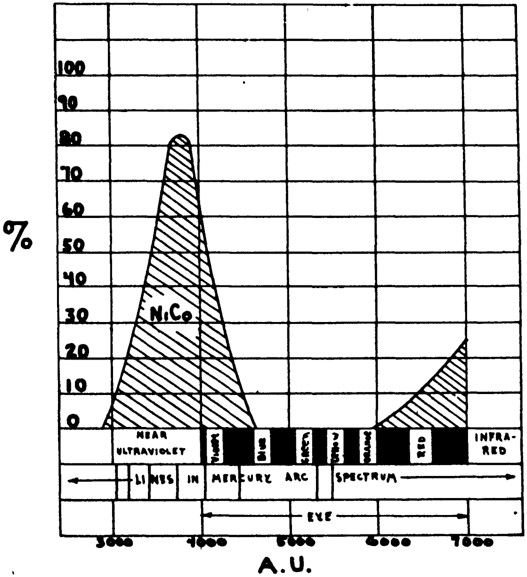
Protracted exposure of the skin to short wavelength radiations may cause a painful or even dangerous erythema. A few moments exposure will do little harm. The above precautions are for those who may employ short wave radiations for long periods. A slight "sunburn" of the eyes while not a serious matter, may be painful for several hours. While the action of short wave radiations of ultraviolet on the human body is not fully understood, it is known that, when indicated, therapeutic doses of ultraviolet may be of considerable value. Short wave radiations of the body should be taken only under the direction and control of a medical expert. It has been established that excessive exposure to short wave radiations can do much harm to the human organism.

FILTERS FOR FLUORESCENCE

No source of ultraviolet radiations, used in the demonstration of fluorescence, is wholly free of visible wavelengths, hence some type of filter is required to remove all or a greater part of the visible which may otherwise overshadow fluorescence. Unfortunately the development of filters has not kept pace with developments in sources of light. Some powerful sources of ultraviolet, rich in short wave lengths, also emit a considerable quantity of visible which completely masks any fluorescence. The high intensity mercury vapor lamp and the carbon arc are examples of units where a filter of some kind is essential.

In general there are two classes of filters which may be used with ultraviolet light units—chemical filters and glass filters. The glass filters are by far the most convenient and practical, but they have distinct limitations. The Corning Glass Works manufactures two types of glass filters intended for ultraviolet units. One type of Corning glass filter is of the "heat resisting" variety and indicated for use on light sources which generate considerable heat. Unfortunately the heat resisting glass filters do not pass wavelengths shorter than about 3200 A.U., hence when this filter is used the light source is limited to wavelengths of from 3200 A.U. to visible range.

The non-heat resisting Corning glass filter, is highly efficient and will pass wavelengths down to approximately 2500 A.U., with a high efficiency in the range from 2537 to 2900 A.U. Owing to the unusual chemical composition of this glass it has very little mechanical strength; its coefficient of expansion is such that it will readily break even at low temperatures. Corning non-heat resisting glass filter can not be successfully used on ultraviolet units which generate heat, but can be freely used on lamps of the ionization of gases types which operate practically as "cold light".



Transmission of nickel-cobalt glass, heat resisting glass filters. Note maximum transmission at approximately 3650 A. U. (*Courtesy General Electric Company*).

None of the glass filters in common use on ultraviolet units are capable of wholly eliminating all visible wavelengths. All permit a small percentage of purple and red to pass the filter, but this is not a serious objection for most practical purposes. The writers have tested various glass filters, used in the demonstration of fluorescence, including the well known Wood's glass of British manufacture, and the series of glass filters of the Jena Glass Company, none of those tested were found to be superior to the products of the Corning Glass Works.

CHEMICAL FILTERS

Various chemical solutions, solutions of aniline dyes, dyed plastics, gelatine, thin films of metal deposited on quartz or special glass, and similar devices have been described for use as filters to eliminate all or part of the visible wavelengths, and yet permit passage of the ultraviolet. For laboratory and analytical purposes where it is desired to isolate certain specific lines in the spectrum, chemical filters have their useful applications, but in general it is necessary to rely upon glass filters for the demonstration of fluorescence in minerals and various other substances.

Some of the recently developed plastics give free passage to ultraviolet radiations, and hold possibilities as substitutes for glass filters. Colorless plastics pass the visible wavelengths as well as the invisible, therefore it would be necessary to incorporate some dye or chemical substance to remove the visible yet pass the invisible radiations. A single thickness sheet of purple colored Cellophane was found (Dake, 1939) to give superior fluorescent colors in some minerals when fitted to a cold quartz tube lamp. While not as effective as a glass filter, the Cellophane does remove some visible radiations. Other colors of Cellophane produced some interesting color combinations. They did not appear to pass the short wavelengths as freely as did the purple. Ordinary dyed Cellophane is not intended as a filter for ultraviolet light sources, yet it would appear that future research may produce a filter from one of the many plastics which would prove superior to, or augment the present glass filters available.

For the isolation of specific bands of ultraviolet for analytical work, L. A. Jones (1930), described a series of eight filters constructed from a combination of Wratten dyed gelatine, Corning glass, and solutions of copper and nickel sulfates. Cells constructed of fused quartz, high silica content glass, and similar materials, and filled with various solutions, to pass ultraviolet radiations but eliminate the visible have been described by a number of writers. The cells containing the solutions are not convenient to handle and have the added disadvantage in that they can not be consrtucted of ordinary glass which is lacking in ultraviolet transmission. Small cells to hold various dye and chemical solutions, may be constructed from quartz glass microscope slides; while of small size these cells find applications in analytical work. Winther (1913) described a filter using a dilute solution of aniline dyes, which in a thickness of one centimeter gave a transmission of 35 per cent at 3650 A.U. Cobalt and nickel sulfate solutions are also effective in transmitting lines at 3650 A.U.

The spectral lines at 2900 A.U. and shorter may be isolated by Cellophane treated with sodium benzoate. For microscopic work, J. J. Fox called attention to the use of bromine and chlorine filters for isolating wavelengths at 2537 A.U. Various research workers have described chemical filters for the isolation of some important wavelengths between 2480 and 5790 A.U. which are used for analytical purposes. Thin plates of fused quartz glass may be coated with metallic silver and used to isolate the shorter ultraviolet radiations. The metallic silver is deposited on the quartz by the reduction of an alkaline solution of silver salt with lactose. P. Carnot (1926) described a substitute for glass filters made by soaking a thin sheet of gelatine in a solution containing 1 per ecnt silver nitrate and 10 per cent ammonium hydroxide for ten minutes. A thin film of metallic silver is then deposited on the gelatine by immersion in a 10 per cent solution of formaldehyde.

In fluorescence microscopy a filter which will remove both the visible and the infra-red radiations is desired for some work. The visible rays tend to mask the fluorescence, while the infra-red radiations heat the lenses and specimen. A 10 per cent copper sulfate solution contained in a quartz cell about two inches thick, comprises a suitable filter for fluorescence microscopy, where a carbon arc is used as a light source. This chemical filter covers a range of from about 3000 to 4000 A.U.

GLASS FILTERS

Special glass filters which pass ultraviolet radiations, and eliminate much of the visible, are by far the most convenient types and are widely used in the field of fluorescence. The use of glass filters on ultraviolet light units appears to be beset with confusion. Each glass filter has its special range of transmission of radiations, and beyond this no more can be expected regardless of the wavelengths emitted by the light source. The filter glasses referred to below, are those manufactured by the Corning Glass Works, unless otherwise stated, and are available through ultraviolet light supply firms and most mineral supply dealers.

No filter glass described here is 100 per cent efficient, and unless the glass is very thick a small amount of visible will pass through the special glass. This could be wholly eliminated by increasing the thickness of the filter, but increasing amounts of ultraviolet radiations would also be lost, thus reducing the efficiency. For certain laboratory purposes complete elimination of all visible light is desired, but for the demonstration of the fluorescence of minerals and most other substances this is not important. The sole purpose of the filter is to eliminate the greater part of the visible light which otherwise may largely or wholly overshadow the fluorescent colors.

Thickness of the filter is important where the light source lacks intensity. In the methods of manufacturing glass filters, various thicknesses are produced. Filters designated as "moulded" are generally approximately 7 mm thick; the "polished" filters are reduced by grinding and polishing to a thickness of from 3 to 5 mm. In general a more vivid fluorescence is obtained by the use of the thinner polished filter. For mechanical reasons large sheets of some glass filters 6½x6½ inches square, can not be supplied by the manufacture, less than 5 to 7 mm. thick. Where it is desired to cover a large aperture with non-heat resisting filter number 986, small squares can be used.

A filter glass accidentally broken need not be discarded; the fracture line may be filled with plastic or glass cement, with little reduction in general efficiency. Care should be used to prevent cement or varnish from flooding the surface of the filter as this may shield out ultraviolet rays. There are two types of glass ultraviolet filters, one is intended for use on the "hot" types of light sources, while the other is non-heat resisting and can generally be used successfully only on lamps which give off very little heat.

HEAT RESISTING GLASS FILTERS

Four glass heat resisting filters, suitable for use on heat generating ultraviolet light units, are manufactured by the Corning Glass Works. These are listed as "red purple ultra" glass filters numbers 584—586—587 597. The standard polished thickness of these filters is approximately 5 mm. but are also available in thickness ranging from 2 to 7mm. The moulded filter can not be used in an optical system where a focus is required; the polished filter is indicated here. In manufacturing a glass of the "ultra" type, it is found that a much higher ultraviolet transmission can be had if a small amount of visible light is permitted to pass. A trace of purple and red is passed by all "ultra' 'glasses except the special number 586.

Heat resisting filter glasses transmit the near ultraviolet region of wavelengths longer than 3100 A.U., while absorbing most of the visible. The maximum transmission lies between 3600 and 3700 A.U., with the best efficiency at 3650 A.U. The majority of fluorescent paints used in spectacular display work, and many of the sulfide minerals, fluoresce vividly under these radiations.

Red Purple Ultra Number 584— filter glass has a maximum transmission at 3650 A.U. and gives off little red colored radiations. This filter, while heat resisting, is not intended for the high temperatures of units like the carbon arc.

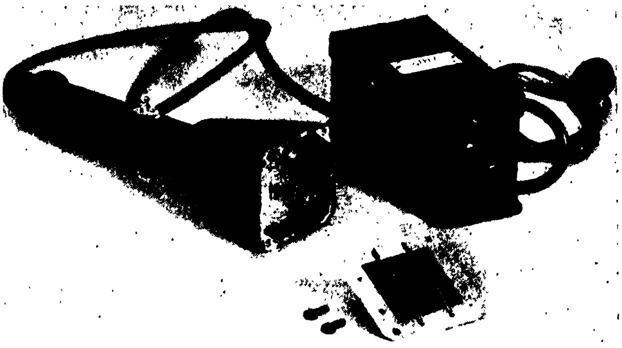
Violet Ultra Number 586— glass filter is intended for examing the fluorescence of organic or other substances which glow very faintly, and must be examined in total darkness. Filter number 586 has an efficiency transmission of only 30 per cent at 3650 A.U. Available in squares up to 6½x6½ inches, 5 mm. standard polished thickness.

Red Purple Ultra Number 587— glass filter transmits less ultraviolet and less visible radiations than number 597. Filter number 587 is heat resisting and intended for use on high temperature light sources like the carbon arc, used in theatrical work, and other applications where it is desired to project a powerful beam of ultraviolet radiations for some distance. Filter number 587 passes no radiations shorter than 3100 A.U. and has an effective transmission of 65 per cent at 3650 A.U.

Red Purple Ultra Number 597— glass filter has a slightly wider range of ultraviolet transmission than number 587. Filter number 597 may be used on hot lamps, except those which develop considerable heat. Both number 597 and 587 are available in 6½x6½ inch squares (or smaller) in standard polished thickness of 5 mm.

Glass filter number 597 has the most efficient transmission of all heat resisting filters. Number 597 has an effective transmission rating of 85 per cent at 3650 A.U., and passes only a small percentage of visible red and purple.

Ultraviolet light sources which generate heat use one of the filters described above. These include units sold under the trade names of NiCo, Sperti, Conti-Glo, Shannon, Wonderlite, and the "Black Light" bulbs manufactured by the General Electric Company, and the Westinghouse Lamp Company. The chemical composition of the heat resisting



COLD QUARTZ TUBE ULTRAVIOLET LIGHT

Cold quartz tube at left, transformer at right, filter glass number 986 in foreground. (*Photo courtesy, H. N. Retherford Company, Los Angeles*).

filters is variable, but most of them contain nickel and cobalt and are often referred to as nickel-cobalt glass. A filter glass known as Wood's glass is of British manufacture and widely used in England. Wood's glass is heat resisting and has approximately the same ultraviolet transmission as the Corning heat resisting filters. Some ultraviolet units of the heat generating type employ a separate unit filter, while other units have the glass filter surrounding the ultraviolet producing filaments.

NON-HEAT RESISTING GLASS FILTER

One ultraviolet glass filter which may be used only on light sources that generate practically no heat is Red Purple Corex A Number 986. This filter is indicated for cold quartz tube types of lamps, or other ultraviolet sources which develop radiations by the ionization of gases. It may be used with light sources like the carbon arc, provided a cell filled with copper sulfate solution is placed between the light source and the filter to absorb the heat radiations. This filter may also be used on a flash light and the sunlight viewing box.

Filter number 986 is the most effective of all glass filters for the transmission of short wavelength radiations. The lowest range of this filter is generally placed at about 2500 A.U. It is outstanding for its large percentage of transmission between 2537 and 2900 A.U., combined with its ability to absorb all the visible light except for a trace of red and violet. When subjected to intense radiation of wavelengths in the region 2500 to 2900 A. U. there is a solarization effect or decrease in ultraviolet transmission for radiations of these wavelengths. After solarization, however, the ultraviolet transmission remains well above that of the heat resisting type of glass filter. The loss of transmission in this filter can be partially restored by carefully heating to a temperature of about 200 C.

Filter number 986 is available in moulded sheets up to 6½x6½ inches, approximately 7 mm thick. Standard polished thickness of approximately 3 mm can be supplied only in smaller sizes, due to the lack of mechanical strength of this glass. The thick moulded filter may be used successfully where the light source is very intense.

It appears that non-heat resisting filters which show deterioration through solarization are those which are used on types of cold quartz tubes where the filter is some distance from the tube, and practically no heat is transmitted to the filter. Seemingly the constant transmission of ultraviolet radiations, accompanied by little heat, promotes relatively rapid solarization of filter number 986. Types of cold quartz tube lamps where the filter is placed close to the tube will develop slight heat in the filter, especially where the unit is burned continuously for ten minutes or more from time to time. Under these operating conditions filter number 986 gives long service without any visible deterioration through solarization.

OBSERVING FLUORESCENCE — GLASSES

To observe true fluorescence when the source of radiations are not confined entirely to the ultraviolet but extends into the violet end of the visible spectrum, D. W. Dana (1935), states it is only necessary to observe the specimen through a filter or goggle with Corning Glass Works' Noviol A, number 038 glass. This filter does not transmit the violet which is usually reflected—rather than emitted as a fluorescent light—by most objects when observed under ultraviolet. When the fluorescence to be observed falls in the blue, this visible violet may be strong enough to mask the reaction.

A similar glass filter—Novial O, number 306—may be used advantageously in the photography of fluorescence according to D. W. Dana. This filter is used as a cap over the camera lens to prevent ultraviolet radiations from reaching the negative, without seriously absorbing the visible fluorescing colors. Photographic film is highly sensitive to ultraviolet radiations, and any ultraviolet light reflected from a specimen under photography may cause a fog on the film.

TESTS OF WAVE LENGTHS

Sources of ultraviolet light vary in their radiations, and various means have been devised for the approximate measurement of the wavelengths. Methods of measuring wavelengths include chemical and physical methods. Chemical methods depend upon the measurement of the extent of a chemical reaction which occurs under the influence of ultraviolet radiations. Chemical methods in general are not wholly satisfactory and accurate. A number of actinometers have been described, an apparatus in which may be placed a liquid or paper moistened with some dye or chemical substance. After a measured exposure to ultraviolet radiations the exposed sample is compared with a known standard. Various dyes may be exposed to ultraviolet light to measure their rate of fading, and thus calculate the approximate wavelengths and their intensity. The photochemical decomposition of other organic substances has also been used to measure ultraviolet radiations.

Physical methods are more accurate and reliable for the measurement of ultraviolet radiations, but often involve the use of expensive apparatus. Spectrophotometric methods, the photometer, and the photoelectric cell all find applications in this field. The results given by these and similar instruments are independent of the personal factor and therefore more reliable than chemical methods, however more convenient the latter may be.

TEST GLASSES

There are a number of glasses manufactured by the Corning Glass Works useful and convenient for the purpose of making an approximate test of the wavelengths emitted by an ultraviolet light unit, or to test the transmission range of a filter. These are known as "fluorescent" glasses.

Fluorescent Canary Number 375— is a yellow appearing glass by ordinary light. It fluoresces a brilliant green under radiation of all regions of the ultraviolet. It also fluoresces slightly under visible blue wavelengths about 4300 A.U. and thus can be used for tracing a beam of light in an optical system. Short radiations cause this glass to fluoresce more strongly than the longer wavelengths. This glass appears to be one of the uranium glasses and fluoresces with the characteristic color ot uranium salts and minerals.

Clear Blue Fluorescing Number 014— is a colorless glass under ordinary light which has the striking characteristic of fluorescing a strong blue under radiations shorter than 3100 A.U. It is very sensitive in the detection of the shorter radiations, including the testing of lamps for therapeutic rays. The strong blue fluorescence of glass number 014 can be readily seen under cold quartz tube types of lamps, with and without filter number 986, but does not appear under lamps fitted with a heat resisting filter. The strongest blue appears under radiations of from about 2500 to 2600 A.U. The fluorescence is confined to the surface of the glass due to a strong absorption for the activating rays.

TEST MINERALS

Until recently very little scientific work has been carried on to learn definitely the wavelength of ultraviolet radiation at which a mineral species will fluoresce the strongest. The special glass filters in common use fail to give sharp cut specific wavelengths, but pass a series of radiations.

Smith and Parsons (1938) described studies in mineral fluorescence made with fused quartz prisms. By the aid of this equipment it was possible to obtain a separation of wavelengths extending from 2652 to 4358 A.U. A resumé, given below, may serve as an aid in the determination of the approximate range of an ultraviolet light source and ultraviolet filters.

Anglesite from Phoenixville, Pennsylvania fluoresces best at 3650 A.U.

Autunite, from a number of localities has been tested and found to fluoresce under both short and long rays. The present writers have observed that the fluorescent secondary uraninites, including autunite, show to the best advantage under radiations at about 2537 A.U.

Calcite from a number of localities was tested. On the average the strongest fluorescence in the majority of specimens was found to be between 2925 and 3128 A.U. Calcite from various localities is highly variable in its fluorescence, but the fiery red of the well known Franklin, New Jersey calcite, unquestionably shows best under radiations (with filter 986) concentrated at 2537 A.U.

Dolomite from Baden, Germany gave a weak green color in the Ångström Units range 2700 to 2804. Above and below this range the material was practically negative.

Fluorite from various localities was tested and in all instances the most brilliant fluorescence was noted under wavelengths longer than 3200 A.U.

Gay-Lussite from Washington fluoresces its best pink color at 3128 A.U.

Gypsum fluoresces a yellowish color at 3650 A.U.

Hackmanite from Bancroft, Ontario, Canada reacts best in wavelengths over 3500 A.U., when a beautiful orange-pink color appears. This mineral is negative under shorter radiations.

Kunzite, the California gem mineral, was found to fluoresce a rather weak orange color under radiations between 3650 and 4047 A.U.

Opal (common) from various localities reacts with a long spread of wavelengths. The common opal from Virgin Valley, Nevada gave variable fluorescence under wavelengths ranging from 2652 to 4047 A.U., but was strongest at 2804 A.U.

Colorless hyalite opal from old Mexico gave the strongest green color at two points, 2652 and 2804 A.U.

Ruby, the pink colored sapphire from North Carolina was found to be wholly negative under radiations below 3650 A.U.

Scheelite from California and Nevada fails to fluoresce under wavelengths longer than 2976 A.U., and radiations shorter than 2804 A.U. are required to produce the strongest blue color.

Sphalerite from Tsumeb, Africa fluoresces over a wide range, but emits the strongest orange color at 3650 A.U.

Wernerite from Ontario, Canada reacts to a rather wide range of radiations, but the characteristic canary yellow color is seen best at 3650 A.U.

Willemite from Franklin, New Jersey is variable; specimens are found that fluoresce over wide ranges, but in general radiations below 3200 A.U. produce the strongest green fluorescence, and the most persistent phosphorescence.

In addition to the above tests, Smith and Parsons showed that the intensity of the ultraviolet light source is not of importance in bringing out more brilliant fluorescence. In short, to double the intensity of the light does not increase the fluorescence in proportion. Large variations in the strength of a given line of wavelengths produce rather small changes in the fluorescence of the mineral specimen. The principal advantage of an intense ultraviolet light source is to enable illumination of a large area, while a more feeble light must be held near the specimen and a close observation made.

CHAPTER SEVEN

THE FLUORESCENT MINERALS

The fluorescence of various minerals is a source of interest and delight to mineral collectors and students of mineralogy. All have dabbled with the phenomenon more or less consistently, but few have tabulated their observations in such a manner as to render the data available to subsequent observers. For many years after the fluorescence of minerals was known few mineralogists carried out scientific studies on the subject. The fluorescence of minerals was long looked upon as a pleasant diversion, with little hope of finding any practical or commercial applications for the phenomenon. Like many other discoveries, at the outset, little thought was given to useful applications.

The applications of fluorescence to many every day problems is growing rapidly. One of the most notable applications of the principal of mineral fluorescence, is the recent development of the fluorescent tube for lighting purposes. Early experiments in developing this important advancement in modern illumination included the use of fluorescent minerals. Observations made by mineral collectors on the fluorescence of the important tungsten mineral, scheelite, led to the present day wide utilization of ultraviolet light for prospecting, mining, and milling of this mineral. The application of fluorescence in the identfication of minerals, and their mining and milling, presents a new and promising field of research.

All observers have noted that mineral species which are luminescent, vary widely in their reactions when exposed to ultraviolet and other radiations. Even specimens of the same species and from the same locality, may vary widely in the shade of fluorescing color, or in intensity, or some may be wholly negative. In attempting to account for the fluorescence of minerals, the prescence of some activating agent, appears to be well established,. but in many instances analytical data is lacking. In the case of the calcite from Franklin, New Jersey it has been shown that manganese in small amounts must be present to bring about luminescence. If the percentage of manganese is too high or too low or lacking, the calcite will fail to fluoresce. The luminescence of calcite is remarkable, and is known in many shades of pink and red, as well as blue, green, yellow, and yellow-white. Possibly variations in the percentage of, or the nature of the activating agent present in calcite can account for the differences in the fluorescent colors.

There are numerous instances of mineral fluorescence where difficulty may be encountered in ascribing a cause. A cavity or pocket in basaltic rock may be partially filled with specimens of the same species; some may fluoresce and some may be negative. In many other instances the character of the activating agent is not known. In other minerals the luminescence is thought to be due to a variable molecular arrangement.

SOME NOTED LOCALITIES

Minerals which fluoresce are found widely distributed in many parts of the world, and in every country where minerals are produced. Every state in the United States produces one or more minerals which show a fluorescence under ultraviolet radiations. Some localities are notable for their production of a wide variety of species. Reference is made below to some of the outstanding localities and states.

Franklin, New Jersey, is easily the most noted locality in the world for the production of spectacular and colorful fluorescent minerals. The large zinc mines situated at Franklin and the surrounding region have produced approximately 150 mineral species, a substantial percentage show luminescence of one type or another. Some of these are found nowhere else in the world.

Some of the ore as well as the gangue minerals from the New Jersey zinc mines show a powerful fluorescence and for many years ultraviolet light has been employed to sort the milling ore from the gangue material.

The fire-red calcite and the powerful green willemite from Franklin are the best known. Calcite is widely distributed but rarely does it show a vivid red fluorescence. Langban, Sweden, is one of the few localities in the world which produces red fluorescence calcite equal to that of New Jersey. The rare mineral calcium-larsenite, which fluoresces a strong yellow occurs at Franklin. So great is the variety of fluorescent minerals from New Jersey, that it is possible to acquire a large and spectacular collection from this locality alone.

California produces a great variety of fluorescent minerals, notably of the non-metallic and rarer species. Among the several California fluorescent gem stones are kunzite, benitoite, and topaz. Scheelite is mined extensively at Atolia and elsewhere in the state. The saline lake deposits of California produce a large number of fluorescent species.

Wyoming rates numerous localities producing fluorescent minerals, notably those of the quartz group. A great deal of the agate, chalcedony, common opal and similar silica minerals found in Wyoming show a strong yellow-green fluorescence. A number of fluorescent saline minerals, and secondary uraninites, occur in Wyoming. The igneous and sedimentary formations of Wyoming are known to be above the average in percentage of radioactivity. It is thought that radioactive substances appearing in minute amounts in the minerals deposited by percolating waters may account for the fluorescence of many Wyoming specimens.

New Mexico and *Arizona* recently produced a number of fluorescent minerals not previously reported from this region.

Texas is best known for the remarkable calcite, which fluoresces pink under long wavelengths and blue under short wavelengths and also phosphoresces strongly.

Ohio is noted for fluorescent fluorite which occurs in profusion at the limestone quarry at Clay Center.

FLUORESCENT MINERALS

The minerals given in the descriptive tabulation below are those which fluoresce distinctly, and are in general suitable for exhibits and collections. Mineral species showing only a feeble fluorescence or uncertain luminescence are included in a separate tabulation. Attention is called to the fact that a mineral sometimes listed as showing fluorescence may be due to a coating of some other mineral, or a fluorescent mineral may be present as a disseminated inclusion or an intergrowth or mixture. Most of the fluorescent uranium (radium bearing) minerals are treated in a separate chapter on *Radioactive Minerals.*

References made to short rays include the radiations given from various cold quartz tube ultraviolet light sources, shorter than 3100 A. U., and with the greater percentage of wavelengths concentrated at approximately 2537 A. U. Long rays refer to radiations from light sources above 3100 A.U., and with the great test concentration at approximately 3650 A. U., as emitted by heat generating units which require a heat resisting filter.

AGATE is widely distributed throughout the world but relatively few localities produce fluorescent examples. The locality of Sweetwater County, Wyoming, is notable for its production of strongly fluorescent agate. This locality has produced innumerable specimens of small water worn agates of the "moss" variety, suitable for gem cutting, and fluorescing a strong green under short rays. The authors of *Quartz Family Minerals,* suggested that the fluorescence of Wyoming agate was due to the inclusion of some uranium mineral. This supposition was later substantiated by the work of John D. Buddhue. Some specimens of Wyoming agate are sufficiently radioactive to affect unexposed photographic or X-ray film.

Agate is often associated with or intergrown with common opal; the latter may fluoresce a green, and the agate negative.

ARAGONITE is variable in its fluorescent colors. The aragonite crystals, associated with sulphur, from Sicily show a strong pink under long rays, and make superb cabinet specimens. A locality in New Mexico produces specimens of limestone and quartz with coatings of aragonite which fluoresce a deep fire red under short rays. Aragonite crystals found near Vernonia, Oregon, fluoresce a cream-white. Bohemian aragonite fluoresces white under short rays and green under long rays. Aragonite from Death Valley, California, fluoresces a pale green under short rays.

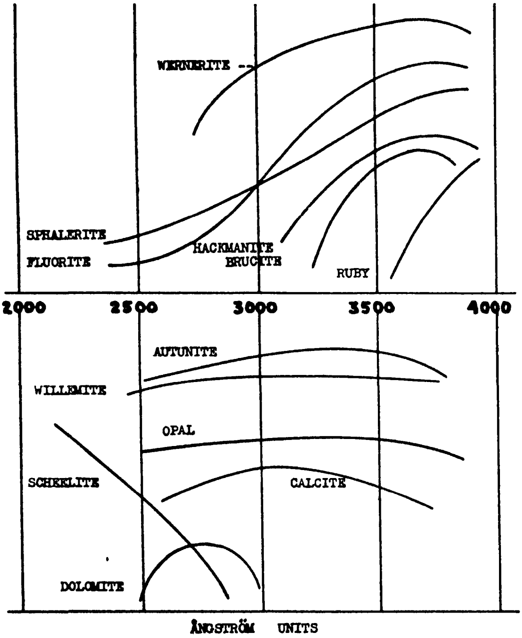
Aragonite from many localities has been tested under various wavelengths. This mineral is more likely to react under long rays, while short rays often cause phosphorescence where fluorescence may be absent.

AUTUNITE, a secondary uraninite, derived from the weathering of pitchblende, fluoresces a powerful yellowish-green characteristic of uranium. This mineral fluoresces well under all sources of ultraviolet radiations. Autunite is often seen as yellow coatings on pegmatite granites which carry radium bearing minerals. Pitchblende (uraninite) does not fluoresce, but the alteration products of this mineral frequently show a strong luminescence, hence this test may be of value in prospecting for pitchblende.

Autunite is common to some of the pegmatites of Connecticut, New Hampshire, and Maine. It also occurs in Mitchell County, North Carolina; the Randsburg district, California; Black Hills, South Dakota, and elsewhere.

BARITE generally fails to fluoresce, but may phosphoresce under short rays. Under long rays the barite of Hexham, England, shows a moderate yellowish-white. Barite, if fluorescent, is best seen under long rays.

CALCITE is one of the most notable and spectacular of all fluorescent minerals. While calcite may fluoresce under various ultraviolet light sources, the short rays of the cold quartz tube, fitted with Corning filter number 986, generally brings out the fluorescing color to the best advantage. Probably more study has been made of calcite than any other fluorescing mineral. W. L. Brown (1934), working with a cold quartz tube and filter, showed that the red fluorescence of calcite was dependent upon the manganese content. Calcite with about 3.5% manganese appeared to give a maximum brilliance; the fluorescence declining gradually with a greater manganese content, reaching zero with the presence of about 17% manganese. It was also shown that calcite free of manganese fails to fluoresce. There is also evidence that the presence of iron and magnesium in calcite tend to act as inhibitors of luminescence Most



The horizontal scale represents wavelengths of ultraviolet radiations in Ångström Units, the vertical scale indicates the relative intensity of fluorescent response. (*Graph by Colonel Julian S. Hatcher*).

calcites having the proper concentration of manganese, to exhibit luminescence, are distinctly crystalline, or show a marked cleavage. M. Allen Northup (1940) suggests that the group of calcites showing a greenish fluorescence may be due to the presence of a hydrocarbon impurity, and the luminescence may be independent of the presence of manganese. Calcite may also exhibit a marked phosphorescence or thermoluminescence.

Pale pink colored crystalline calcite from the Chisos mountains, Texas, is one of the most remarkable of all phosphorescing minerals, rating second only to willemite. Under some lamps this calcite will fluoresce a pale pink and phosphoresce a strong blue, while under short rays both the fluorescence and the phosphorescence are a strong blue. The blue phosphorescence remains for several seconds and shows the unusual behavior of becoming a deeper shade of blue as it expires.

Fluorescent calcite is known from many localities but the specimens from Franklin, New Jersey, are but far the best known, most spectacular, and variable. The range of red fluorescence seen in Franklin calcite will vary fom a pale pink to a deep fire red. Some of the specimens show a short red phosphorescence, deeper in color than the fluorescing red. Much of the calcite from this locality is associated with willemite and other strongly fluorescing minerals to offer spectacular and pleasing color combinations. The so-called "black" calcite of Franklin, New Jersey, fluoresces a bright scarlet red. The dark color of this calcite is due to included manganese dioxide. Other localities in New Jersey produce fluorescent calcite, including some limestone quarries, Paterson, Sparta, Sterling, and Prospect Park.

Fluorescent calcite is found at many localities in Wyoming. Some specimens show a scarlet red equal in quality to that of New Jersey. Near Baroil, L. E. Bowser collected specimens of calcite associated with chalcedony, the former fluorescing a bright pink, and the latter mineral a vivid green.

A locality in southern California produces a clear, colorless variety of calcite known as Iceland spar which fluoresces a deep pink. Other California localities include, Avenal Creek, Riverside, Tuolumne County, near Hollywood, Red Rock Canyon, and the Mojave Desert region. Specimens of fluorescent calcite showing various colors under short rays are found widely distributed in the desert regions of Southern California, Arizona, Nevada, Utah, and other western states. Limestone stalactites which fluoresce a pale green under short rays, have been collected from the caverns of New Mexico by R. E. Anderson of Lovington.

At the Oregon King Mine, three miles northeast of Ashwood, Oregon, J. Lewis Renton, collected specimens of bladed calcite on quartz crystals; the calcite fluoresces a strong pink. The calcite associated with the zeolites at Ritter Hot Springs, Oregon, often fluoresces a pale green. The Tri-State Mining District, centered around Joplin, Missouri, produces a calcite fluorescing a cream-yellow color.

Massive calcite from the mines of Langban, Sweden, a noted mineral locality, fluoresces a vivid red under short rays and a pink color under long rays. Some of the Langban calcite is equal in quality to the New Jersey specimens. Calcite found in combination with fluorite at Cumberland, England, fluoresces a deep red, while similar specimens from a locality in Germany present a straw-yellow fluorescing calcite.

CALCIUM-LARSENITE. One of the rare minerals found at Franklin, New Jersey, is calcium-larsenite. Under short rays this mineral fluoresces a vivid yellow color, and may be intergrown with calcite, willemite, and other fluorescing minerals. Calcium-larsenite was found only in limited amounts in restricted areas in the zinc mines at Franklin, hence specimens of this mineral are scarce.

CARNOTITE. Specimens of pure carnotite from two localities tested by the writers failed to fluoresce. Carnotite from some localities may be intergrown with some secondary uraninite or an alteration product exhibiting fluorescence. Some writers have reported fluorescent carnotite.

CHALCEDONY (See also under AGATE). Many localities in Wyoming yield chalcedony showing a strong green fluorescence under short rays. Like in the case of agate, it is thought that the characteristic green fluorescence of the Wyoming chalcedony is due to the presence of some uranium salt. Large masses of colorless chalcedony are found at Specimen Hill, north of Medicine Bow, Wyoming, show a green fluorescence similar to the agates of Sweetwater County, Wyoming. The agatized wood and agate casts of wood from Eden Valley, Wyoming, may also show the characteristic uranium green under short rays.

The igneous rocks and sedimentary formations of many parts of

Wyoming are known to be radioactive to an abnormal degree. It is suggested that the percolating waters or the silica gel from which the chalcedony and agate were derived could have readily carried small amounts of fluorescent uranium salts, dissolved from the igneous rocks and sedimentary formations. Some of the milky quartz, quartzite, and dark colored jasper found in Wyoming may also show the characteristic green fluorescence. John Pitts of Riverton, Wyoming has collected small water worn specimens of agate and chalcedony in Sweetwater County which shows visible inclusions of some yellow colored uranium mineral.

Fluorescent chalcedony is also reported from localities in Arizona and New Mexico. In some specimens the strongest green fluorescence is due to the presence of areas and bunches of common opal, while the chalcedony reacts only very weakly. The pseudomorphs of chalcedony after coral from Tampa Bay, Florida fluoresce a feeble green; this may be due to some extraneous substance derived from salt water.

CLINOHEDRITE. One of the minor fluorescent minerals from Franklin, New Jersey is clinohedrite which may show a bright orange color under short rays and a pinkish color under long rays. This species is variable in its reaction.

COLEMANITE. The borate mineral, colemanite, found at various localities in California is variable in its fluorescence. Crystallized specimens often fluoresce a green color under long rays. Colemanite may also show phosphorescence. John Melhase (1935) states that all the minerals from the saline lakes of California are more or less luminescent.

CUPROSCHEELITE. Specimens of nearly pure cuproscheelite from Guanajuato, Mexico tested by the writers gave a marked yellowish-white fluorescence under short rays with filter. The color in ordinary light was a dull greenish. Specimens of scheelite are sometimes reported as fluorescing a yellowish color, and this may be due to the presence of cuproscheelite. Scheelite is a calcium tungstate, while cuproscheelite is a copper-calcium tungstate.

CURTISITE. The hydrocarbon mineral, curtisite, from Skaggs Springs, California fluoresces a yellowish-green under both short and long rays. At the Mirabel mine near Middletown, California curtisite occurs in dolomite—both minerals fluoresce.

DAKEITE. See Schroeckingerite

FLUORITE. From a historical standpoint, fluorite rates as the most important of luminescent minerals. Many of the early researches in the field of luminescence were carried on by studies of fluorite While fluorite may fluoresce under short rays, the strongest reactions will generally be noted under the long rays.

The fluorite produced at a number of localities in England gives a remarkably strong fluorescence. Fluorite occurs in a number of colors, and this often has a bearing on its luminescence. All green, lilac, and purple fluorite from Weardale, Alston Moor, and Allenheads, England gives a similar strong blue fluorescence, while the yellow, brownish-yellow, and colorless fluorites from the same localities are negative. British fluorites may be noted in numerous large museum and private collections.

The noted limestone quarry at Clay Center, Ohio yields large masses of a brown colored fluorite which fluoresces a yellow-green or yellowish-white, and may also phosphoresce strongly. Massive fluorite of a green color from near Keller, Washington fluoresces a strong blue; some specimens being nearly equal to those of the noted localities in England. The green fluorite from Azusa and Afton, California, and Jefferson County, Montana, also fluoresce a vivid blue. Large quantities of fluorite are mined in the region around Rosiclare, Illinois, which may show phosphorescence, but rarely fluorescence. W. C. Shortle (1939) reported an occurrence of fluorescent fluorite from near Chatham, New Hampshire. Phosphorescent fluorite occurs at a number of localities in New Hampshire and Connecticut.

Other luminescent properties of fluorite is treated elsewhere. Fluorite, especially the colorless variety, may sometimes contain minute disseminations of petroleum oil that fluoresce a blue color. This pseudo fluorescence of fluorite can generally be detected by the lack of uniform luminescence throughout the specimen.

GYPSUM. Of 34 gypsum specimens, from various localities, tested by P. Walther (1935), under long rays, only 8 were found to react, with green color predominating. A brownish colored gypsum from a Michigan locality fluoresces a dark green under short rays. Gypsum from the saline lakes of southern California and other southwestern United States localities is often reported as showing a marked green fluorescence. The Salton Sea Basin is notable for its production of fluorescent gypsum, associated with various luminescent saline minerals. The alabaster variety of gypsum, widely used for ornaments and art objects, is described elsewhere.

HACKMANITE. Rating as one of the most unique of all luminescent minerals, is the hackmanite from Dungannon Township, Ontario, Canada. W. Scott Lewis (1940) called attention to the reversible photosensitivity of hackmanite, and its changing color under the influence of different wavelengths of light.

Under both short and long rays, hackmanite is luminescent. Under short rays, with filter number 986, it fluoresces a strong orange-yellow, while without the filter, the fluorescent color will appear as a pale pink which persists by exposure to daylight.

HALITE. The most notable locality producing fluorescent halite (common salt) are the saline deposits near Amboy, California. The halite found here shows a vivid red fluorescence under short rays with filter. Halite from other localities has been reported by Peter Zodac (1936) as phosphorescing a faint green.

HYALITE. See Opal.

HYDROZINCITE. The ores in the zinc mines of Utah and Nevada, are often coated with a basic zinc carbonate, hydrozincite, which fluoresces a vivid blue under short rays. Under long rays some specimens may fluoresce yellow. Excellent specimens of hydrozincite have been found at the noted locality of Good Springs, Nevada, and in Beaver County, Utah.

LIMESTONE. See Calcite.

OPAL. The strong green fluorescence of colorless hyalite opal is thought to be due to the presence of minute amounts of uranium. This assumption is probably a correct one, for the secondary uraninite minerals fluoresce under all ultraviolet radiations, in the same manner as hyalite opal, and with the same characteristic yellow-green color. Even the small argon bulb with its feeble and limited radiation is sufficient to bring out the hidden beauty from a colorless hyalite opal. Stone Mountain, De Kalb County, Georgia is one of the best known localities for hyaline opal. According to J. Roy Chapman (1939), the hyalite opal at Stone Mountain occurs mainly in seams and thick coatings on granite. The locality is an abandoned granite quarry a short distance from Stone Mountain proper. Plenty of material is available, but must be worked from the matrix. Night prospecting has been successful in locating the hyalite.

Spruce Pine, North Carolina; Bedford, New York, and Bagdad, Arizona are other notable localities for hyalite. Bohemia produces superb specimens of hyalite opal coating basalt but several specimens tested by the writers failed to fluoresce. While on a recent field trip to Mexico, W. O. Stewart obtained some specimens of rhyolite showing large cavities containing chalcedony linings, which in turn are coated with colorless transparent hyalite opal. The hyalite shows the characteristic strong green fluorescence under all radiations, but the chalcedony is wholly negative. The specimens obtained by Stewart were labeled, "Cerro delo Rose de Castilla, Mina del Cubo, Guanajuato, 1897". The mines around Potosi, Mexico have produced hyalite opal for many years, although the fluorescence of this material has been known only recently.

Common opal is widely distributed but few occurrences of the fluorescent type have been reported. At Virgin Valley, Nevada, there are numerous mines and prospects which have produced quantities of both common and fire opal, but only one property produces luminescent opal suitable for specimen purposes, yet the deposits are all geologically contemporaneous. Common opal occurs associated with the fire opal in all the Virgin Valley workings, but in this combination both are non-fluorescent, while the single deposit of fluorescent opal carries no fire opal. The Common opal of Virgin Valley, Nevada has been mined in large masses over twelve inches in diameter. It fluoresces a strong yellow-green under all radiations. The best Virgin Valley opal for fluorescence is that having a pale yellow color, and often referred to as "semi-opal". Limited amounts of common opal showing dendritic markings is associated with the fluorescent opal. Recently, Mark Foster, operating a property adjacent to the fluorescent opal, encountered brightly colored common opal, which fluoresces a strong yellow-green.

The common opal associated with chalcedony, found at various Wyoming localities, often exhibits a strong yellow-green fluorescence. Some of the common opal found in the desert regions of Nevada, Arizona, New Mexico, and California may also prove luminescent. Specimens of opalized wood from Nye County, Nevada show areas of luminosity. Specimens of agatized and opalized wood from Eden Valley, Wyoming also exhibit areas of pink or green fluorescence under short rays. Generally these luminous portions appear where the original wood structure is completely lacking, and may be secondary depositions. In general the fossil woods fail to show a uniform fluorescence throughout the specimens. Agatized and opalized woods sometimes reported as fluorescing, can often be ascribed to coatings of some fluorescent mineral like calcite or aragonite.

PECTOLITE. The white radiating fibrous pectolite from West Paterson and Bergen Hill, New Jersey appears to be the variety most likely to show fluorescence. Under short rays of the spark discharge or cold quartz tube some pectolite fluoresces or phosphoresces a yellowish color.

PETROLEUM. Petroleum oils and various petroleum products often fluoresce a strong blue, yellow, or green under both short and long waves. The testing of possible petroleum bearing sands is treated in a separate chapter. Various refined petroleum products like kerosene, paraffin, vaseline, and lubricating oils fluoresce strongly. Medicinal ointments with a petroleum base also fluoresce in varying colors and intensities.

POWELLITE. Under short rays, with filter, powellite fluoresces a marked yellowish-white similar to cuproscheelite. Powellite is a calcium molybdate with calcium tungstate. Scheelite is a calcium tungstate, while cuproscheelite is a calcium tungstate with some of the calcium replaced by copper.

There appears to have been some confusion in the three tungsten minerals mentioned above. Scheelite has been reported as fluorescing a yellowish color, and it is possible that either cuproscheelite or powellite was the mineral under test rather than scheelite. The writers have tested numerous specimens of scheelite from various localities, and have noted none which luminesce other than the characteristic blue.

Powellite occurs in some of the tungsten mines of California and Nevada. One specimen of powellite tested by the writers was from a mine near Quinn river crossing, Nevada, and showed large areas of powellite in a quartz matrix. The composition of the powellite tested for fluorescence was verified by the usual chemical methods. Considerable reliance is being placed on the use of ultraviolet light in the prospecting, mining, and milling of tungsten bearing ores, hence attention is called to the fact that tungsten minerals other than scheelite may show a marked fluorescence.

SCAPOLITE. See Wernerite.

SCHEELITE. Tungsten is one of the important strategic metals, and scheelite is a valuable tungsten mineral. Scheelite fluoresces a characteristic blue color under short rays, and is most marked if the cold quartz tube is fitted with filter number 986. The applications of ultraviolet radiations in the prospecting, mining, and milling is treated in the mining section. See also cuproscheelite and powellite.

Scheelite occurs at a number of localities in the United States including the Atolia and Randsburg districts in California; Mill City, Nevada; Murray, Idaho; Baker County, Oregon; Jardine, Montana; Silverton, Colorado; Silver Hill, Washington; Monroe, Connecticut; and also at various localities in Utah, Arizona, and Wyoming.

While scheelite is generally assumed to always show luminescence, reports have been recorded of scheelite which fails to fluoresce under short rays. Some of the scheelite from Silverton, Colorado and Battle Mountain, Nevada has been reported negative. No phosphorescent scheelite has been noted.

SCHROECKINGERITE—(dakeite) Schroeckingerite was first described by A. Schrauf (1873) as a new hydrated uranium-calcium carbonate, found at Joachimstal. At the original locality, the mineral was found in limited amounts, and no quantitative chemical analysis was made.

In 1936, on Lost Creek in the Red Desert about forty miles north of Wamsutter, Wyoming, a large deposit of a yellow mineral in gypsite was found. Specimens were tested (by Dake) under ultraviolet radiations and the characteristic yellow-green of uranium was noted. Specimens were sent to Esper S. Larsen of Harvard University, where a complete quantitative analysis was made. Since complete data was lacking on schroeckingerite, Larsen (1937) gave the name dakeite to the mineral found at the Wyoming locality. Later (1939) it was shown by R. Novacek, that the two minerals are probably identical, and that preference should be given to the original name.

The Wyoming locality has produced large quantities of specimens, and these are to be seen in nearly every collection of fluorescent minerals. Schroeckingerite fluoresces a very strong yellow-green under both long and short rays, but is seen best under the cold quartz tube with filter number 986. Lost Creek has cut through and exposed the three-foot thick seam of impure gypsite which carries the yellow mineral, hence specimens are readily obtained. The mineral occurs as small bright yellow masses, and can be easily hand picked from the matrix before drying. The origin of schroeckingerite at the Wyoming locality has not been definitely established, but the mineral was no doubt derived from the weathering of some primary (pitchblende) deposit.

SELENITE. The selenite variety of gypsum, is more likely to exhibit phosphorescence rather than fluorescence. Peter Zodac (1936) described selenite crystals from the clay pits near Hudson, New York, with a marked whitish, pale blue, and yellow phosphorescence. The selenite crystals from the well known locality of Ellensburg, Ohio phosphoresce a pale blue.

Selenite, associated with chalcedony, occurring near Hay Springs, Nebraska fluoresces a pale yellow under short rays and filter. Much of the selenite of Wyoming is luminescent. Selenite frequently carries inclusions of various kinds and these may cause areas of fluorescence within the selenite.

SPHALERITE. The best known fluorescent sphalerite, is the granular, black colored material from Tsumeb, South Africa, which fluoresces a strong orange under long rays, and less powerful under short radiations. The sphalerite (cleiophane) from Franklin, New Jersey is not constant in its luminescence, some specimens give an orange color under both long and short rays. Some of the Franklin sphalerite is strongly phosphorescent. The mines of Beaver County, Utah produce luminescent sphalerite.

TORBERNITE. The secondary uraninites, torbernite and meta-torbernite, fluoresce strongly under all ultraviolet radiations. Torbernite fluoresces with the characteristic yellow green, while meta-torbernite exhibits a bluish-green, Mitchell County, North Carolina has yielded excellent specimens.

WERNERITE. One of the most popular fluorescent minerals is wernerite (scapolite), which fluoresces a vivid yellow under long rays, and less marked under short rays. The most noted locality is a quarry in Ontario, Canada where the wernerite is mined as a by-product. There are two types of wernerite available, a compact, sub-translucent variety, suitable for gem cutting, and of superior fluorescent ability. The other type is the more common, opaque variety, and usually has non-fluorescent matrix material attached. Few minerals fluoresce a strong yellow color equal to wernerite.

WILLEMITE. Most connoisseurs of fluorescent minerals agree that the fluorescent and phosphorescent willemite of Franklin and Ogdensburg, New Jersey, is the most spectacular of all luminescent minerals.

A silicate of zinc, willemite occurs associated with other zinc minerals at Franklin, and is mixed extensively for its metallic content. Willemite occurs in numerous colors, including white, green, reddish-brown, and pink. The granular, fibrous, and massive form is much more common than crystals. The Franklin deposit has been known since 1650, and actively mined since about 1861, with a production to date of thousands of tons.

Not all varieties of willemite show the characteristic green luminescence; according to C. Palache, the slightly manganiferous willemites fluoresce the strongest, and occurs in the white fibrous form. The white fibrous willemite also phosphoresces the best, some specimens will continue to glow for hours after a charge under the open cold quartz tube. Specimens of willemite from Franklin, New Jersey, lacking manganese or carrying a very high manganese content, may only weakly fluorescent, or may be negative. The green and the reddish varieties fail to phosphoresce.

Artificial willemite (zinc orthosilicate) when pure fails to fluoresce, but when the proper amount of manganese is added as an activating agent, it will fluoresce fully as strongly as the natural mineral. Various chemical analysis indicate that the strength of luminescence coincides with the percentage of manganese present. Varieties of willemite containing up to about two per cent of manganese are known to display the strongest luminescence, while the presence of over four per cent manganese tends to quench fluorescence. A large collection of New Jersey willemites will present numerous shades and intensities of green. The differences will be easily noted when the specimens are arranged for close comparison. Calcite in a similar diversity of shades of pink and red occurs with willemite at Franklin. Willemite is often found in thin capillary films between plates of mica, which can be noted under ultraviolet.

The ore minerals of Franklin, New Jersey are often complicated patterns of deposition and intergrowth, and seemingly endless in number.

Specimens viewed in ordinary light may appear more or less homogenous, but under ultraviolet radiations each mineral will stand out in sharp and clear color contrasts. By this means a study can be made of the deposition of the various minerals. Non-fluorescent species, surrounded by color stand out in contrast.

Willemite is variable in its luminescence. Some specimens will fluoresce strongly under long waves, while others react only to short rays. Liebisch (1921) showed that the strongest fluorescence was excited in white and green willemites from Franklin under radiations from 2537 to 2652 A. U. Hence the cold quartz tube (with filter) will excite willemite to the best advantage. Radium radiations and X-rays also cause strong fluorescence and phosphorescence in willemite.

WOLLASTONITE. The large quarry at Riverside, California produces wollastonite which phosphoresces a yellowish-orange when charged heavily with short rays from the open cold quartz tube.

ZIPPEITE. The luminous radioactive mineral zippeite has been described from several localities including the noted radium bearing ores of the Great Bear Lake region of Canada. Zippeite a secondary uraninite is a product derived from the weathering of primary uraninites including pitchblende, and fluoresces the characteristic uranium green. At Great Bear Lake, zippeite is not found in the ores at depth, but develops as a coating when the ores are exposed to weathering. In the ore dumps, coatings of zippeite will form in less than six months exposure.

The fluorescent minerals given in the following list are those which fail to show a strong or marked luminescence, and are in general not suitable for display in collections of fluorescent minerals. Short rays refer to the radiations from ultraviolet units having the largest percentage of wavelengths concentrated at approximately 2537 A.U. Long rays refer to units having the largest percentage of wavelengths concentrated at approximately 3650 A.U. Phos. indicates phosphorescence.

Mineral	*Locality*	*Short Rays*	*Long Rays*
Albite	Bedford, N. Y.	Phos.	
Albite	Newry, Maine	Phos.	
Alumnite	Saxony	White	White
Alunite	Marysville, Utah	White	
Anglesite	Leadhills	Yellow	Yellow
Anorthoclase	Franklin	Blue	
Apatite	Bohemia	White	Brown
Apatite	Hull, Quebec	Yellow	
Apophyllite	Paterson, N. J.	Yellowish	
Axinite	Franklin	Red	Red
Barylite	Franklin	Blue	
Borax xls.	Borax Lake, Calif.		Greenish
Celestite	Clay Center, Ohio	White (phos.)	
Cerussite	Freiberg, Saxony		Yellow
Cerussite	Good Springs, Nev.	Pale blue	
Clinohedrite	Franklin	Orange	Pinkish
Colemanite	Death Valley, Calif.	White	Greenish
Dolomite	Lake Co. Calif.		Blue-white
Dolomite	Northumberland	White	White
Elaterite	Utah	?	Brown
Epsomite	Death Valley, Calif.		Pale blue
Fluorapatite	Strafford, N. H.	Orange	
Glauberite	Borax Lake, Calif.	Phos.	
Gyrolite	Bohemia	White	White
Hanksite	Searles Lake, Calif.	Phos.	
Hardystonite	Franklin	?	
Hexagonite	Edwards, N. Y.	Red	Pink
Hydromagnesite	Gustine, Calif.		Greenish
Hydrozincite	Beaver Co. Utah	Blue	Yellow
Hydrozincite	Good Springs, Nev.	Blue	
Leucite	Arizia, Italy		Orange
Meyerhofferite	Death Valley, Calif.	Phos.	
Nasonite	Franklin	Blue	
Ozocerite	Brazil		Brown
Priceite	Death Valley, Calif.	Yellowish	
Pyromorphite	Klemenslust		White
Smithsonite	Belgium		Green
Smithsonite	Good Springs, Nev.	Green	Green

Mineral	*Locality*	*Short Rays*	*Long Rays*
Sodalite	Moultonboro, N. H.		Orange-red
Strontianite	Alston Moor, Eng.	White	
Sulphur	Lassen Peak, Calif.		Yellowish
Thaumasite	Paterson, N. J.	White (Phos.)	
Trona	Searles Lake, Calif.	Blue	Blue
Vesuvianite	Ludwig, Nev.		Yellowish
Wavellite	Hungary		Green
Witherite	Hexham, Eng.		Yellow

LUMINESCENCE OF METEORITES

The luminous trains. which falling meteorites sometimes leave, has been observed by many, but little is known regarding the phenomenon. It appears that meteorites are not entirely devoid of luminescence from causes other than heat. Apparently the first observation of this kind was made by Flight while examining some of the minute particles of oldhamite which Storey—Maskelyne had previously discovered in the Bustee, India meteorite.

Flight discovered that when the meteorite was exposed to the light of burning magnesium ribbon, the oldhamite particles emitted an orange phosphorescence when the magnesium was extinguished. Oldhamite is composed of approximately 90 per cent calcium sulfide, and over 3 per cent of the remainder is magnesium sulfide. The former is recognized as a conspicuous phosphor, while magnesium is a well known activator.

John D. Buddhue (1939) tested nine stone meteorites under a cold quartz tube and filter number 986 but failed to note any luminescence, except from a thin coating of calcium carbonate, deposited on the specimens after reaching the earth. Buddhue also examined the spectrum of gases given off when meteorites are warmed in a vacuum. He discovered that powdered meteorites were phosphorescent. Powdered Holbrook, Arizona meteorite gave a faint but long lived phosphorescence. Buddhue (1940) also tested in a similar manner the recently fallen Washougal, Washington stone, which gave a much brighter but shorter yellow phosphorescence. The spectrum of the phosphorescence appears to be continuous.

In a paper read by Kaplan (1939) before a meeting of the Society for Research on Meteorites, suggestions were made pertaining to the dust particles derived from the meteorite. The phosphorescence of the dust train may depend upon the presence of a surface such as that of a dust particle. The recombination of atoms to form molecules of the surface of the meteor, releases tremendous heat which could make dust particles glow.

According to John D. Buddhue (1940), the intense heat of the meteor is somewhat against the production of dust particles. The effective temperatures of meteorites during their fall, as calculated from the spectrum of the resulting meteors, is sometimes well above the boiling point of iron and silicon. The constituents of the meteor may therefore be completely vaporized, and in the absence of anything to condense upon, may remain vapor. The spectrum of the general glow of the night sky shows the presence of free atoms (vapor) of sodium, and probably calcium, which are thought to be derived from meteors.

Buddhue (1940) states that the cause of the phosphorescence known as meteor trains is unknown, but may be due, in part at least, to nitrogen, and perhaps also to dust particles. Meteor trains seen in daylight are a different matter. They are even more rare than the night trains. The color of the day trains is usually reddish gray, and their attitude is only about 40 miles, and may be as little as 25 miles. Buddhue points out that their nature is also uncertain, but believes they are probably smoke clouds; another point in favor of the production of dust by falling meteorites.

CHAPTER EIGHT

THE RADIOACTIVE MINERALS

URANIUM MINERALS

The radioactive minerals seem to be of universal interest with their relation to fluorescence. The rather widespread fallacy that all radium bearing minerals are highly fluorescent is perhaps one cause of this interest. This is in spite of the recognized fact that a few, but not all of the radium bearing minerals are highly fluorescent. The latter has provided a valuable adjunct for rough tests as to the uraniferous nature of minerals which invariably presupposes radium and other radioelements.

As is generally known radium bearing minerals are always the ores of uranium. At least, no mineral has been reported which contains radium without uranium or vice versa. Of the three types of radioactive minerals only one type contains varieties preponderately fluorescent. These three general types include:

(I) Uraninites, those richest in uranium and which include such crystalline varieties as broeggerite, cleveite, and certain uraninites found in the United States and Africa.

(II) Columbium titanium tantalates, salts of the rare earths and uranium such as euxenite, ampangabeite, samarskite, semiresite, and others.

(III) Secondary uraninites, the weathered or altered varieties of Type I minerals such as schroeckeringite (dakeite), autunite, bassetite, meta-torbernite, zippeite, and others.

The primary uraninites are non-fluorescent although their weathered products, the secondary uraninites are often highly fluorescent. The fact that outcropping of uraninites like pitchblends are usually coated with alteration products which often fluoresce indicates that prospecting for radioactive minerals by ultraviolet light is rather important. It supplements other methods in the respect of being available more frequently than electroscopes or Geiger—Mueller counters which are the more positive detectors of radioactive minerals. Details on prospecting for radium minerals by this principle is discussed in detail elsewhere here.

Practically all fluorescent uranium minerals emit in the yellow and green regions irrespective of exciting wavelengths. Intense fluorescence does not appear to be recognized for longer wavelengths, e.g., red or orange. A vivid yellow or yellow-green luminescence has been observed in most studies on the uranium salts.

Ultraviolet light of 2537 A.U. wavelength and thereabouts generally excites luminescence in uranium minerals more effectively than long wavelengths such as 3650 A.U. The portable cold quartz tube units are particularly well suited for the secondary uraninites while black bulb sources are usable but not as adequate as the former. An illustration of this is by studies made on schroeckingerite (dakeite). The fluorescence of sparsely distributed particles of this mineral in its matrix is visible when excited with long wavelengths but tests on the same specimen with short rays produce fluorescence so great as to almost cover the matrix.

In 1940 Miexner studied the luminescence of uranium minerals and found that they may be classified into strongly luminescent, weakly luminescent, and non-luminescent according to their appearance under ultraviolet light. The investigations qualify the fact that primary uranium minerals are usually non-fluorescent while secondary uranium minerals are sometimes fluorescent.

The strongly luminescent minerals are the uranium phosphates, arsenates, and sulfates which fluoresce a characteristic intense yellow-green color. The uranium carbonates produce an intense green fluorescence (see table). The non-luminescent uranium minerals include the silicates and uranium micas of composition $M_2\ (UO_2)\ _2(XO_4)_2.8\text{-}12H_2O$ where M may be copper, iron, lead, bismuth, manganese, or uranium dioxide; and X may be phosphorous, arsenic, vanadium, or sulfur. Others of this class are zeunerite, fritzscheite, bassetite, phosphuranylite, tujamunite, walpurgite, betafite, ellsworthite, ianthinite, cuprosklodowskite ($CuO.2UO_3.2SiO_2.6H_2O$), kasolite, curiite, fourmarierite, uranospherite, hatchettolite, and johannite.

The studies of Miexner did not reveal any connection between fluorescence and chemical composition although De Ment (1940) pointed out that fluorescent uranium minerals often have greater solubilities than the non-fluorescent varieties such as micas and silicates. Also, that approximately two-thirds of the well known fluorescent radioactive minerals have specific gravities between 3 and 4.

FLUORESCENCE OF URANIUM MINERALS

Strongly Fluorescent:—

Autunite	Yellow-green
Beta-uranopilite	Yellow-green
Chalcolite	Yellow-green
Johannite (variable)	Yellow-green
Meta-torbernite	Yellowish-blue
Schroeckingerite (dakeite)	Green
Torbernite	Yellow-green
Uranocircite	Yellow-green
Uraniferous hyalite	Yellow-green
Uranophane	Yellow-green
Uranopilite	Yellow-green
Uranospathite	Yellow-green
Uranospinite	Yellow-green
Uranothallite	Green

Medium Strong:—

Gummite (variable)	Violet
Beta-uranotil	Yellowish
Uranotil	Yellowish
Zippeite	Yellowish

The above list of fluorescent uranium minerals includes only the better known species. Some of the rare secondary uraninites, and the alteration product minerals are omitted. The occurrence of secondary uraninites as coatings on uraninite (pitchblende) is discussed in the section of "Uses of Ultraviolet Light in Mining".

J. De Ment, V. L. Minehart, and V. P. Barta (1940) studied the luminescence of radioactive minerals under X-rays. As was to be expected, the majority of the secondary uraninites showed a strong fluorescence. Many varieties phosphoresced strongly under X-ray excitation although the same specimens do not ordinarily phosphoresce with ultraviolet radiation as the exciting agent. Primary uraninites like carnotite and pitchblende (uraninite) did not luminesce. Uranium containing agate from Sweetwater County, Wyoming (cf. elsewhere with ultraviolet rays) fluoresced a yellowish-green color with no difference being noted between th specimens with visible inclusions of secondary uraninite and those without the inclusion, i.e., translucent agate. A strong phosphorescence of several seconds duration was noted in these agates after exposure to X-rays produced at 83 Kv. and 20 ma. (see table).

Hyaline opal containing uranium, as a secondary uraninite, fluoresced a strong yellowish-green color and phosphoresced a dull whitish-green color after exposure to X-rays of the same character. Autunite fluoresced a color similar to that when excitation with ultraviolet radiation is used and phosphoresced a dull green. Schroeckingerite (dakeite) fluoresced a yellow-green color but no phosphorescence was noted. Meta-torbernite fluoresced a yellow-blue and did not phosphoresce while gummite did not luminesce.

URANIFEROUS MINERALS UNDER X-RAYS

(83 Kv./20 ma., 0.5 mm.Al)

	Fluorescence	*Phosphorescence*
Autunite	Yellowish	Dull green
Carnotite	None	None
Pitchblende (uraninite)	None	None
Gummite	None	None
Schroeckingerite (dakeite)	Yellow-green	None
Meta-torbernite	Yellow-blue	None
Uraniferous agate	Yellowish-green	Whitish-green, dull
Uraniferous opal	Yellowish-green	Whitish-green, bright

Interest in the luminescence of uranium minerals existed before radioactivity was discovered and, therefore, before this property was known in uranium. The investigation on the luminescence of uranium compounds began with Stokes and A. Becquerel in 1852, although as early as 1833 Brewster mentioned a yellow glass which was probably the canary glass so well known for its highly fluorescent properties. The fluorescence of this glass is ascribed to the presence of traces of uranium acting as an activator. The first objective studies by Stokes were on the few compounds of uranium that he was able to prepare. He also studied autunite, calcium uranyl phosphate, and chalcolite, copper uranyl phosphate.

Becquerel studied uranium compounds during the course of investigations with the phosphoroscope and was impressed with their strong emission. Becquerel noted the duration of emission and found it to be three to four thousandths of a second and the rate of decay in accordance with his empirical relationship later investigated by Nichols and Howes (1919) with similar results. Later, in 1872 Becquerel found other uranyl salts active and obtained data on their spectral bands. The studies of H. Morton and H. C. Bolton the following year on 85 uranium compounds showed not all specimens to be fluorescent. In 1919 Nichols and Howes added important data on the characteristics of the spectra of uranyl salts. Becquerel and Onnes (1903) found that at temperatures of −185° C. caused the spectrum of uranyl salts to resolve into a number of much narrower bands. This fact alone has been of significance since it affords a means of studying the structure of the spectra of the uranyl compounds and may be used to augment spectroscopic studies on the nature of uranium itself.

The difficulty encountered in differentiating the rare secondary radioactive minerals is well known. A qualitative spot test procedure has been used by the writers to roughly discriminate specimens appearing the same under ultraviolet light. For example, autunite and schroeckingerite (dakeite) often appear about the same. By spotting the surface of the specimens with chemical reagents, e.g., hydrochloric acid, nitric acid, sodium hydroxide, hydrofluoric acid, and others, alterations in fluorescence color are produced because of the different products developed from the reaction. These differences enable discrimination of two specimens that cannot be otherwise subjected to the usual analytical methods. Spot tests may also be performed with fragments several millimeters in diameter as well as on the surface of a large specimen. A set of standard reagents and a series of known radioactive minerals makes it possible at times to identify a species. The test appears to be useful since data on the properties of radioactive minerals is often scant and unreliable. The final consideration in use of this test consists of strict standardization of working conditions and discretion in application.

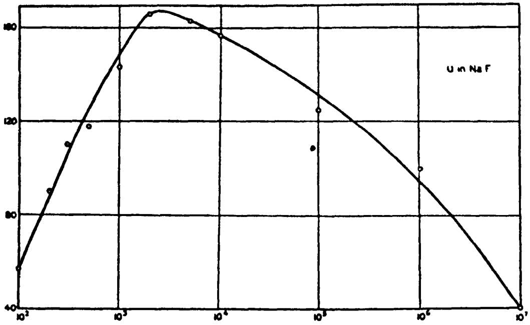
URANIUM AS AN ACTIVATOR

Uranium as an activator has been established in hyaline opal, as well as certain agates and glasses. Trachytic derived hyalite from Mexico and North Carolina fluoresces an intense green color, presumably due to the presence of minute amounts of uranium likely in the form of secondary uraninites.

The moss agate from Sweetwater County, Wyoming fluoresces a color and intensity characteristic of secondary uraninites. Large masses of colorless chalcedony found elsewhere in Wyoming have a green fluorescence similar to the agates from Sweetwater. Agatized wood and agate casts of wood from the same vicinity fluoresce similarly but not as intensely. Milky quartz, quartzite, and dark jasper also fluoresce with this green color. More recently other agate producing localities have been found in Wyoming and often this material fluoresces a green color. The localities are one-hundred or more miles apart but are all on the same general geological horizon. The rocks and sedimentary formations of central Wyoming, including Sweetwater County, are known to be radioactive to an abnormal degree.

In a large specimen of fluorescent Wyoming moss agate found by Pitts (1939) inclusions of a canary yellow mineral on one side provided basis for studies since this specimen was typical of those found in the locality. The inclusion was about six millimeters under the surface and fluoresced intensely under both short and long wavelength ultraviolet light. The yellow fluorescence was similar to that of the secondary uranites. The inclusion was found radioactive by its effect on a photographic plate.

Spectroscopic examination of Wyoming agate made by J. D. Buddhue (1939) failed to definitely establish the presence of uranium. However, in view of other evidence and the sensitivity of spectroscopic methods tests of greater delicacy were performed on the same specimen. A chemical examination by T. G. Kennard showed uranium in amounts greater than a few parts per million. Further studies by Buddhue on fluorescent chalcedony from the same locality by spectroscopic methods definitely excluded autunite as the activating substance since bands obtained did not coincide with those of autunite. The presence of phos-



Uranium in Sodium Fluoride. Curve for the optimum—a vivid yellow fluorescence may be produced by one molecule in 10,000,000 and still be easily measured. At a dilution of one molecule to 2000 optimum brightness occurs. This affords an indirect method for indicating the presence of radium in minerals. (*Nichols, Howes, and Wilber*) phorus, which would have indicated autunite or chalcolite since both are phosphates was not demonstrated either. However, Buddhue is of the opinion that the fluorescence of Wyoming agates and chalcedony is due to an unidentifiable uranium compound. This is apparently present in small amounts and probably contains the uranyl radicle and may be a new mineral species since its fluorescence spectrum appears to be unlike that of uranium compounds studied. Since vanadium was found to the extent of about 0.1% it might be possible that Ferghanite, hydrated uranyl vanadate, is the cause as its color, sulfur yellow, is about the same color as the inclusion noted in the Wyoming moss agate.

The presence of radioactive elements in water to activate fluorescence was studied by Francesconi and Brund (1934). These investigators found that greenish fluorescence could be directly attributed to the presence of these elements.

In fused borax beads and in non-sulfide phosphors uranium as an activator has been significant. The practical application of this is the delicate test of Papish and Hoag (1927) derived from the data of Nichols and Slattery. Essentially, traces of uranium salts fused with sodium or potassium metaphosphate, borax, or sodium or calcium fluoride produces a bead with an intense lemon-yellow fluorescence. Papish and Hoag used sodium fluoride in their tests and obtained results which were somewhat faulty since columbium was found to produce a similar fluorescence. The use of potassium fluoride as a solvent for uranium gives a less intense fluorescence but more specific one since other elements do not interfere with it. The bead tests are important in that they provide an indirect means of testing for *radium* in minerals by rendering the suspected sample soluble and fusing into beads with potassium fluoride and examining the product under ultraviolet light. The writers have used this with good results.

The sensitivity of the bead test is shown by the modification used by H. Eitel (1928) for detection of uranium in the kidney cortex, the only organ in which uranium is deposited in cases of poisoning. By ashing the organ and fusing portions of the ash with borax it was found that one part of uranium in 500,000 parts kidney ash could be detected by the characteristic fluorescence.

Uranium salts in the solid state, unlike most other inorganic substances, fluoresce intensely when both pure and dry. The measurement of the duration of fluorescence of uranium salts was made by F. Perrin and extended studies were performed by Achard, et al, who found that for low concentrations of some salts of the alkali metals the intensity of the fluorescence was found to be a decreasing exponential function of the concentration of uranium.

THORIUM MINERALS

The lesser known radioactive minerals containing thorium have not been studied as extensively for luminescence as the uranium minerals. It appears that thorium salts are generally non-fluorescent and few thorium minerals are known that fluoresce intensely or characteristically. An exception to this might be some zircons or others where thorium is sometimes associated as an impurity, however, this is a secondary consideration. Studies by the writers on 27 thorium compounds excited by long wavelength ultraviolet light demonstrated a number with pale blue, violet, or lavender fluorescence. Fluorescent thorium minerals are noted elsewhere. The *actinium minerals,* generally associated with the others and lanthanum, have not been studied extensively either.

CHAPTER NINE

LUMINESCENCE OF GEMS

Many species of gem minerals and minerals used for ornamental purposes exhibit luminescence when exposed to radiations of ultraviolet, cathode, X-rays, and those emitted by radium. The luminescent and fluorescent properties of some gems are a distinct aid in their identification, but sole reliance should not be placed on this method of determination. Numerous workers who have studied the luminescence of gems agree that the variability of the reactions in different specimens of the same species renders determination unreliable in many instances.

Gem minerals of the same species, originating from different localities, may vary in their luminescent properties, or may even fail to react to any type of radiation. Even gem minerals of the same species and from the same locality are known to vary. The degree of color in the gem may have an influence on its luminescent properties. The presence of a minute amount of impurity, not detectable by any ordinary chemical means, may wholly modify luminescence. For example, colorless hyaline opal from some localities, exhibits a powerful yellow-green under ultraviolet radiations, while the same mineral from other localities is wholly negative. The presence of a small amount of some secondary uraninite mineral is thought to account for the fluorescence exhibited by some hyaline opal.

The possibilities of distinguishing natural gems from the synthetics has been studied by a number of workers. Various natural stones differ from their manufactured substitutes in luminescent properties, but owing to numerous factors which enter into the observations, complete reliance can not always be placed in the results obtained. Very slight differences in the chemical composition of the manufactured stone may lead to a false conclusion. While the examination of natural and synthetic gem stones under ultraviolet light is more convenient, cathode and X-ray radiations give more reliable luminescent reactions and are generally more sensitive.

This is especially true in the distinction of natural ruby and sapphire from the manufactured poduct.

A search of the literature pertaining to the luminescence of gem minerals will indicate a variance of findings in the same species. This can be charged to the reasons stated above. The following table indicates wavelengths which have been found to be most satisfactory, and under which some colored gems fluoresce best. Attention is called to the fact that all existing specimens of the gems listed below are not fluorescent.

Gem	*Color*	
Beryl	Pale blue	3274 A.U.
Diamond	Yellowish	3200 A.U.
Diamond	Blue-white	3150 A.U.
Emerald	Green	3200 A.U.
Kunzite	Pink	3050 A.U.
Ruby	Red	3000 A.U.
Spinel	Purple	3248 A.U.
Spinel	Pink	3000 A.U.
Spinel	Blue	4023 A.U.
Topaz	Pale yellow	2618 A.U.
Topaz	Dark yellow	2294 A.U.
Topaz	Blue	2961 A.U.
Tourmaline	Green	3512 A.U.
Tourmaline	Pink	3064 A.U.
Zircon	Reddish-brown	2618 A.U.
Zircon	Blue-green	4023 A.U.

Some workers have studied the use of color filters for the observation of the fluorescent colors of gems. The color filters are an aid in eliminating the color of the gem itself. Doublets and triplets when composed of luminescent and non-luminescent portions can be readily detected when brought under the proper type of radiation.

Agate and chalcedony seldom exhibit luminescence, and only a few localities in the United States have produced examples. The well known moss agate of Sweetwater County, Wyoming is one of the most outstanding examples of agate showing a strong fluorescence under ultraviolet. The green fluorescence of this material is probably due to the presence of some uranium compound as shown by the recent work of John D. Buddhue. . The moss agate of Wyoming fluoresces a strong yellow-green, and is best under short wavelengths with filter 986. The colorless chalcedony found at the other Wyoming localities exhibits a similar fluorescence.

Alexandrite may fluoresce a weak dark red under ultraviolet radiations. It is usually negative to X-rays and red or orange under cathode rays.

Amber, a fossil resin, widely used as a gem and ornamental material, fluoresces a bright greenish-yellow to a bluish-white under ultraviolet. Ambroid (pressed amber) fluoresces in the same manner, although the color noted is less pronounced.

Bakelite, phenol-formaldehyde, urea-formaldehyde, and various resin-like plastics either fail to fluoresce or react only weakly. Some resin-like plastics prepared from casein and cellulose may give a bluish-white fluorescence.

Most of the natural fossil resins show a distinct fluorescence, and the cause of this is thought to be due to the included hydrocarbons.

Benitoite, a gem stone found only in California, fluoresces a strong blue under both long and short wavelengths of ultraviolet.

Beryl when exposed to ultraviolet usually fails to fluoresce or shows only a feeble color. The cathode radiations may cause colorless beryl to luminesce a reddish color. The aquamarine variety of beryl is also usually negative under ultraviolet, X-rays, cathode, and radium emanations. Emerald may show a distinct fluorescence which will set it apart from other green stones. X-rays luminesce emerald a weak red, and this is true of stones from practically all localities, while cathode rays bring out a deeper red color.

Chrysoberyl fails to fluoresce under ultraviolet and X-rays.

Diamond is a crystal form of carbon, but inclusions of amorphous carbon are frequently noted in the gem. The cause of fluorescence in diamond may be due to the presence of minute inclusions of some hydrocarbon, but this has so far not been substantiated by analytical work.

Diamond is one of the most interesting of all gems showing luminescence, and yet one of the most variable. The luminescence of diamond has been known for many years, and very early writers called attention to the phosphorescence of some gems after exposure to sunlight. A strong pale blue color is by far the most common fluorescing color, but pale green, orange, and reddish have also been noted under ultraviolet radiations.

The writers recently tested a lot of 550 carats of diamond bort originating in South Africa. The specimens consisted of small crystals and fragments averaging about one half a carat in weight. Under radiations of from 3200 to 4000 A. U. less than 3 per cent of the diamond fluoresced a strong pale blue. A small number of fragments emitted a pale green.

Under the cold quartz tube and filter 986, the same number of stones fluoresced blue. The green fluorescing diamonds gave a stronger color under the short wavelengths, and a few reddish and orange stones were noted which did not fluoresce under the long wavelengths. Similar results have been noted in smaller lots of diamond bort tested by the writers.

Under X-rays diamonds generally show at least a feeble luminescence, the color being variable with the color of the gem and the locality of origin. Cathode radiations will also cause most diamonds to fluoresce, with a stronger color than noted under X-rays.

It has been stated by some observers that the diamonds from certain African mines appear most likely to fluoresce, while stones fom other workings or other countries, seldom if ever, show this phenomenon. It is most probable that diamonds from any mine or locality may show fluorescence. The writers have tested lots of bort from Brazil which fluoresced in percentages about equal to the bort originating in Africa.

Garnet from many localities has been tested for luminescence by numerous workers, and only in rare instances has luminescence been reported, and these are open to question. Garnet fails to luminesce under ultraviolet, X-rays, or cathode radiations. On the other hand red color spinel usually shows a strong red fluorescence under ultraviolet. At times there may be some difficulty in distinguishing a cut gem of red garnet from a red colored spinel, hence the strong fluorescence of spinel may serve as a valuable supplementary test.

Kunzite, the pink colored spodumene from California fluoresces a weak to fairly strong reddish-yellow. Hiddenite the green colored spodumene fluoresces a weak reddish to lilac color. Some kunzite exhibits phosphorescence. Under cathode radiations kunzite luminesces a strong orange-yellow.

Opal often shows a marked fluorescence under ultraviolet, especially hyalite and common opal. Precious opal may also fluoresce weakly. The colorless hyalite opal found in North Carolina, Georgia, and San Louis Potosi, Mexico, while of little value as a gem stone, fluoresce a powerful green under both long and short radiations of ultraviolet.

Pearls, both native and cultured, often fluoresce with colors that vary with the locality of origin. The reason for this is still obscure, but the composition of the water may be a factor for consideration. There is no difference between the fluorescence of natural and cultural pearls. Artificial pearls as a rule fail to fluoresce unless they contain some fluorescing pigment like a uranium compound.

Peridot is considered as being non-luminescent under any type of radiations.

Quartz crystal when colorless usually fails to fluoresce, but smoky quartz from some localities may show a marked brownish-yellow reaction. Citrine quartz is generally negative under ultraviolet, while some amethyst fluoresces weakly. Many specimens of crystallized quartz show a distinct luminescence under cathode rays.

Ruby from various localities presents variable luminescent reactions, some of which are a distinct aid in distinguishing the gems originating from different localities. Ruby from Siam generally fluoresces a weak red under ultraviolet, while a similar colored stone from Burma or North Carolina may react a strong red under the same radiations. Ruby from Ceylon may fluoresce a strong yellow. Under cathode radiations, ruby from most localities wil luminesce a strong bright red, but the stones from Ceylon will generaly appear as a yellowish-red.

Under ultraviolet radiations, all shades of synthetic ruby generally fluoresce a strong red. The cathode rays also cause most synthetic ruby to fluoresce a strong red; the synthetic material appears to respond more readily to cathode rays, compared to the natural gem, and both the natural and artificial may show phosphorescence under these radiations. Luminescence can not be considered a reliable means of distinguishing natural ruby from the manufactured substitute.

Sapphire, colorless and the colorless synthetic sapphire are likely to fluoresce under ultraviolet. The natural stone may appeal a strong orange-yellow and the colorlees synthetic may fluoresce an orange-red to a reddish-blue. Under cathode rays colorless sapphire, natual and synthetic, appear as a violet red.

Dark green sapphire is usually negative under all radiations, but dark green synthetic sapphire may fluoresce dark red under ultraviolet and dark reddish-orange under cathode radiations. Yellow sapphire from Ceylon and Australia may fluoresce orange-red to orange-yellow under ultraviolet; the yellow colored synthetic stones more often show only a feeble color or fail to fluoresce. The cathode radiations cause most natural yellow colored sapphires to exhibit a light to dark red luminescence. Light blue sapphire from Montana will usually fluoresce a reddish-blue under ultraviolet and a bright red under cathode excitation.

Spinel, especially the red colors, usually fluoresce a marked red under ultraviolet, and the more pronounced the red of the gem, the stronger will appear the red fluorescence. Under cathode rays red colored spinel is generally negative or fluoresces only a very weak red.

Blue, green, violet and other shades of spinel ae usually negative to ultraviolet. Under cathode rays synthetic spinels in this color group either fail to fluoresce or lack features of distinguishing value. However, some dark blue synthetic spinel may fluoresce a strong red under ultraviolet and a similar color under cathode radiations. Slight variations in the shade of color in both natural and synthetic spinel appears to cause wide variations in luminescence.

Topaz when colorless fails to fluoresce under ultraviolet but may exhibit a pale blue or yellow under cathode rays. Pink, pale blue, light yellow, and dark yellow topaz usually fails to respond under ultraviolet. Under cathode radiations, the pink colors fail to respond, while the yellow shades often fluoresce a pale blue.

Tourmaline rarely shows marked luminescence under ultraviolet, cathode, or X-rays. The light yellow shades and colorless may exhibit slight fluorescence.

Willemite is generally found as an opaque gem material, and is therefore usually cut as a cabochon. Practically all the willemite found at Franklin, New Jersey, shows a strong green fluorescence. Some of the compact and colored varieties of willemite are well suited for cabochon cutting, and while not a hard wearing stone, the gem makes an excellent addition to collections of fluorescent gem stones.

Zircon usually fails to fluoresce under ultraviolet. The blues and dark reds may show a slight luminescence, and some colorless zircon from Australia fluoresces a marked yellow color. Under cathode and X-rays the luminescence of zircon is generally feeble or lacking.

FLUORESCENT GEM COLLECTIONS

A number of gem minerals, minerals, and ores that can be worked into cabochon styles, show an excellent fluorescence, and it is possible for the lapidarist to build up a spectacular and fascinating collection of fluorescent gem stones. Gem materials best suited for facet cut styles have been described above, and below are given some well adapted for cabochon cutting.

No attempt will be made here to refer to all fluorescent minerals suitable for lapidary treatment. Some which fluoresce only weakly would find little place in a collection. Hence only the better known species are mentioned. Cabochons or facet cut gems blend in well and always attract attention when exhibited with collections of fluorescent minerals. No special technique is required to cut cabochon gems or sections from fluorescent specimens. In general most of the minerals showing strong fluorescence are softer than quartz and can be sectioned and worked with ease. For complete and modern methods of gem stone cutting technique the reader is referred to, The Art of Gem Cutting, The Mineralogist Magazine, April 1938, Portland, Oregon.

Practically all the minerals mentioned below are available from mineral supply houses and are inexpensive. Collections of fluorescent gem stones confined to cabochon styles hold fascinating possibilities. It is not at all strange that a ground and polished surface on a fluorescent mineral will increase its brilliancy 25 per cent or more under ultraviolet light. The smooth worked surface on a cabochon is free of the pits, depressions, and projections pesent on the rough mineral, and which cast shadows to detract from the vividness of the fluorescence. A high polish on the finished stone is not essential, removal of the deep scratches will suffice to bring out the best fluorescence possible in the material.

Kerosene is generally used as a lubricant for the lapidary saw, and this liquid may be absorbed by the gem to temporarily mask some of the fluorescence. Most of the kerosene can be removed by washing the stone in some solvent like gasoline or commercial cleaning fluid. The presence of kerosene permeating the stone is not serious, for the liquid slowly volatilizes. at ordinary room temperatures, and will evaporate from the stone within several days. Kerosene in common with many petroleum products fluoresces a strong blue under all wave lengths of ultraviolet.

Agate and chalcedony seldom show a marked fluorescence, and despite the wide distribution of these varieties of quartz, few localities produce fluorescent examples. The state of Wyoming is the principal producer of fluorescent agate and chalcedony. The small water worn pebbles of moss agate from Sweetwater County, Wyoming, fluoresce a strong uranium green, and are well adapted for cabochon cutting. North of Medicine Bow. Wyoming is a locality which produces large masses of colorless chalcedony which fluoresce a strong yellow-green. Other localities in Wyoming produce fluorescent agate and chalcedony suitable for gem cutting. The cause for fluorescence in Wyoming agate is doubtless due to the presence of minute amounts of uranium, carried along as an impurity in the percolating silica solutions. It is possible to obtain a radiograph on X-ray photographic film with some specimens of Wyoming moss agate.

Amber, while generaly worn as beads, may also be worked into cabochon styles. This and other fossil resins often fluoresce markedly.

Aragonite in the massive form, especially when intergrown with other fluorescent minerals, is often suitable for gem cutting. Depending upon the locality, aragonite fluoresces either pink, red, or cream-white.

Calcite from many localities is suitable for gem cutting, and finds wide use in collections of fluorescent gem stones. The massive calcite, intergrown with various other minerals, from Franklin, New Jersey serves as spectacular cabochons. The New Jersey calcite fluoresces in shades of from pink to deep fire-red, and is best seen under cold quartz tube with filter number 986. The Franklin locality produces intergrowths of calcite, calciumlarsenite, and willemite which fluoresce red, bright yellow and strong green respectively. These three minerals all in the same cabochon made a superb color combination.

Cuproscheelite occurs in compact massive forms, fluoresces a yellowish color, and may be worked into cut stones.

Fuorite has a well defined cleavage and must be worked with care while cutting. The massive forms of fluorite are better adapted for gem cutting. Fluorite from many localities fluoresces strongly under long wavelengths of ultraviolet.

Gypsum and selenite generally fail to fluoresce strongly, but the material from some localities finds use as a gem cutting material.

Hackmanite from Ontario, Canada fluoresces strongly and specimens suitable for cabochon cutting are available.

Opal in the precious varieties fluoresces less strongly than do the common and hyaline varieties. The common or semi-opal from Virgin Valley, Nevada, is pale yellow in color under ordinary light, while under all ultraviolet light sources the mineral glows a strong yellow-green. A common opal with inclusions of dark moss-like markings from Virgin Valley, Nevada also shows a strong fluorescence. Both types are well adapted to gem cutting. Colorless hyalite opal, when fluorescent, is also used as a gem cutting material. Under ordinary light a cabochon of hyalite opal appears as a limpid, congealed drop of water, which turns a vivid yellow-green under all ultraviolet radiations.

Quartz crystal when colorless rarely, if ever, exhibits fluorescence under ultarviolet light. The inclusions often noted in quartz crystals may show fluorescence. G. B. Gibford of Riverside, California recently collected some remarkably unique quartz crystals in San Diego county, California. The specimens found by Gibford are clear colorless quartz crystals, about one inch in length and showing phantoms. Along the planes of the phantom are invisible inclusions which show a strong green fluorescence. The identity of the included material causing the fluorescence has not been determined.

Scheelite fluoresces a vivid pale blue and can be worked into cabochons. The richer scheelite ores are best adapted for lapidary treatment.

Sphalerite from Tsumeb, Africa is a black, granular to massive, zinc sulphide. Under ultraviolet the material glows a strong orange color. The massive sphalerite is best suited for lapidary work. Intergrowths of fluorescent sphalerite and wurtzite from Frisco, Utah may also be used for lapidary cutting.

Wernerite from Ontario, Canada exhibits a strong canary-yellow fluoescence. The compact, sub-translucent variety is excellent for cabochon cutting.

Willemite occurs in numerous colors under ordinary light. The fluorescence of the willemite fom Franklin, New Jersey is highly variable and spectacular, and includes various shades of green. Some specimens phosphoresce strongly and may continue to glow for hours after a single "charge" of ultraviolet radiations. The compact, fine grained, and subtranslucent varieties are best for gem cutting. Willemite from Franklin is often intergrown with other fluorescent minerals to offer pleasing color combinations.

CHAPTER TEN

SOME NOTABLE FLUORESCENT COLLECTIONS

Prior to ten years ago very little attention was given by museums and individuals to the possibilities of building colorful collections of fluorescent minerals, and few exhibits of this kind were known. At that time ultraviolet light sources were not as highly developed, and most units were cumbersome and costly.

About 1932 the little inexpensive argon bulb appeared, to be followed by various types of "black bulb" and "black light" lamps operated from a small transformer. These in turn were followed by various improved and less costly units as convenient and efficient sources of ultraviolet radiations both of the short and long wave types. With the improvement in ultaviolet units more and more attention was devoted to collections of fluorescent minerals. Museums, institutions, and private collectors soon learned that the colorful and spectacular beauty of a well arranged collection of fluorescent minerals brought about wide public interest.

At the present time there are thousands of collections of fluorescent minerals in the United States. Numerous large museums have and are continuing to install exhibits and augment those already on public view. Museum curators have noted collections of fluorescent minerals are a never ending source of attraction to visitors.

So far as can be learned the first museum to install a collection of fluorescent minerals was the British Museum of Natural History in London. In 1903 this institution arranged a small exhibit in a dark room. A minute amount of radium salt was used to excite the specimens to fluorescence, and only a small number of specimens could be viewed at one time. The room in which the London exhibit was arranged was small; only space for the operator and one visitor. The popularity of this exhibit exceeded all expectations, visitors stood in line for days to await their turn to view the glowing minerals and gems excited by the emanations from radium.

For some years following 1903, little was done on the installation of public exhibits of fluorescent minerals. In 1929 the Philadelphia Public Museum installed the first museum collection in the United States, and from that time there have been numerous installations. During the first few years of its installation over 200,000 visitors viewed the Philadelphia Museum collection. Eighteen large and showy specimens comprised the first exhibit and these included wernerite, aragonite, common opal (Nevada), fluorite, willemite, Calcite (New Jersey), hyalite, autunite, sphalerite (Africa), brucite, and amber. Two carbon arcs fitted with Corning heat-resisting filters were used as ultraviolet light sources. The lighting system was so arranged that the specimens would first be shown under ordinary light and then under ultraviolet. A duplicate collection was loaned to the Century of Progress Exposition at Chicago in 1933, by the Philadelphia Museum. This same exhibit upon its return to Philadelphia was loaned to the Wanamaker store and placed in a large show window. The plate glass window was painted black except for a narrow strip through which pedestrians could peer. Six large NiCo tubes were used to excite fluorescence.

Since 1933 additional thousands of people have viewed fluorescent collections throughout the country. There are many excellent public collections of fluorescent minerals in the country and below reference is made to some. The list given here is not complete, but many outstanding ones are enumerated and briefly described. Many colleges and educational institutions have installed fluorescent collections, and some of these are open to the public.

MUSEUM COLLECTIONS

One of the most notable of museum collections is that of the Cranbrook Institute of Science, Bloomfield Hills, Michigan. This remarkably beautiful exhibit was installed some eight yeas ago, and since then has been continuously improved by the curator, William B. Colburn. Beauty and quality and not quantity has been the keynote at Cranbrook; each specimen has been selected as one of the largest and best of its kind available.

The Cranbrook Institute of Science fluorescent collection is housed in a special dark room in Mineral Hall. The specimens are arranged on black velvet, in a large recess in the wall and the front covered with plate glass. Four large NiCo tubes supply the ultraviolet radiations, which are ample to fully illuminate the ten foot frontage and several feet depth. The ultraviolet lights operate automatically, with an interval between ordinary illumination and the invisible radiations to permit observation of phosphorescence. Since its installation many thousands of visitors have viewed the Cranbrook collection.

Probably the largest museum exhibit of fluorescent minerals is that of Paterson Public Museum, Paterson, New Jersey. This museum has specialized in the spectacular Franklin, New Jersey, specimens, and hundreds of specimens from this locality are included in the exhibit. Various light sources are used in the Paterson collection, including both long and short radiations.

The Griffin Observatory Museum at Los Angeles contains an excellent collection of fluorescent minerals. While not large, the Griffin collection is one of quality, and includes an assortment of the best fluorescing species. The illumination by short wavelength radiations gives a spectacular effect.

The Santa Barbara Museum of Natural History at Santa Barbara, California, has an excellent exhibit of fluorescent minerals. Numerous spectacular California and New Jersey specimens are included. The display is well arranged and illuminated by powerful cold quartz tubes.

The Field Museum of Chicago contains an automatically operated fluorescent exhibit using NiCo tubes as a light source. The Houston Museum of Natural History at Houston, Texas, has a similar installation. Some excellent exhibits of fluorescent minerals may be seen in a number of Atlantic coast museums and educational institutions.

The Spokane Public Museum of Spokane, Washington, has a small but colorful exhibit. The specimens have been selected to show best under the cold quartz tube without filter. A six foot length of Mineralight tube, backed by a reflector gives ample radiations to cover a large area. The Spokane Museum exhibit uses both ordinary and ultraviolet light, operated semi-automatically, with an interval between to permit observation of phosphorescence. The Spokane exhibit was installed by Charles Fernquist.

Visitors to the Georgia State Museum at Atlanta are impressed with the splendid fluorescent exhibit. The display is arranged in an alcove, with a convenient switch to enable change to be made from ordinary to ultraviolet light, at the option of the operator. NiCo tubes are used in the Atlanta exhibit. The collection at the Academy of Science Museum, Golden Gate Park, San Francisco, attracts thousands of visitors annually. The Golden Gate Park exhibit uses a NiCo tube operated by the viewer. The specimens are arranged in a large case and viewed through slots at the side. Dr. Warren D. Smith, Department of Geology, University of Oregon at Eugene, has arranged a colorful exhibit of fluorescent minerals in Condon Hall Museum. Germicidal tubes and filter 986 is used as a light source for the Condon Hall Museum exhibit.

During the past six years many of the mineralogical societies throughout the country have sponsored public lectures and demonstrations devoted to mineral fluorescence. These public lectures often attract gatherings numbering up to 1000 or more persons, and have been instrumental in developing wide public interest in the phenomena.

PRIVATE COLLECTIONS

There are hundreds of large and excellent private collections of fluorescent minerals and gems scattered throughout the country. Some of these are closed to the public, but in many instances arrangements can be made to view same. In building a collection of fluorescent minerals due consideration should be given to the type or types of ultraviolet light sources to be used. With the recent appearance of numerous and efficient ultraviolet light sources for both long and short wave radiations, many installations include both types of light sources, thus covering the entire range of mineral fluorescence. Collectors and museums in the eastern part of the United States have been inclined to favor the iron spark lamp and the NiCo tube, while western collectors and museums generally favor the cold quartz tube light sources. Both have their advantages and distadvantages.

To enjoy the benefits of a collection of fluorescent minerals, and to enable the individual to carry on studies of the fluorescence of vaious substances, elaborate and costly ultraviolet equipment is not required. Recently, light bulb manufacturers have made available powerful but inexpensive long wavelength units, of the "black bulb" type, with self contained filter that can be operated from an 110 volt, alternating current light socket. Improvements and price reductions have also been made in the higher priced units. A great deal remains to be done in the systematic study of the fluorescence of various substances, and doubtless the future will witness many additional applications of fluorescence in the sciences, arts, and industries.

The list of private collections of fluorescent minerals given below is by no means complete, as practically every mineral collector in the country has at least a small collection of luminescent minerals. Only a few of the outstanding cabinets are referred to here.

The Sutter Fluorescent Show of Walter Sutter of Tacoma, Washington has probably been viewed by a larger number of persons than any other private collection in the country. It has been estimated that during the past six years the Sutter Flourescent Show has been viewed by no less than 500,000 people. The Sutter fluorescent collection is in two parts, a permanent installation in the Sutter Tacoma residence, and the portable part known as the Sutter Fluorescent Show. These include hundreds of large specimens having a total weight of over four tons. Many of the large size Sutter specimens are outstanding for their typical quality. The portable collection has made numerous appearances at mineralogical conventions hobby shows, and lay gatherings. The non-portable portion of the Sutter collection is built around a fireplace in his home and is combined with Chinese art objects, with a pleasing effect. Several sources of ultraviolet are used to illuminate the Sutter fluorescent fireplace.

The Sutter Fluorescent Show is outstanding for the spectacular beauty of the specimens, as well as the convenient and effective manner in which the several sources of ultraviolet are operated. The portable exhibit is complete with a large black tent, so the set-up may be made in a large illuminated hall and yet obtain proper darkness, when specimens are viewed under ultraviolet radiations. A robot, electrically operated controls the switches for the several units. This enables the operator to carry on with a descriptive lecture as the different types of radiations appear. The robot can be timed to cause various light units to appear at varying or constant intervals. Combinations of different types of ultraviolet radiations can be obtained under the robot control system. The robot can be set to require from about five to fifteen minutes to complete the entire series of changing fluorescent colors in the exhibit.

The ultraviolet lighting equipment used in the Sutter portable exhibit includes (1) a battery of argon bulbs, (2) a standard length of NiCo tube, (3) a battery of 250 watt "black bulbs", (4) an 8 foot length of 9mm diameter unfiltered cold quartz tubing, (5) a 4 foot length of cold quartz tubing completely covered with filter number 986, (6) 15 watt Germicidal tubes, and (7) standard fluorescent lighting tubes for illumination with ordinary light. An illuminated indicator is included to show changes in ultraviolet illumination as they are delivered from the robot control. All illumination units are fitted with reflectors and placed in concealed positions.

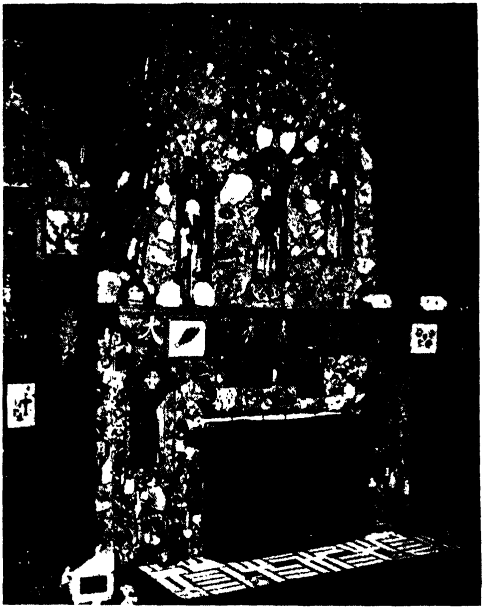
In New Jesey and New York there are a number of noted private collections of fluorescent minerals. The J. L. Smith, Chester, New York collection is rich in large and rare specimens from the noted locality of Franklin, New Jersey. Egbert McElroy of Monroe, New York also has a magnificent cabinet of Franklin minerals. One of the best collections in New York City is that of John Grenzig of Brooklyn. Paul Walther of Elizabeth, New Jersey has one of the most comprehensive private collections, which includes a large number of species. The Walter C. Shortle collection at Laconia, New Hampshire is notable among the private collections in the New England states.

One of the most unique fluorescent exhibits in the country is the Fluorescent Cave of Professor H. E. Murdock of Bozeman, Montana. The Murdock collection of minerals and other fluorescent substances is arranged in an underground cavern. Numerous ultraviolet units are used in the Murdock Fluorescent Cave.

In Wyoming the L. E. Bowser, Baroil; W. A. Brox, Rawlins, collections are noteworthy. At Lovington, New Mexico the Dr. R. E. Anderson fluorescent collection comprises one of the most complete in the country. The

E. Mitchell Gunnell, Denver, Colorado, collection rates as one of the best in the state.

A number of excellent collections of fluorescent minerals may be seen in Portland, Oregon, including those of J. Lewis Renton and Dr. Courtland Booth. Both exhibits are illuminated by several types of powerful sources of ultraviolet. One of the most complete collections of fluorescent minerals



WALTER SUTTER FLUORESCENT FIREPLACE

The Sutter fluorescent fireplace of Tacoma, Washington has ben viewed by thousands of visitors during the past five years. Fluorescent minerals are used in combination with Chinese art objects. Fluorescent minerals from many localities are represented.

in the country is the exhibit in the laboratories of The Mineralogist Magazine, Couch Building, Portland, Oregon.

One of the best private exhibits in Seattle, Washington is the Verah Landon cabinet, illuminated with both short and long wave ultraviolet units. California has dozens of superb and spectacular exhibits of fluorescent minerals, including those to be seen in museums, institutions, dealers stocks, and in private cabinets.

Some of the best commercial stocks of fluorescent minerals and supplies may be seen at the following firms:-

John Grenzig Co., Brooklyn, N. Y.
Warner & Grieger Co., Pasadena, Calif.
Smith Agate Shop, Portland, Oregon.
Chesbert Co., San Francisco, Calif.
Shortman's Minerals, Easthampton, Mass.
Pacific Mineral Mart, Long Beach, Calif.
American Mineral Exchange, Houston, Texas.
W. Scott Lewis, Hollywood, Calif.
Harry Ross, New York City
H. N. Retherford Co., Los Angeles, Calif.
Ultraviolet Products Co., Los Angeles, Calif.
R. W. Tuthill Co., Michigan City, Indiana.

FLUORESCENT FIREPLACE CONSTRUCTION

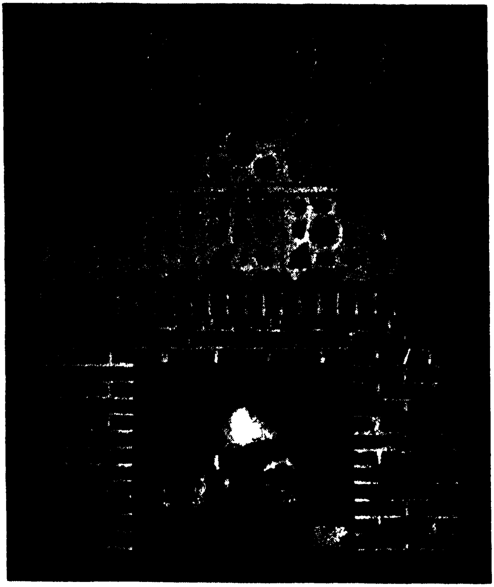
Fluorescent minerals are finding wide applications as an ornamental stone. Large massive specimens of fluorescent minerals may be fashioned into book-ends, pen holders, paper weights, and similar ornaments. Sawed into sections, like tile, massive specimens may be used as an effective table top covering. Fireplaces faced with fluorescent minerals hold wide possibilities; installations of this kind are well adapted for a fireplace in a den, basement recreation room, or a night club. It is possible to face a fireplace with a selection of fluorescent minerals to give a pleasing effect in ordinary light, and a spectacular color transformation under ultaviolet light.

In the construction of a fluorescent fireplace, a number of methods can be used to place the specimens in position. One of the first fireplace exhibits in the country was arranged by A. N. Goddard of Detroit, Michigan in 1934. The Goddard installation makes use of a fireplace which has been rebuilt to exhibit minerals, and not used for fire. The Goddard method makes use of the original fire pit, where the minerals are arranged on black shelves and suspended from wires. Two large NiCo tubes are concealed at each side of the fire pit as sources of ultraviolet. The specimens are first viewed in ordinary light. Covering the entire original Goddard fireplace are numerous illuminated glass cases and shelves where non-fluorescing minerals are displayed. A special case conceals the fluorescent minerals in the fire pit, so these may be viewed as a final climax. The Goddard method is effective and has the advantage that rough specimens may be used and the exhibit changed at will.

The fireplace installation of Walter Sutter of Tacoma, Washington embodies a combination of features, both in construction and in illumination. The Sutter fireplace is of considerable size, 15 feet high and 10 feet wide at base, with the mantel 5 feet above floor level. The uncut fluorescent minerals and ornaments, facing the fireplace below the mantel, are attached with cement and are a permanent installation. Above the mantel both rough and sawed specimens, are attached so as to be freely removable, being held in position by wire or resting in niches in the brickwork. Lengths of cold quartz tubes, concealed both above and below the mantel supply short wavelength radiations, while a carbon arc spotlight, with heat-resisting filter, hidden in the ceiling gives long wavelength ultraviolet.

One of the most simple and convenient means of facing a fireplace with fluorescent mineals is the use of square plaques carrying sawed sections of fluorescent minerals, and where ultraviolet units may best be attached to ceiling or on each side. The plaques shown on the fireplace illustrated cover the portion only above the mantel, are 15 in number and each is 13 inches square. If the plaques are all of equal size, it will be possible to readily change their positions. Owing to constuction reasons it is not advisable to make a plaque of this type much larger than 13 inches square.

Construction of plaques is simple. A wooden framewok 13 x 13 x ¾ inches is first made. The wooden framework is placed on a large sheet of glass, the sawed sections of fluorescent minerals are placed in position, inside the wood frame. Plaster of Paris is poured over the specimens to fill the frame flush with the top. When the plaster has set the plaque is removed from the glass, and any slight excess of plaster which has run over the face of the specimens may be trimmed away. The sawed specimens need not be over ¼ inch in thickness, and in no case should be over ¾ inch, the



FIREPLACE FACED WITH
FLUORESCENT MINERALS

Fireplace of H. C. Dake using cut sections of fluorescent minerals and plaques for mounting. The plaques rest on a track and can be readily removed from fieplace front. The ultraviolet lighting system attached to ceiling is not shown. (*Photo by Gus Brockmann.*).

thickness of the wooden frame work.

The smooth sawed surface of the specimen will appear on the face of the plaque against a background of white plaster paris. The contrast is pleasing, but if a dark colored background is desired, a pigment or dye may be incorporated in the plaster, or the plaster may be painted after it has set for several days. The wooden framework may be painted or may be constructed of the western black locust wood which (unvarnished) fluoresces a vivid yellow-green. The smooth sawed surface of the specimens fluoresce effectively since it is free of depressions and ridges which otherwise cast shadows.

Plaques as a fireplace facing have many advantages. They can be placed on a track rest, and slide into position from the side of the fireplace, can be moved about on the installation and are readily portable. A facing of this kind can be installed without damage to the fireplace front. The wooden track upon which the plaques rest are easily attached to the fireplace by driving a few nails into the mortar between the bricks. Other uses for the plaques will suggest themselves.

The majority of fluorescent minerals are not extremely hard and can be readily sectioned by the saws employed in lapidary work. If a poured plaque is not satisfactory, it is easily possible to remove framework, and by gently tapping the plaster with a light hammer the sawed specimens can, in most instances, be broken out intact.

Numerous fluorescent minerals are suitable for sectioning and used for fireplace facing, ornamental tile, and numerous other purposes. The fluorescent ore minerals from Franklin, New Jersey are well adapted for sectioning and make spectacular and pleasing color contrasts. Other minerals suitable for plaques include wernerite, scheelite, massive fluorite, calcium-larsenite, massive calcite, willemite, common opal, and aragonite. Fragments of fluorescent minerals may also be applied to plastic Plaster of Paris or cement to give a stucco affect.

CHAPTER ELEVEN

ANTIQUES — CERAMICS — GLASS — ART OBJECTS

The applications of fluorescence to detect frauds in antiques is still in its infancy but holds many possibilities. W. D. Quattlebaum (1935) was one of the first to make a systematic study of the fluorescence of antique glassware. Using short wavelength radiations, Quattlebaum found that no shade of blue fluorescing glass appeared to have been manufactured in America later than 1864. It is well known that in 1864, American glass manufacturers adopted a soda-lime flint in place of the lead-flint fomula used previously. It was amply shown that the old American glasses of the lead formula gave a blue fluorescence, while the non-lead glasses were either negative to ultraviolet or gave a greenish-yellow luminescence.

Quattlebaum also pointed out that practically all old Continental glass gives a greenish-yellow fluorescence. Some of the old Bohemian and some modern Slovakian glasses fluoresce greenish. The fluorescence of the Bohemian and Slovakian glasses has been attributed to the presence of minute amounts of uranium in the sand used in the manufacture of the glasses.

Practically all the glass made in England for table use from about 1700 to 1800 gives a blue fluorescence. The same is true of American glass made for table use prior to 1864—and particularly that of the New England and Pittsburg districts—from about 1800 to 1864.

Repairs or replacements of an antique glass object can frequently be detected by the use of some type of ultraviolet radiation. For example, a pair of candlesticks with dangling glass prisms, should fluoresce equally if all parts are contemporaneous. The cheap modern glasses which often contain minute amounts of uranium fluoresce with a characteristic yellow-green color under both long and short ultraviolet radiations. Glasses from different sections of the world and from different manufacturing areas rarely fluoresce with identical color. This is due to the fact that different sand deposits and different formulas were utilized.

Fluorescence analysis as applied to glass is in use in the laboratories of glass specialists. W. B. Lester (1931) found it possible to differentiate between glasses colored with manganese and selenium. According to M. Guillott (1934) iridescence in glass is due to calcium carbonate formed in the presence of sodium bicarbonate, but oxides of the alkaline earth metals, zirconium and uranium, are usually added to produce fluorescence. Efforts have been made to learn which constituents in glass are most likely to cause fluorescence, but no specific generalizations can be made.

Optical glasses of the same formula, but from different manufacturers, show marked distinct differences in fluorescence. The differences in shade may be subtle, but they are sufficient to permit a manufacturer to distinguish his product from that of another in the finished (lens) form. The cause of the differences in the fluorescence of optical lens glasses of the same form is thought to be due to the presence of minute traces of rare earth elements. Some have suggested that the crystalline structure of the glass may account for a variation in luminescence. The fluorescence which some glasses acquire after exposure to X-rays, radium radiations, and ultraviolet radiations may provide a further means of identification. Very old glasses may undergo decomposition with aging, with accompanying changes in fluorescence. Imitation of very ancient glass by surface treatment may be revealed in ultraviolet light.

Fluorescence is very valuable in museum work and practically every large institution is equipped with one or more ultraviolet light units. Paintings, books, documents, ceramics, glassware, sculpture, ivories, fossils, old marble, alabaster, textiles, postage stamps, and many other objects are often counterfeited, altered, or repaired. The searching rays of invisible light will frequently clearly reveal these subterfuges.

Forged postage stamps as well as those which have been cleverly altered or patched are generally exposed under ultraviolet radiations of the correct type. The success of detection of spurious postage stamps depends largely on the fact that any addition of color ink, or mucilage differing in chemical composition from the original will cause a difference in fluorescence. The mucilage on the back of the stamp often shows a fluorescence which varies in color and intensity according to the origin of the stamp. A patch or an addition to the edge or corner of a stamp will generally be clearly revealed by ultraviolet light, by reason of the use of a different paper and ink, and by the joint line itself.

Reprints and forgeries can be detected in postage stamps unless identical paper, ink, and mucilage are used in the spurious product. In some instances two issues of the same stamp may be differentiated under ultraviolet light. Eradicated cancellation marks may also be rendered visible under ultraviolet. Black inks as a rule do not fluoresce or react only feebly. In examining postage stamps under ultraviolet light it is well to have a known genuine and unaltered specimen for comparison alongside the suspected spurious or tampered specimen. All specimens should be examined under both long and short wavelength ultraviolet units fitted with a proper filter to remove visible radiations.

Old parchments and other valuable papers may be examined under ultraviolet light. Erasures were made by rubbing with fine sand, and some ancient parchments show as many as three different writings, with only the last visible under ordinary light. Some interesting historical facts have been revealed in examining old parchments under ultraviolet light. J. Grant has given a method of revealing faded writing on paper. The underside of the paper is smeared with vaseline and mineral oil. The oily mixture penetrates the paper more rapidly at the point where there has been no writing, and since the oil is fluorescent the faded writing stands out clearly against the fluorescent background. The fluorescence of paper itself is often a clue to its age and composition. Old paper does not contain fluorescent sulphides and the fluorescence of rag differs from that of wood pulp paper.

Imitations and genuine specimens of ceramics may be differentiated under ultraviolet light. Surface alterations may be easily noted, for the metallic surface glazes are seldom fluorescent, while patches and restorations made with paints, plasters, or clays usually fluoresce. One of the recent developments in ceramics has been the production of artificial teeth which fluoresce in a manner similar to natural teeth. The fluorescence of the artificial teeth, especially when set in a pink colored translucent plastic, adds much to their resemblance to the natural.

Old marble fluoresces differently from freshly cut or old recut marble. Old marble usually shows a mottled white or yellowish-white color, while recently cut marble fluoresces a uniform purple. G. A. Richter (1929) examined the statue of Diogenes in the Metropolitan Museum of New York City under ultraviolet light. He concluded that from the mottled appearance of the base and the lower portions that these are of ancient origin, while the upper portion is of more recent date.

In paintings, repairs, overpaintings, counterfeits, and spurious signatures may be difficult to detect under ultraviolet light, hence tests are generally made under both ultraviolet and X-rays. E. Botolfsen tells of a Mona Lisa said to have been executed by Bernado Lunini. Examination under ultraviolet light indicated the work had been done nearly 100 years after the death of Lunini, and the signature was obviously spurious. Pigments* of various types, varnishes, oils, and organic dyes all react under ultraviolet light in a characteristic manner. During certain periods in the history of art, only certain types of paints were used by artists, hence a fraud can often be revealed on the basis of the approximate date of the execution of the work. Many of the modern coal tar colors used in paints fluoresce strongly, while some of the older metallic pigments show only a feeble fluorescence or are wholly negative.

Modern varnishes and glues fluoresce differently from those used in past years, hence antique furniture may be distinguished from modern replicas by this means. Fluorescence analysis has enabled oil varnishes on old violins to be distinguished from the spirit varnishes used on modern imitations. Oil varnishes were always used on old Stradivara violins.

* Many formulas for fluorescent paints and pigments will be found in *The Chemical Formulary* by H. Bennett (Chemical Publishing Co., Brooklyn, N. Y.)

BACTERICIDAL ULTRAVIOLET RADIATION

The lethal effects of ultraviolet radiation on micro-organisms and fungi constitute a distinguishing property of this radiation. The bactericidal effect of ultraviolet light was first noted in sunlight since the latter has long been known for its power to kill certain micro-organism. As early as 1903 Barnard and Morgan demonstrated that bactericidal action is limited to radiations of wavelength shorter than 3000 A.U. Later, Gates showed that the bactericidal action of ultraviolet light depends on wavelength since an increase in lethal action occurs when the wavelength decreases from 3000 A.U. to a maximum at approximately 2660 A.U. It was further noted that bactericidal action decreases to a minimum for wavelengths of 2375 A.U. but again increases to a maximum for wavelengths below 2375 A.U.

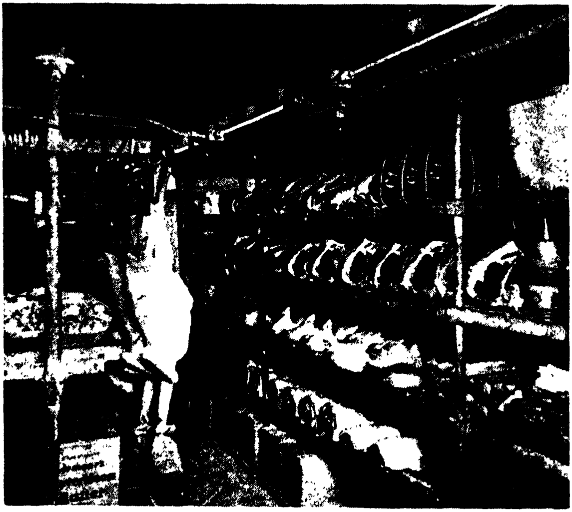
Only recently has an attempt been made to use these facts for practical purposes. The development of a suitable source of abiotic radiation by H. C. Rentschler and R. James was the result of several years research and was aided immensely by a tantalum photoelectric ultraviolet meter devised by them. By means of this instrument the quality of radiation as well as its quantity could be studied.

The lamp devised by Rentschler and James is known as the Sterilamp. Its tremendous significance for sanitizing and sterilizing has not yet been fully realized.

The Sterilamp consists of an evacuated glass tube with special transmission characteristics. Usually these tubes are about a half an inch in diameter and of varying lengths. In the ends metal electrodes are sealed and coated with an electron emitting material such as Strontium oxide and Barium oxide to minimize voltage drop. In the tube, a small amount of inert gas is present, or, a mixture of gases which permit ionization at room temperature to occur and allow the arc discharge to start instantaneously when the electrodes are energized. The starting voltage is generally a function of the length of the tube, ranging from 400 to 800 volts in the commercial units. In addition, the tube contains small amounts of mercury vapor at four to ten millionths of an atmosphere pressure. The pressure results in a negligible amount of visible light but produces the two well known mercury lines at 2537 and 3650 A.U. The quality of the special glass is to obtain maximum transmission of wavelengths longer than 2000 A. U. but to absorb shorter wavelengths such as the 1850 and 1940 A.U. lines. Approximately 95% of the emission occurs at 2537 A.U. Shorter wavelengths produce ozone which has an objectionable, if not injurious, effect on the nasal membranes. Ozone may cause undesirable changes to occur in foods. The small amount of energy emitted in the visible region of the spectrum consists of a pleasant light blue light.

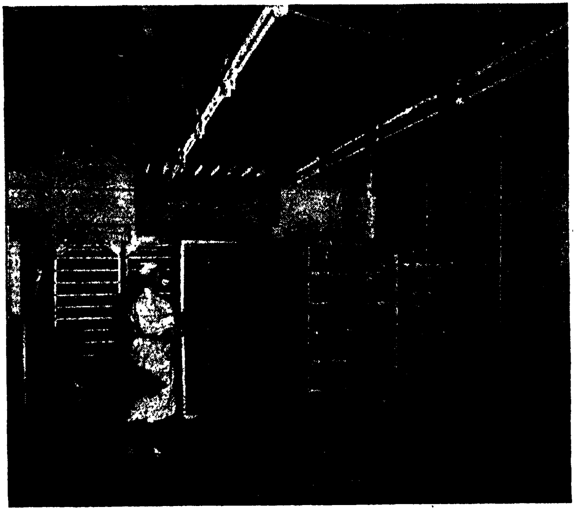
Probably the most striking application of the Sterilamp has been in surgery where large reductions in infection have been obtained by D. Hart (1936) and others. In use the lamps are mounted over the operating table, in the ventilators to sterilize the air, in instrument cases, refuse containers, or other places where pathogenic micro-organisms may occur. With such radiation, wound healing has been more rapid and with less reaction when wounds are reopened for the second and third stages than in those cases where radiation has not been used. The post-operative condition of the patient is greatly improved in instances where sterilizing lamps are used in conjunction with operative procedure. Results by Hart showed practically all cases examined to have been less post-operative pain with more rapid convalescence in the cases where radiation was used. By sterilizing the air in the operating room with bactericidal radiation Hart found the mortality rate to be more than cut in half by the elimination of cases of severe wound infection which resulted in death. Hart's work has been on extrapleural thoracoplasties and other operations. For the method of mounting bactericidal lamps over operating tables see the accompanying illustrations and the references in the Bibliography.

Other applications of the Sterilamp are as significant. These applications may be divided into three groups, (I) where direct radiation can be utilized, (II) where semidirect radiation must be used, and (III) where totally indirect radiation is necessary.



Typical installation of open ultraviolet tubes in a walk-in refrigerator. One of the problems in refrigeration has been the development of fungi and molds. The problem has been largely solved by the powerful bactericidal action of ultraviolet radiations below 2500 A.U. The bactericidal tubes consume very little energy and practically no heat which is of importance in a refrigerator.

In the first group the most important application is in the hospital operating room. Bactericidal radiation has already proven highly successful in meat preservation since it prevents spoilage due to the molds and bacteria unavoidably present in these products. Although refrigeration inhibits growth of micro-organisms it does not have the highly lethal effect possessed by ultraviolet light. Reduced temperatures usually result in lower relative humidities which cause dehydration or shrinkage in bread is caused by the growth and development of an organism known to belong to the mesenteric group of bacteria. Rope bacteria may exist as either vegetative cells or spores, the latter of which are more resistent to high temperature than the vegetative cells from which they are formed. The vegetative cells are sensitive to several agents. According to data supplied by George F. Kirkwood, antiseptic methods for prevention and control of mold and rope are of several kinds. Among the agents for mold, acetic acid applied to the crust of bread, fumigation with ethylene oxide, and ultraviolet light are suggested. With the intro-



Installation of open ultraviolet (short wave radiations) light tubes in the cooling room of a bakery to provide a sterile environment around the product. The bactericidal action of the ultraviolet radiations, aids in preventing the development of mold and fungus growth after the bakery product is wrapped for shipment. (*Westinghouse Electric Comphany photo*).

duction of a practical source of ultraviolet light molds and ropes may be destroyed by direct irradiation.

In the second group of applications of abiotic radiation, where semi-direct radiation is resorted to, nurseries may profit by the change in conditions not otherwise possible under the circumstances. Semi-direct radiation is also used in public gathering places such as offices and school rooms. Semi-direct radiation is used to protect occupied areas from direct effects of the lamp.

Indirect radiation finds numerous uses in the ducts of ventilating and air conditioning systems. Lamps placed at points where air is circulating or recirculating allow bacterial control.

Ultraviolet light is a powerful *odoricidal* agent as well as a bactericidal agent. For the destruction of odors bactericidal lamps may be used. This is of importance for refrigerators or other closed spaces where foods are stored since transference of undesirable odors and flavors is a constant source of annoyance. In many manufacturing processes the destruction of obnoxious odors is desired, and may be accomplished by use of short wavelength ultraviolet radiations. Powerfully odoriferous materials are reduced in minutes by radiation from a bactericidal tube or a quartz mercury lamp. For example, substances like chloroform, skatole, ethyl sulfide, and cresol are reduced in olfactory intensity from 2 to 1 in 6, 0.50, 0.25, and 5 minutes respectively.

Other uses of bactericidal lamps are numerous and are increasing rapidly. For example, utensils, glasses, liquid foods, the surfaces of drinks, jams and canned foods, barns and poultry houses, coolers and display cases, surgical and barber cases, containers for foods, solid foods, pharmaceuticals and their containers, and a host of others respond to this method of sterilization. Indirect benefits from the applications of sterilizing ultraviolet radiations will be great.

CHEMISTRY

The observation of substances under ultraviolet radiation provides many advantages over examination in white light. The detection of small differences, with ultraviolet light, is well known to those familiar with its nature. For split second detection of substitutions, adulterations, imperfections, and deficiencies in pure research or in industrial laboratories the ultraviolet lamp is an instrument of increasing importance. Among the many advantages provided by examination of substances in ultraviolet light the detection of small differences is, of course, of primary importance. Of somewhat secondary importance are factors such as the little or no alteration produced in the specimen by this technique; the small amount of sample required for study; the rapidity with which such studies may be performed; and, the absence of intricate or expensive apparatus. It is important to note the small amount of handling required for fluorescence analysis. In many instances the specimen may be examined in its original container.

Although it is not possible to present more than a fraction of the many applications of fluorescence methods to chemistry the wide range and the sensitivity of the simple techniques described here may, it is hoped, lead to greater use of ultraviolet light to augment and/or supplement the more stereotyped examination of substances in white light.

In using ultraviolet light in chemical studies several points should be emphasized. Probably most obvious is the strict standardization of procedure required if results are to be considered at all reliable or reproducible. Although highly purified inorganic salts are usually not markedly fluorescent most technical grade substances are usually fluorescent due to the presence of small amounts of impurities which act as activators. The presence of water in inorganic substances may act as an activator. In a study of 348 pure, thin layered, inorganic substances a slight change in color of fluorescence was produced in 20.5%, on addition of water. In 1927 Petrikaln demonstrated that the fluorescence intensity of quinine sulfate was diminished considerably after intensive drying. The state of dispersion, i.e., particle size, may effect the fluorescence of substances. Reference is made to the chapter on technique and elsewhere for data on procedure in fluorescence analysis.

In 1925 E. Bayle and R. Fabre showed that the curves obtained by plotting the wavelength of the fluorescent light against the intensity of the fluorescent light provide a criterion of purity of the substance being observed. They found that the peaks gradually rise to stable maxima as the impurities are removed from the substance. This may be used with advantage in many studies involving the two factors concerned.

Fluorescence titrimetry depends upon changes in intensity and/or color of a fluorescent substance with changes in the pH of a solution. Heretofore, titrimetry of dark colored liquids such as fruit juices, wines and others has been restricted in some cases and is impossible in others unless special treatment such as dilution is made. However, with the addition of a fluorescent indicator the titration may be carried out in the usual manner under ultraviolet light. Often the sensitivity of fluorescence titrimetry exceeds that of titrimetry in white light with other indicators.

Most frequently used indicators are eosin, fluorescein, acridine, beta-naphthol, umbelliferone, resorufin, phloxine, quinine, naphthionic acids and naphthol sulfonic acids. Umbelliferone may be used as an indicator for titrating in regions just below that of phenolphthalein. One cubic centimeter of an acid solution in 250 cubic centimeters of water may be titrated with 0.01 N. alkali with the change occurring at pH 6.5 to 7.6 with a colorless and then blue fluorescence.

A few particles of fluorescein or quinine on the surface of alkaline and acid solutions, respectively, and illumination with ultraviolet light aid in following the meniscus as well as reading the graduations on the buret with titrations in ultraviolet light.

INDICATORS

Indicator	*Color Change*	*pH Range*
Fluorescein	Colorless to green	4.0 — 4.5
Eosin	Colorless to green	2.5 — 4.5
Umbelliferone	Colorless to blue	6.5 — 7.6
Resorufin	Yellow to pale orange	4.4 — 6.4
Erythrosin	Colorless to green	4.0 — 4.5
Cotarnine	Yellow to white	12.0
Salicylic acid	Colorless to blue	3.0
Dichlorofluorescein	Colorless to green	4.0 — 6.0
Benzoflavine	Yellow to green	0.3 — 1.7
Acridine	Green to violet	4.9 — 5.1
Phloxine	Colorless to yellow	3.4 — 5.0

Fluorescence capillary analysis was described by Danckwortt and Pfau (1933). It consists of the capillary separation of the components of a solution and differentiating these by their fluorescence or appearance under ultraviolet light. The procedure is to fix a strip of filter paper vertically with one end in the solution to be examined. The liquid will be drawn up by the capillary attraction and when the moistened portion is examined under ultraviolet light characteristic zones will be found. The media used consists of strips of spot test paper, used in microchemistry, two or three centimeters wide and twenty to fifty centimeters long. The paper is cut in the same direction, if standard procedure is to be used.

By fixing the strip with one end several millimeters under the surface of the liquid for 24 hours, under highly controlled conditions, records may be obtained and compared with strips prepared with solutions of known composition. The photometer may be used to obtain data concerning the intensities of the various zones and this data plotted. Color and length of the zones are the important features of this method. The solvents used for specimens should be optically inert and non-fluorescent.

Nevertheless, the use of suitable fluorescent solvents often yields results not otherwise obtainable, since in the latter alterations may be produced, which are characteristic of the sample or which produce results more easily observed.

Schlieren, changing regions of refractivity in an otherwise optically homogenous medium, provides a positive means to detect very small differences in refractive index, density, purity, adulteration, and other properties of substances. Schlieren analysis is often used where restricted amounts of samples are to compared, as in microchemistry. De Ment (1936) applied the use of fluorescent substances to Schlieren analysis. The addition of fluorescein in amounts below the threshold sensitivity of the Schlieren reaction made it possible to extend the limits of identification.

Fluorescein, or other such indicator, was added to the static sample and analysis made in the usual way only in a quartz cell and with a quartz pipet. High intensity ultraviolet radiation of short wavelength provided oblique illumination to indicate the movements of the highly fluorescent thread of static sample emerging from the pipet. Both ascending Schlieren and descending Schlieren may easily be seen by this modification.

The *measurement of ionization constants* with the aid of fluorescence was described by J. Eisenbrand (1930). He found the fluorescence intensity of quinine sulfate solution to increase almost linearly with the increase in concentration. The fluorescence intensity was also found to be affected by the absorption of light by the solution according to Beer's Law. The ionization constants of substances such as quinine sulfate, B-naphthol, and methoxyquinoline were determined by the formula:

$$K = \frac{(0.01\ I[OH])}{(1 - 0.01\ I)}$$

The results obtained with this relationship are in good agreement with the determinations by other methods.

Electrographic fluorescence analysis was described by De Ment (1940). It does not utilize any new principle except the use of fluorescent electrolytes and examination under ultraviolet light. It depends on the anodic solution of the metal specimen and the deposition of metal from the specimen onto or into the paper. The procedure is to impregnate paper with a suitable reagent, e.g., quinine-fluorescein solution ($pH = 3.5$), and "fix" the metal in the paper which may then be recognized by its characteristic fluorescence.

The apparatus used consists of (cathode) an aluminum plate placed on bakelite and (anode) the metal specimen. A piece of spot test paper saturated with an inert electrolyte is placed on the aluminum plate and covered with a second piece of paper saturated with the reagent. The specimen is placed on this paper and brought into intimate contact by screwing down a small pressure disc to complete the circuit. After several minutes or more the reagent paper is removed and the paper inspected under ultraviolet light (see table.) Subsequent development with an agent such as hydrogen chloride, gas, ammonium hydroxide, or acetic acid may be required.

Only a "molecular thickness" of specimen is removed by this method. In using the technique it is apparent that the amount of metal deposited in the paper depends on the e.m.f. impressed. With a mixture of metals the least noble metal will go into solution first.

ELECTROGRAPHIC FLUORESCENCE ANALYSIS

Anode	*Fluorescence*
Indium	Deep violet, dull
Thallium	Deep green, dull
Tin	Rose
Ruthenium	Red-brown
Antimony	Whitish

Aluminum may be detected with delicacy by the morin test. In order to test for aluminum in the presence of other metals which give color reactions or precipitations with morin the test solution is precipitated with potassium hydroxide, a drop of the filtrate is acidified on a black spot plate with 2 N. acetic acid and a drop of morin reagent (saturated methanol solution) is added. A green fluorescence indicates a positive reaction.

A modification of greater sensitivity consists of impregnating filter paper with fresh morin solution, drying and treating with a drop of neutral or slightly acid solution of the specimen and drying again. The addition of two or three drops of 2 N.hydrochloric acid produces a green fluorescence in ultraviolet light. As little as 0.005 gamma of aluminum with a concentration limit of one in 10,000,000 may be detected. For large dilutions control tests should be made.

The majority of *arsenic* compounds thus far studied do not seem to be markedly fluorescent. Of these the trioxide and the triiodide fluoresce a bluish-white and a light yellowish-white respectively. The calcium and magnesium ammonium arsenates fluoresce whitish. By modifying the Gutzeit test for arsenic A. A. King found it possible to detect as little as one gamma of the substance. The mercuric chloride test paper used in the Gutzeit test examined in ultraviolet light show a black appearance in regions not otherwise seen in white light.

Metals are usually regarded as non-fluorescent. The surfaces of freshly cleaved metals and elementary materials seem to appear slightly different in ultraviolet light than older surfaces on the same specimen. For example, in observations on 25 elementary substances by one of us (J. D.) differences were noted in metals such as rhenium, thallium, gallium, bismuth, and others. Whether this is due to a small degree of luminescence in the metal itself; to the additive effects of residual violet and blue radiations; to the fluorescence or the additive effect of an oxide or other coating on the specimen; or, to a combination of these is subject to question.

Colorimetric reactions may be carried out with a sensitivity of a much as ten times that ordinarily possible according to J. Grant. This is stated to apply particularly to matchings of sulfide colors produced from metals such as cadium, lead, bismuth, arsenic, and antimony. The colored precipitates produced when *heavy metal ions* react with *calcium carbide* in aqueous solution may be characterized by examination in quartz tubes in ultraviolet light.

The pentoxides of *columbium* and *tantalum* fluoresce with a whitish shimmer in ultraviolet light. Organic salts of *vanadium* are markedly fluorescent and this may be used for purposes of detection and identification.

Rhenium may be detected in small quantities by fluorescence analysis. Tougarinoff (1934) found that 0.01 milligram could be detected by the characteristic fluorescence developed. A yellow-green fluorescence is produced on adding one cubic centimeter of the sample solution to dimethylglyoxime reagent and heating. Dimethylglyoxime reagent is prepared by adding 3 drops of a saturated alcoholic solution of dimethylglyoxime to 3 cubic centimeters of a 25% solution of stannous chloride in concentrated hydrochloric acid.

Beryllium may be detected in minerals by the test of Zermatten (1933). The sample is fused with sodium carbonate and the melt dissolved in 5-normal hydrochloric acid and tetrahydroxyflavanol and sodium hydroxide. A yellow-green fluorescence is produced. In the test of Satoh (1934) the nitride of beryllium with a blue fluorescence is produced by passing ammonia for 4 hrs. over beryllium containing 10% alumina at 1000°C. The only other fluorescent nitrides known are those of aluminum and boron both of which require activation by silicon and carbon respectively. The fluorescence of beryllium sulfide has been examined by Tiede and F. Goldschmidt (1929).

A specific test for *zinc* consists of adding sodium hydroxide to the solution and then acidifying with acetic acid. On adding urobilin to this and examining in ultraviolet light a bright green fluorescence is produced.

Fluorescence analysis may be augmented in some instances provided *statistical analysis* of data is also used. In studies by Izmailov and Schraiber (1939) it was found that harmine, harmoline, and quinine could be determined quantitatively if the results were in the form of curves. The determination of harmine with 2% accuracy was accomplished in solutions of concentrations between $5x10^{-9}$ and $1.5x10^{-5}$%. Accuracy of 4% was obtained in concentrations between $1.5x10^{-5}$ and $2x10^{-8}$%.

Salt formation may be used for identifying metals which often produce non-fluorescent compounds. Eisenbrand found that apoquinine and 6-hydroxyquinoline increase in fluorescence in the presence of certain metallic salts. The zinc, magnesium, and cadium derivatives of 8-hydroxyquinoline are highly fluorescent. Strongly fluorescent solutions are produced when an alcoholic solution of 8-hydroxyquinoline is added to an alcoholic solution of the nitrates of lanthanum, thorium, strontium or magnesium. Alcoholic solutions of cadmium and zinc acetates as well as the chlorides of calcium and lithium produce similar results.

Fluorescence analysis provides a delicate means for indicating the presence of *uranium* and subsequently *radium* should the uranium tests be conducted in minerals since the two are invariably associated in nature. Details on the bead test for uranium may be found in the chapter on *Radio-active Minerals*.

The *rare earths* may be tested in several ways. Bead tests have been used by several investigators. By fusing rare earths with borax or potassium metaphosphate beads phosphors are often produced which fluoresce highly even in large dilutions. Nichols and Howes made observations on the salts of samarium, neodymium, europium, thulium, terbium, dysprosium, terbium, erbium, praeseodymium, and yttrium. Traces of these elements were put into solid solution in various solvents, i.e., calcium oxide, calcium fluoride, borax, sodium phosphate, sodium fluoride, and aluminum oxide. For results of these tests reference is made to the table in the chapter on theory. Other studies by Haitinger included rare earths dissolved in borax or potassium phosphate beads. Great sensitivity was obtained in these studies also (see table).

In studies by the writers rare earth salts were converted into tellurite, salicylate, silicate, citrate, aluminate, and others and examined in ultraviolet light when both wet and dry. Results of these studies indicate that discrimination between closely related rare earth elements is possible provided they are examined in both wet and dry phases where differences often become more apparent.

BEAD TESTS FOR RARE EARTHS

Rare Earth	*Fluorescence of bead (cool)*	*Sensitivity, one in*
Cerium oxalate	Blue	10^4
Europium	Red	500
Samarium	Orange	1000
Holmium	Yellowish	–
Thulium	Lavender	–
Dysprosium	Yellow	1000
Terbium	Yellow-green	5000
Gadolinium	Yellow	100

Studies on the luminescence of thorium oxide activated by rare earths by Wick and Throop (1934) might provide a basis for future methods of detection of rare earths. In these investigations three sets of specimens were prepared, in which thorium oxide contained as activators praseodymium, samarium, and terbium. The concentrations of these varied by known amounts. The specimens activated by praseodymium varied from 1 atom of Pr in 100 molecules of thorium oxide to 1 atom in 100,000 molecules; those activated by samarium from 1 atom in 15.5 molecules to 1 atom in 2000 molecules; those activated by terbium from 1 atom in 10 molecules to 1 atom in 40,000 molecules.

The intensity of luminescence of specimens in each set was measured and the concentration of greatest brightness, the optimum concentration, determined for each of the following sources of excitation: cathode rays, ultraviolet light and hydrogen flame. The results show that the optimum concentration is different for each of the sources of excitation used. In all cases the concentration required for the optimum under cathode rays is less than that for the other methods of excitation used.

The phosphorescence of *ice* has been previously noted by several investigators. According to Armstrong (1924), Sir James Dewar found that pure water frozen is phosphorescent while tap water is not. Precht (1902) suggests that the triboluminescence of ice on cooling may be considered to be a pyroelectric effect or a piezoelectric effect due to molecular changes in sudden expansion or contraction. Studies by Wick (1940) found ice to be phosphorescent at temperatures almost down to the temperature of liquid air. Ice from a cooler was found phosphorescent at this low temperature, as was ice prepared by pouring water into liquid air or by freezing distilled water in an electric refrigerator. Ice at low temperatures was also found to be triboluminescent, emitting a glow when ground in a cold mortar. The intensity of this light is increased by exposing the ice to the light from an iron spark at a low temperature before grinding. The results of this investigation, on a frozen solution of naphtha show the same effects. The water is triboluminescent at a low temperature and this is markedly increased in intensity by exposure to ultraviolet radiations from an iron spark.

J. De Ment (1940) examined specimens of *deuterium oxide* and *deuterium* under ultraviolet radiation, X-rays, heat, and electrical discharges. A five gram specimen of 99.9+% D_2O showed no fluorescence under ultraviolet radiation of wavelengths between 2200 and 4000 A.U. As was to be expected, from its viscosity, a specimen of 95% D_2 was not excited by ultraviolet radiation either. In the same specimens luminescence was not excited by X-rays (83 Kv./20 ma.) or electrical discharges (20–120 Kv./5–30 ma).

As has been discussed in the chapter on theory, the intensity of fluorescence depends on several factors: (I) the concentration of the fluorescent substance in solution, (II) the intensity, as well as the wavelength, of the exciting light, (III) the nature of the fluorescent substance, (IV) the nature of the solvent, (V) the pH and the temperature of the solution, and (VI) the effect of interfering substances present in the solution.

Fluorometry is the measuring of the concentration of fluorescent substances by determining the intensity of the fluorescent light they emit under standard conditions. In some cases the substances to be assayed need not be fluorescent, but may be converted into a fluorescent substance by a suitable form of treatment. In most fluorometric analyses, the intensity of the fluorescent light emitted by a solution of unknown concentration is compared either directly or indirectly with the intensity of the fluorescent light emitted under similar conditions by the same substance in known concentrations. The factors II, IV, V, and VI, should be constant in the comparison of the known and the unknown, if it be demonstrable that a variation of these factors could cause a change in fluorescent intensity. Whenever possible, the interfering materials mentioned in VI should be eliminated by an appropriate chemical procedure. These materials may interfere (1) by fluorescing, (2) by absorbing the exciting light, (3) by absorbing the fluorescent light, and (4) by quenching the fluorescence.

Vitamin B_2 solutions fluoresce yellowish-green when irradiated with blue light with the greatest amount of wavelengths between 4300 and 4400 A.U. In determinations of this vitamin by fluorophotometric methods a special filter is employed to produce pure blue activating light. As a standard; a riboflavin solution of 0.1 gamma per cubic centimeter is used. Comparison of the unknown solution with the standard may be performed by plotting the relationship between the intensity of the transmitted light and the fluorescent light in galvanometer units. Another way is to plot the curve between the concentration of the B_2 standards and the deflection of the galvanometer.

While it is well known that riboflavin occurs in many substances such as are found in foods, medicinals, and others, difficulties may be encountered due to the activity of interfering materials. To avoid this, in cases where these interfering substances are in excess, it is essential to dilute them to a point where they no longer affect the fluorescence. In some cases, ultraviolet radiation does not produce satisfactory results since it produces luminescence in too many substances. More accurate determinations for riboflavin are obtained when exciting light of wavelengths between 4300 and 4400 A.U. is used.

The determination of vitamin B_1 was accomplished fluorophotometrically by Hennessy and Cerecedo in 1939. For assay of this material an ultraviolet filter with a peak of 3700 A.U. is used. In the fluorophotometer the photocell is protected by filters which prevent the exciting light from acting on the cell itself and from wavelengths above 4700 A.U. By use of this filter combination results are obtained in accordance with the Lambert-Beers Law.

Fluorophotometric methods of analysis are applicable to many substances other than those mentioned. Many distinct advantages over the biological methods of assay are possible with substances such as vitamins A, B_6. C, E, nicotinic acid, cholesterol, androsterone, carotene, bilirubin, hemoglobin, porphyrin, oestrin, Nessler's Solution and glucuronic acid when present in other materials. Wavelengths of 5100 A.U. are for the estimation of sulfanilamide.

Certain organic substances may be identified by melting with fluorescein chloride. The procedure is to fuse the sample with anhydrous zinc chloride and fluorescein chloride, the product of which is rhodamine dyestuffs from all compounds containing NH_2—NH— or $N(CH_3)$— These vary characteristically according to the amine used. In testing, a drop of the specimen is evaporated to dryness with hydrochloric acid in a test tube and the residue fused with fluorescein chloride, and twice this amount of anhydrous zinc chloride, on an air bath to 250-260°C. The heating is continued until the zinc chloride just melts. When the melt is cool, it is dissolved in hydrochloric acid and examined under ultraviolet light. The amines may be distinguished according to fluorescence as well as color in white light (see table). The sensitivity of these tests is as low as 10 gamma in the case of glycocoll ester hydrochloride.

FLUORESCEIN CHLORIDE TEST FOR AMINES

		Color	*Fluorescence*	*Limit*
Ammonium chloride	NH_4Cl	Pink	Yellow-green	30γ
Hydroxylamine Hydrochloride	$NH_2OH.HCl$	Pink	Yellow	20γ
Hydrazine sulfate	$NH_2.NH_2.H_2SO_4$	Orange	Yellow	20γ
Methylamine hydrochloride	$CH_3.NH_2HCl$	Red	Yellow	10γ
Glycocoll ester hydrochloride	$\underset{NH_2.HCl}{\underset{\vert}{CH_2}}.COOC_2H_5$	Pink	Yellow	20γ

Fluorescein chloride may be used to differentiate aromatic amines and aliphatic amines. With fluorescein chloride aromatic amines do not fluoresce while aliphatic amines do.

Tetraalkyl rhodamines are formed on melting secondary aliphatic amines with fluorescein chloride. Four gamma may be detected in certain instances, e.g.,

Amine	*Fluorescence*	*Limit*
Diethylamine	Orange-red	4γ
Piperidine	Orange-red	4γ
Aceturic acid ester	Orange-yellow	20γ

The fluorescence of fluorescein was used in 1877 by von Baeyer in an experiment which demonstrates the extent to which the substance possesses this striking property. In order to trace the course of a river fluorescein played a novel role. A solution containing 10 kilos of fluorescein was sunk in the Danube river near its head springs. After about 60 hours the characteristic fluorescence of fluorescein appeared in a small river which emptied into Lake Constance and then into the Rhine river. The fluorescence was detected as long as 36 hours after being placed in the Danube.

In the test of Ekhert a number of organic substances may be identified by using a reagent composed of 10% paradimethylaminobenzaldehyde in sulfuric acid. The procedure is to cover one cubic centimeter of an alcoholic solution containing 0.01 gram of the specimen with one cubic centimeter of concentrated sulfuric acid. The reagent is added to this mixture. By agitating and examining in ultraviolet light characteristic colors appear. For example, benzene fluoresces deep brownish-red, naphthalene a dark greenish-brown, and phenanthrene a greyish blue.

The Voges-Proskauer reaction depends on fluorescence of end-products. If a solution of *protein* is shaken with a small amount of 10% sodium hydroxide solution and a drop of 1% diacetyl solution a green fluorescence is produced. The fluorescence of albumen facilitates examination of eggs. Under long wavelength ultraviolet light solutions of horse serum (protein) fluoresce yellowish-green or yellowish although this may vary according to the specimen.

Salicylates usually fluoresce strongly although the color varies with the type of salt. Salicylates of the alkali metals usually luminesce violet very strongly while heavy metal salicylates may fluoresce green or blue. Rare earth salicylates usually fluoresce bluish under long wavelength ultraviolet light. Methyl and ethyl salicylates fluoresce green and amyl salicylate fluoresces lavender; the organic salicylates of greater molecular weight than these often luminesce violet.

Benzoic acid fluoresces a weak medium-blue color while its salts luminesce to a greater extent in many cases. White to violet fluorescence is shown by most alkali metal benzoates. Both meta and para sodium hydroxybenzoate fluoresce violet shades.

According to Radley and Grant, chemically pure *alcohols* show either a weak fluorescence or else none at all. Where a weak fluorescence is present this usually appears as a violet tinge and may be due to effects from the source of light rather than luminescence. Although this is true to a certain extent for the simpler alcohols it does not hold closely for the higher members. Substances such as menthol and eugenol, which are both alcohols, fluoresce pale greenish and brownish respectively. A number of alcohols luminesce green of varying shades among which are nonyl, alcohol, cinnamic alcohol, citronellol, and some specimens of terpin hydrate.

Formaldehyde may be detected by fluorescence analysis in concentrations as small as 1 part in 5x10^{-5} by the blue luminescence produced when a solution of the specimen in ethanol is added to Tommila's reagent which consists of naphthoresorcinol in hydrochloric acid. With the same reagent *glyoxal* may be detected in concentrations as small as 1 part in 10^{-5} by the bluish-green fluorescence produced.

Feigl, et al., (1935) distinguished the various *dicarboxylic acids* by reactions which produce fluorescent end-products.

Fluorescent end-products are often produced when organic chemicals are dissolved in concentrated sulfuric acid and examined in ultraviolet light. Shades of violet are shown by compounds such as xanthone and dihydroanthracene while substances such as phenazine oxide and anthraquinone fluoresce faint orange. Tones of green are shown by dihydroacridine, xanthene, phenoxazine, and phenazine although phenoxazonium salts do not fluoresce.

Continued crystallization has removed fluorescence from substances otherwise luminescent. Quinine, eosin, anthracene and others, after several score crystallizations, became non-fluorescent although after keeping in air or heating the fluorescence was found to re-appear.

In long wavelength ultraviolet radiations the derivatives of cochineal do not fluoresce markedly. Nitrococcinic acid and coccine appear purple-brown and deep violet, respectively.

Waxes examined by J. Radley (1932) had a characteristic fluorescence and mixtures were often detected by alterations in this characteristic fluorescence. Carnauba wax fluoresced bright yellow color mottled with brown. The fluorescence is so strong, from this wax, that its fluorescence may be detected in chloroform solutions of as low as 1%. This provides a useful means for detecting carnauba wax in mixtures since in solutions it produces a brilliant milky-blue or bluish-violet. Chloroform solutions of most other waxes do not fluoresce intensely and some do not fluoresce at all. Chinese wax fluoresces white with a blue tinge while Japan wax fluoresces ivory. The fluorescence of beeswax is regarded as an uncertain test for purity by E. Kraus (1933). The addition of paraffin or ceresin to beeswax may intensify the fluorescence. Foreign beeswax fluoresces orange-brown; white beeswax fluoresces white with a bluish tinge and English beeswax fluoresces brownish-yellow with a green tinge.

Soaps were examined by the writers. Specimens of pure castile soap fluoresced a bright yellow-white. Shampoo soap samples fluoresced intense blue and blue-green. Saddle soap fluoresced green while cheap handsoaps fluoresced pale blue indicating a preponderance of non-saponified fat. Other soaps fluoresced yellow and blue. Fluorescence analysis aids in detecting impurities and adulterations in soaps. The use of ultraviolet light for accelerated rancidity tests is described by Hagen (1931).

CRIMINOLOGY

In the field of criminology wider use is being made of ultraviolet light. All modern laboratories engaged in legal work and crime investigations are equipped with ultraviolet units. The fact that innumerable substances show a characteristic fluorescence, including parts of the human anatomy and some secretions, offers many possibilities in this field.

Human teeth show a well defined fluorescence and, curiously enough, the fluorescent color of the teeth of the white race differs from that of the Oriental. This holds true even after death and decomposition of the body. The classic story has been told of solving a noted murder mystery in Chicago by the difference in the fluorescence of the teeth of the Oriental. If the teeth have been subjected to considerable heat the fluorescence is destroyed. The cause of fluorescence of the human teeth is not definitely known, but may be due to the mineral apatite which is present in the enamel of the teeth.

The impressions left by fingers contain traces of organic matter, such as oils and fats, which fluoresce under ultraviolet radiations. Finger prints left on multi-colored backgrounds may be difficult to photograph by ordinary means. When dusted lightly with anthracene or some other fluorescent powder, finger prints may be easily photographed under ultraviolet light. In this manner finger prints may be photographed with a sharpness not otherwise possible.

Old scars, tatto marks, which have been removed by chemical means, the lesions of skin diseases, not visible under ordinary light, may be revealed under ultraviolet radiations. Dyed hair can be readily detected if the dye is fluorescent. Various remedies and products sold under trade marked names are sometimes counterfeited. To detect the fraud the manufacturer may add minute amounts of some harmless fluorescing substance. As a means of identfying newly-born babies in hospitals, a form of ' branding" may be done with ultraviolet light, thus eliminating the possibility of confused identity. The slight mark made by ultraviolet light on the tender skin of the infant will remain sufficiently long to eliminate any errors while the baby is confined in the hospital nursery.

Various bodily secretions and excretions fluoresce a characteristic color, and this may be of considerable value in the field of forsenic medicine. Certain drugs are excreted principally by specific organs, hence this may prove of vital importance in proving some point in a legal manner. Stains left on garments may be revealed by ultraviolet light—semen fluoresces a blue-white. Stains left by nasal secretions, pus, perspiration, and the discharge from leucorrhea also fluoresce under ultraviolet radiations. According to C. T. Symons (1930) urine stains fluoresce yellowish, while those due to semen show bluish.

The clothing of a criminal suspect or that of a dead body may reveal numerous valuable clues. The occupation of the suspect may also be revealed by exposure of the clothing and shoes to ultraviolet light. Many inks, paints, varnishes, chemicals, drugs, and petroleum products fluoresce with characteristic colors, and those engaged in handling products of this kind will be revealed by exposing the clothing and hands to ultraviolet light. Moreover, laundry marks on clothing are now frequently printed in bold letters with inks invisible under ordinary light. Fluorescent laundry marks fluoresce under long rays of ultraviolet light, hence can be revealed by any of the "hot" types of ultraviolet units. Sorting of garments thus marked is carried out in the laundry under a battery of ultraviolet lights. The large bold marks stand out clearly. Unmarked cloth may also fluoresce, and serve as evidence in criminology. Fragments of glass, matches, pieces of paper and cloth, and other objects found as clues on the scene of a crime may be compared under ultraviolet light with objects found on the person or property of a suspect. Glass from the headlights of an auto suspected of involvement in an accident has been identified by fluorescence. Fragments of glass may also be found in the clothing or skin of the injured. The ladder in the noted Lindbergh kidnap case was subjected to fluorescence analysis.

Suspected thieves have been trapped by treating paper money with anthracene powder. Minute amounts of the highly fluorescent powder will gather on the hands and clothing of the individual handling the money so treated. Or the floor may be lightly dusted with anthracene and later revealed on the shoe sole of the person passing through the treated room. Anthracene powder fluoresces a strong yellow-green under all types of ultraviolet radiations.

One of the many industrial applications of fluorescence — laundry mark in fluorescent ink, exposed to ultraviolet radiations. (*Courtesy General Electric Company.*)

Some medicinal products, like eye waters, containing hydrastis fluoresce strongly and will be clearly visible under ultraviolet light even after repeated washings of soap and water. Many ointments contain petrolatum or lanolin bases, the former fluoresce bluish and the latter yellowish. On the basis of fluorescence it is possible to distinguish between many ointments which may be used to dress wounds or which may be applied to skin diseases. Traces of ointment may remain on the skin after repeated washings or may accumulate under the finger nails. The well known medicinal ointments—Mentholatum and Ungentine—fluoresce strongly and with characteristic colors. Ointments of this kind are sometimes used on the face in theatrical work where the performers work under ultraviolet light. Stains left by ointments on garments also show characteristic fluorescence.

The use of ultraviolet light in the examination of documents is of great value and the bane of forgers. Firms and individuals who write checks of large size may imprint an invisible water mark on the check. Before the check is passed by the bank the paper is examined under ultraviolet light. If the fluorescing mark is not present the check is a known forgery, no matter how well the signature may be executed. Variously colored inks and marks may be used, and may be changed from time to time. This method of identifying checks has been the means of eliminating large losses to some banks. Blank checks imprinted with invisible fluorescing inks are difficult to duplicate owing to the slight differences in the fluorescence of similar inks and pigments used in inks.

Where revenue stamps, postage stamps, and similar documents are suspected of being forged it is possible to add minute amounts of some fluorescing substance to the printing ink. By this means counterfeit can be readily detected no matter how perfect the spurious engraving may be. Different lots of inks vary in fluorescence hence it becomes possible to determine if the signatures on documents were all made with the same or different inks. This is sometimes of importance in legal work. Erasures made by chemical or mechanical means can also be detected under ultraviolet light. Chemical substances used in bleaching an ink will also change the fluorescent color of the paper or leave a stain which will fluoresce. Mechanical erasures rarely completely remove all the ink, enough will generally soak into the paper to become visible under ultraviolet light. Photographs made of altered or forged documents by ordinary and ultraviolet light for comparison purposes may be of considerable value as legal evidence in court. In photographing the document under ultraviolet light, it is not damaged in any manner; it is not even necessary for the photographer to touch the document. In examining documents, both long and short wave ultraviolet units should be used with the proper filter for each unit. Old parchment documents of historical interest often reveal as many as three different writings, one over the other. Sheepskin and parchment paper was at one time costly, so it was often the custom of writers to salvage old "paper' 'by erasing previous script.

Paper money used as payment for ransom, blackmail, or for the purchase of narcotics by police agents, may be first imprinted with an ink invisible under ordinary light. Inks containing minute amounts of some fluorescing uranium salt would prove advantageous as these show the characteristic yellow-green fluorescence under any ultraviolet unit. For special purposes activated calcium tungstate may be used to produce fluorescence in the ink, and would react only under short wavelength radiations. Fluorescing substances may also be incorporated in the paper during the manufacturing process. Special papers of this kind are difficut to duplicate and may be used for valuable documents like bonds, insurance policies, and other papers of value which are subject to counterfeiting, alteration, and forgery. The possibilities in this field are numerous, yet full advantage of this has not been taken. Watermarks on paper often exhibit a characteristic fluorescence, which may vary in different lots of the same quality paper from the same manufacture. Paper pulps bleached by different methods will also differ in fluorescence. Watermarks applied to paper by means of a stamp using an oily or waxy substance usually fluoresces strongly in contrast to the remainder of the paper. Watermarks made by a roller impression before the paper is finally dried do not fluoresce as clearly and strongly.

Many substances have been utilized for the purpose of writing messages invisible in ordinary light. Prisoners are often ingenious in devising means of sending out messages in an ordinary letter which can be read only under ultraviolet radiations. As invisible inks such substances as saliva, vinegar, salt water, fruit juices, milk, tea, soap-suds, urine, and other body excretions have all found use. All these substances fluoresce enough to render the writing visible under ultraviolet light.

Various glues, adhesives, and sealing waxes differ in fluorescence. Letters or parcels which have been opened and resealed with a different adhesive can be detected through the difference in the fluorescence of the sealing substances. Sealing adhesives with a dextrin base fluoresce distinctly, while the gum arabic adhesives show only slight fluorescence. Pastes with a starch base fluoresce bluish. Glue made from waste animal matter fluoresces strongly. Casein glues fluoresce bluish. Sealing waxes which appear identical in color under ordinary light often show marked color differences under ultraviolet light. Valuable sealed parcels which have been opened and cleverly resealed, may be revealed by the addition of a different sealing wax.

An interesting application of fluorescence was suggested by Dake (1941). By use of highly fluorescent pigments *tattoo marks* could be made. These marks, in ordinary light, would be invisible but under ultraviolet light would show to a striking degree since ultraviolet light would penetrate the skin enough to excite the pigment. The applications of this might be numerous and significant. For example, in criminology and related studies fluorescent tattooing would present definite advantages.

FLUORESCENT LIGHTING

For centuries man has been familiar with the "cold light" emitted from the firefly and other forms of life, but it has been only within the past seventy-five years that investigators have been enabled to account for the cause of certain phosphorescences in living creatures. For over a quarter of a century, E. Newton Harvey of Princeton University has studied the "living light" emitted from various forms of land life and fish. In 1926, Harvey called attention to the fact that "animal light" is not essentially different from ordinary light, except in its mode of production. This difference is expressed when we term animal light as "cold light" or a luminescence. The electric light bulb is a "hot light" or an incandescent.

While superior to the old-fashioned kerosene lamp and the Welsbach mantle, the incandescent light globe has many disadvantages. Unfortunately about 98% of the energy consumed by the incandescent lamp is radiated in the form of heat, and only 2% emitted as visible light.

Hence it will be seen that incandescence is not an economical way of producing light because it is impossible to obtain visible light rays without heat. Luminescence, or cold light, consists only of visible light.

During the past twenty years numerous workers have studied the possibilities of utilizing some form of cold light to replace the incandescent tungsten filament electric light. With the recent development of the fluorescent lighting tube, the incandescent light globe will go the way of the old-fashioned gas lamps. While the efficiency of the modern fluorescent tube has not reached that of the firefly, the new lighting tubes operate practically as cold lights and consume much less energy in proportion to the light emitted when compared to incandescent light sources. Often a 15 watt fluorescent tube will give a more efficient light where formerly a 100 watt incandescent bulb was required. The fact that the new fluorescent ligthing tubes operate practically cold renders them invaluable for many lighting purposes in addition to the economy factor.

It is of interest to note that as early as 1912, W. S. Andrews devised an experimental vacuum tube for testing the fluorescence of various substances. The principal of the fluorescent tube used by Andrews is identical to that of the modern fluorescent lighting tube. Unfortunately the practical applications of this tube were not realized in 1912.

The modern fluorescent lighting tube is a mercury vapor tube generating ultraviolet radiation through the ionization of gases. The inside of the glass tube is coated with various artificial minerals and chemicals, which fluoresce by the ultraviolet radiations generated within the tube. The light emitted is from the fluorescing substance. Two small tungsten filaments, one at each end of the tube, serve to "start" the ionization of the mercury vapor. Once the contained mercury vapor becomes ionized, the small tungsten filaments cease to glow. A small "choke" coil is used as an auxilliary unit. The fluorescent lighting tube can be operated in the same fixture used for the germicidal tube, widely used as a bactericidal unit.

In the development of the fluorescent lighting tube, considerable difficulty was encountered in obtaining a suitable substance to coat the inside of the tube. At the outset, powdered fluorescent minerals were used, but finally artificial activated minerals and chemicals were found more uniform and reliable. Fluorescent lighting tubes are available in a variety of colors in addition to the "daylight" tube. A tube coated with calcium tungstate (scheelite), for example will glow blue, while a coating of zinc ortho-silicate (willemite) will yield green Other colors are easily possible, and a mixture of various chemical powders produces a "daylight" tube.

MEDICINE AND BIOLOGY

In the medical and biological sciences numerous studies have been made pertinent to the possibilities of ultraviolet light as a tool for solving problems which do not respond to the other methods of investigation. In medicine and its related sciences, as in chemistry, applications of fluorescence in ultraviolet light are, at present, relatively small. It is hoped that greater applications of luminescence will be made since present indications are that procedures described herein may lead to more definite and specific conclusions of diagnostic value in medicine than by many of the other methods now favored.

Probably the teeth fluoresce more intensely than any other external part of the human body. In health, teeth fluoresce an intense bluish-white although they may have a greenish or yellowish-white tinge. In older persons with defective health the fluorescence shifts into the longer wavelengths, i.e., becomes reddish.

The teeth of oriental races tend to fluoresce a yellow-white and in some instances this may be used to discriminate between bodies since fluorescence of teeth continues after death. Porcelain teeth are discussed in the ceramic section. The teeth of some individuals phosphoresce under short wave radiations of ultraviolet.

The *eye* is markedly fluorescent. This was noted in 1896 by Helmholtz and later by others. The eye was noted to fluoresce by Roentgen soon after his discovery of X-rays. Some investigators regard the fluorescence of the eye as a protective mechanism to change injurious ultraviolet light or X-rays into harmless visible light, i.e., fluorescent light and emit it in that form. Under high intensity sources of ultraviolet light of short wavelength the fluorescence color of the eye, in living subjects, appears to be a medium bluish color with greater intensity when the eye is normal to the beam than when the eye is at right angles to the beam. Isolated portions of the cornea and sclerotic coat fluoresce a bright blue and regions of the cornea fluoresce yellowish or green. The fluorescence of the eye during different states of disease has not been studied to any great extent.

Skin deficient in pigment is more fluorescent than highly pigmented skin. Untanned areas of the skin often fluoresce a bluish-white or blue color while tanned regions do not fluoresce. The skin of persons belonging to the white race fluoresce although members of the black race usually do not. The harder portions of the skin, e.g., calloused regions, fluoresce more than do softer portions except fatty tissue. Scars, pigment spots, lacerations, abrasions, and traces of skin diseases, as well as deposited chemicals, may usually be seen under ultraviolet light. In fact any conditions which alter the character of the skin cause a variation in appearance under ultraviolet light. The contents of the sweat glands, especially if filled with acnaceous matter, fluoresce yellowish-green. A considerable difference, however, in the fluorescence of the contents of sebaceous glands on the same skin region is reported by one investigator. The glands studied contained material which fluoresced an intense yellow; a yellow-green; red; pink; and in a small percentage the plug fluoresced red on the base and yellow on the upper end. Pale blue and greenish fluorescence were also noted.

Since erythema patches on persons of the white race appear dark in ultraviolet light, and are white on persons of the dark races, it is possible that the dosage of radium and X-ray may be estimated by fluorescence methods. Studies by Goodman (1928) indicated this. The fluorescence of scars due to burns by X-ray and radium has been noted by several investigators. In one case studied by E. B. Knerr (1937) numerous pearly-white fluorescent patches were scattered over the back of hands and fingers which had been injured by X-rays as early as fifteen years previously. These scars were also the result of frequent slight exposures to X-rays over a period of years although they had not progressed through the skin. Other instances of fluorescent scars due to X-ray injury are known to be of greater age than the case cited.

A limited amount of work has been done on the fluorescence of the serum of the blood by O. Reche (1931). Reche terms the examination of sera under ultraviolet light *fluorescence serology.* It was found that the blood-group determined the shades of greyish-blue and greyish-green fluorescence although no particular intensity was noted in the fluorescence spectra from the sera of healthy persons. In studies on over one-hundred cases Reche found the color and intensity of fluorescence to vary considerably according to the nature of the disease. Of importance is that different thicknesses of the same serum specimen fluoresced with different colors. Although no correlation between the colors of the different thicknesses of sera was found, it is possible that this method may be used for diagnostic purposes. A check is obtained by the variation in fluorescence color for various thicknesses of sera examined (see table).

FLUORESCENCE SEROLOGY

Modified, after O. Reche

Serum from	1 *mm.layer*	*7mm. layer*	$\Delta\lambda$ *for a change in thickness*	*Intensity*
Syphilis	Yellow	Yellow-green	<	Bright
Gastritis	Yellow	Yellow	≅	Bright
Influenza	Yellow-white	Brown-grey	>	Dull
Rheumatism	Blue-grey	Violet	<	Bright
Nephritis	Yellow	Yellow	≅	Dull
Arteriosclerosis	Blue, light	Blue-green	>	Bright
Aortitis	Blue, light	Brown-grey	>	Bright

Since fluorescence of blood sera is not due to the presence of foreign material in the blood but to changes induced in the sera through disease processes it is possible that fluorescence serology may have great possibilities in warning of impending disease. The fluorescence of uranine is not changed on addition of sera from healthy men but it is reduced in intensity on addition of sera from carcinomatous persons.

Blood corpuscles may often be discriminated by their appearance under ultraviolet light. This is particularly augmented if fluorescent dyes are used and examination is made with the luminescence microscope. Two varieties of leucocytes are visible under ultraviolet light. In one, a granular leucocyte, there is a fairly intense fluorescence, in the other, a transparent leucocyte, there is a weaker fluorescence. In both the nucleus appears dark. For identification of blood stains by fluorescence methods see the section on criminology.

By staining tissues with fluorescent chemicals (dyes), detail is often brought out that is not visible by other methods. The tissues of animals as well as the tissues of plants respond to *fluorochromes* (see table) in the same way that they respond to ordinary dyes.

TABLE OF FLUOROCHROMES

Berberine sulfate
Chelidonium
Chrysorubine
Coriphosphine O
Geranine G
Geranine S
Neutral red extract
Fluorescein
Rosol red
Rhodamine 6G
Thiazol yellow
Thioflavine
Trypaflavine
Phosphine 3R
Primuline yellow
Esculin

Pontachrome blue-black R (with aluminum mordant)
Dimethylglyoxime (with rhenium mordant)
Tetrahydroxyflavanol (with beryllium mordant)
8-Hydroxyquinoline (with zinc or cadmium mordant)

Various tissues have been studied by fluorescence methods. Examination of unaltered specimens does not ordinarily yield as much information as tissue which has been treated with fluorochromes. Glandular tissue is markedly fluorescent, e.g., suprarenal tissue fluoresces deep orange-red color and thyroid tissue fluoresces a red-grey color while testicular tissue appears grey-red under ultraviolet light. Finger nails usually fluoresce bluish-white, becoming more fluorescent with short wavelengths. Fatty tissue fluoresces a bluish-white color. Studies by Haitinger and Hamper (1933) were particularly augmented by the use of fluorochromes. For example, these investigators stained tissue specimens with a solution of Thioflavine-S (which fluoresces blue in neutral solution) and obtained blue fluorescence for fat cells, cell nucleii, and medullary layers. Shades of yellow were noted in muscle tissue and collagen cells. The fluorescence of brain tissue has not been studied extensively although C. van Ledden-Hulsebosch considers it possible to discriminate between perception and emission centers by fluorescence.

The presence of *hematoporphyrin* appears to be the cause of red fluorescence in certain tumors and urine according to the studies of Policard (1924). E. Derrien and Turchini (1924) found the red fluorescence produced in the Harder glands of rats, abscesses, amniotic fluid of sheep, keratin, and quills of animals due to porphyrin. By plotting the pH-fluorescence-intensity curve, it is often possible to identify the exact porphyrin according to H. Fink and Hoerburger (1931) who examined some 34 porphyrins by this method. In these studies it was found that the fluorescence intensity is a function of the constitution and is independent of outside influences except in the case of halogens.

Dermacenter andersonii, Rocky Mountain wood tick, fluoresces according to E. B. Knerr (1937). Under ultraviolet light the tick has a bright diamond-shaped fluorescent spot on the dorsal surface. Other organisms such as Pediculus pubis (adult and nit) fluoresce. Trichophytosis (ringworm) may be detected from similar afflictions of the skin by its characteristic fluorescence. Other human parasites are known to be markedly fluorescent. The practical application of this may have diagnostic value.

Extensive work on the luminescence of animals (bioluminescence) has been performed by E. N. Harvey. According to Harvey (1919) a survey of the animal kingdom discloses at least 36 orders containing one or more forms known to produce light and several more orders containing species whose luminosity is doubtful. It is likely that recent study has raised this number. In the plant kingdom there are two groups containing luminous forms. The chapter on *Types of Luminescence* contains additional information on bioluminescence.

Chlorophyll was one of the first substances studied for fluorescent properties. This substance, green under white light fluoresces a deep red under ultraviolet light, in most cases. Some samples of commercial chlorophyll do not fluoresce and this appears to be due to the replacement of magnesium with other elements to make the material better suited for the preparation of tinctures and solutions. *Phaeophytin,* the hydrogenated derivative of chlorophyll has the same red fluorescence as chlorophyll. The continued exposure of chlorophyll to ultraviolet light will cause the fluorescence to disappear. De Ment (1940) obtained an intense blue-green fluorescence in one sample of commercial chlorophyll after long exposure to alpha rays from radiothorium. A. Dusseau (1930) attempted to correlate the fluorescence color of chlorophyll extracts from wheat with the nature of the species.

Chlorophylls and polychromoproteins have been studied by M. Fontaine, et al. (1931). C. Dhere (1934) found pyocyanine hydrochloride solution to dissociate into a free base which has no fluorescence while solutions in chloroform have a yellow-green fluorescence. Reduction of the free base with sodium hyposulfite in the presence of zinc powder produces a substance which fluoresces.

In 1940 Najjar and Wood noted a specific reaction in urine which was apparently dependent on the store of nicotinic acid in the body. When urine was absorbed on zeolite and eluted with potassium chloride, the eluate on treatment with caustic soda developed a bluish fluorescence. Although the cause of this bluish fluorescence was not ascertained it could be measured by the fluorophotometer. After the ingestion of nicotinic acid the excretion of this substance increased. This led to the suggestion that in *pellagra* the excretion of this material might be diminished or absent and the quantity of this substance excreted in the urine, might serve as a measure of the deficiency of nicotinic acid.

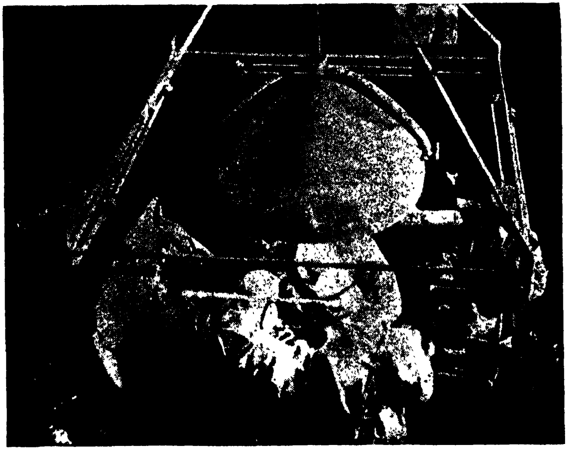
In 1941, Najjar and L. E. Holt, jr. studied typical pellagric patients. They found two fluorescent compounds in the urine. Both provided criteria by which to recognize states of nicotinic acid deficiency. In one, a normal substance disappeared which ordinarily produced fluorescence on alkalinization. In the other, an abnormal substance appeared and did not require this treatment to produce fluorescence. It is interesting to note that fluorescence was expressed by them in Najjar-Wood units, one unit being the fluorescence produced by 1 microgram of quinine sulfate dissolved in dilute sulfuric acid.

Fluorescence methods are particularly applicable for the precise determination of vitamins. C. F. Poe (1940) used the fluorophotometer (see the section on chemistry) for studies on the vitamin content of foods to determine the requirements for military use. In these investigations determinations were made in an effort to ascertain whether dried foods contain as much vitamins as fresh foods, a fact which, if established, would be of economic as well as military significance.

Most *suturing material* is markedly fluorescent under all wavelengths of ultraviolet light. Specimens of sutures examined in their original containers under long wavelengths fluoresce intense blue-green to pale yellowish-white. Kangaroo tendon has a pale yellowish-green color; "silkworm-gut" fluoresces strong blue-green; horse hair is practically void of fluorescence; catgut fluoresces bluish-white to yellowish-white while chrome gut fluoresces a strong amber color. The age, source, processing, and manufacturer determine the fluorescence of suturing materials. These facts are of significance for medico-legal studies and toxicology.

The use of short wavelength ultraviolet radiations has been suggested for the dissipation of accumulated static electricity on microtomes (L. E. Griffin, 1939) This is to prevent adhesion between sectioned specimens which, otherwise, is a source of annoyance to the operator. This method has been used with excellent results for the dissipation of static electricity on glassware by other investigators. Many possibilities lie in the practical application of this fact.

Luminography is the photography of fluorescing objects with an ordinary camera. In certain cases it presents advantages over the other procedures possible to use. Luminograms of tissues and biological specimens are particularly useful since many structures are visible in ultraviolet light which are not visible in ordinary light. Some micro-organisms show structures under ultraviolet light which are invisible in ordinary light. For paleontology and related fields luminograms provide convincing evidence to augment more stereotyped procedures when investigations are presented for the first time. An application of luminography is for studies on the nature of the surface of highly polished metal, wood, or plastic. For the detection of flaws as well as determination of their configuration fluorescence methods are suggested. At present, radioactive greases are used to radiographically detect discrepancies in highly polished surfaces. A more practical technique seems to be with the use



Westinghouse Sterilamp installation over an operating table in the Duke University hospital. Photo during an actual operation on the lung of a tubercular patent — an operation which lasted over one hour.

of intensely fluorescent greases (which may be either drying or non-drying) in ultraviolet light, the results of which may be photographed by an ordinary camera.

Bactericidal ultraviolet lamps are being rapidly installed in hospital surgeries. The accompanying illustration shows a typical installation of eight ultraviolet units arranged in pairs, one pair to each side of a square, and operated prior to, during, and after the operation, producing a safety screen of sterilized air around the patient and surgeons. Late in 1936, more than 200 operations were performed under these radiations. In a certain type of operation, 34% of the patients developed infection from pathogenic bacteria in the air. Four per cent of these died. After the ultraviolet units were installed no infection resulted from this particular type of operation.

MICROSCOPY

The application of both ultraviolet light and luminescence has directly aided man in seeing objects in more minute detail and with more exactness than would have been otherwise possible. Of the forms of microscopy both fluorescence microscopy and ultraviolet microscopy depend on fundamental principles not obtainable by other agents. The application of luminescence to electron microscopy has directly aided in development of this method of investigation, the tremendous importance of which has not yet been fully realized. The applications of luminescence to ordinary microscopy have not been as extensive.

Perhaps the use of stains such as eosin or fluorescein in histological work might be considered an application since these substances owe their color in part to fluorescence under visible light. Little application of luminescence or ultraviolet light has been made to ultramicroscopy atlhough it seems apparent that this field might profit considerably if such applications were made. Microscopy with polarized ultraviolet light has been only scantly investigated and little reliable data has been obtained.

Fluorescence microscopy consists of the observation of fluorescing substances with a microscope. The fluorescence microscope furnishes a means for studying all substances which fluoresce. Illumination is the distinguishing characteristic of this form of microscopy, an iron or carbon arc or other source of ultraviolet light being used for illumination of the specimen. In this instrument all visible light is eliminated from the field. This is done by means of two cells, one with quartz windows containing a 25% copper sulfate solution, in water, to cut off the visible red and infra-red radiations. The other, having special ultraviolet transmitting properties but which absorbs the yellow, green, and blue and containing a dilute solution of p-nitrosodimethylaniline to eliminate the violet. The cells, however, may be substituted by glass filters such as number 986 or others described elsewhere herein.

The other elements in the illuminating system are the same as used in ordinary microscopy except that the lenses are made of quartz, which is transparent to ultraviolet radiation. The substage condenser and collective lens at the light source are both of quartz and since most instruments are used in a vertical position a quartz prism is used. In order to focus the ultraviolet light in the condenser a uranium glass screen (Corning Glass Co. number 375) is placed at the iris diaphragm. This screen, in fluorescing, indicates that the condenser is receiving ultraviolet light. For studying specimens the uranium glass screen is removed.

In examining objects for fluorescence it is necessary to mount them on a special quartz or Corex glass slide (Corning numbers 791 and 970) since these transmit ultraviolet radiations and do not fluoresce themselves. The ordinary cover glass is used as well as the ordinary glass objectives and oculars. These glass elements fluoresce to some degree themselves as does the human eye. To prevent this a special absorbing glass is mounted in the eye cap. With the aid of this absorbing glass a dark background is established and the effects of fluorescence are greatly enhanced.

For fluorescence microscopy with reflected ultraviolet light the cover glass should obviously be transparent to both visible and ultraviolet light and should not fluoresce under the latter. In this form, light of high intensity is required although with an advantage over microscopy by transmitted light since it reduces transmission of the ultraviolet light through a lens system. Chamot and Mason (1930) described fluorescence microscopes with dark field illumination. In these the object is self-luminous against the dark background and minute details appear brilliantly contrasted. The results are superior in many ways to those obtained with transmitted ultraviolet light.

Ultraviolet microscopy differs from fluorescence microscopy in that resolution is due to the short wavelengths of ultraviolet light and not to luminescence of the specimen. Reviewing the capabilities and limits of the microscope, the word "resolution" stands out as most important. Since resolution is the distinct separation of two small details in structure, it follows that all other qualities of a microscope are useless without this prime factor. High magnification is useless if not accompanied by a proportionate high resolving power. This is determined by the numerical aperture of the objective and the wavelength of light used for illumination,

$$R = \frac{\lambda}{2\ \mathrm{N.A.}}$$

The numerical aperture, or N.A. of an objective is limited by several factors. The most important are the focal length and angular aperture. In reducing the focal length of high powered objectives to 1.9 millimeters the practical limits are reached since some working distance must be allowed. Aperture angle is widened to approximately its greatest degree by use of immersion oil between the objective lens and the object. Therefore, there is but one element possible to change . . . the wavelength of light. As may be seen from the formula, the shorter wavelength of light the greater the resolving power.

In the use of short wavelengths two serious obstacles are present. In one, the finding of a material with the necessary physical characteristics that will allow it to be made into a lens passing ultraviolet light with sufficient intensity; the other, the difficulty of focusing an invisible beam.

In an older form of ultraviolet microscope the cadium line at about 2750 A. U. wavelength was used. It gave vastly superior resolution to the best microscopes using ordinary light. Although it remains the best ultraviolet microscope its chief drawback consists of the requirements of special quartz lenses to cut off the line at 2750 A.U. and the use of photographic plates with the focal distance obtained by interpolation of values obtained with two plates exposed at different distances. The latter procedure is both expensive and time consuming.

A newer instrument using wavelengths of 3650 A.U. gives resolution of from 12% to 19% better than that obtained with visible light microscopes. A mercury-quartz lamp is used as the source of light and heat resisting glass filters are used to cut off undesirable wavelengths.

The optical system is of glass and is corrected to focus in the visible regions for wavelengths at the same point but of 1800 A.U. less wavelength. Therefore, focusing is positive and in the visible while results are obtained in the ultraviolet and are recorded on one plate without interpolation. As is apparent results are obtained by photographic means.

Electron microscopy overcomes limitations in resolving power due to the wavelength of light. Instead of visible light or ultraviolet light the electron microscope uses electronic radiation of wavelengths as low as 50 A.U. and, at present, giving magnifications of almost 200,000 diameters as contrasted to the 2000 diameter limit of visible light microscopes and the 5000 diameter limit of ultraviolet light microscopes. There are indications that electronic radiation of less wavelength may be developed, for example, 0.01 A.U. and with such magnification will probably photograph molecules.

The development of the electron microscope involved the direct use of luminescence. Since electronic radiation is not visible to the eye fluorescent screens were used to render the effects visible. These screens were usful for experimental work in both focussing and specimen tests. A fluorescent screen at the point of focus allows the human eye to see in great detail the shadow cast by the specimen in the path of the beam of electrons. In some instruments the final image is 3½ inches in diameter. By replacing the fluorescent screen with a photographic plate a permanent image is obtained.

The available magnification, with no loss in resolution, is possible with electron radiation as given by

$$\lambda = \sqrt{\frac{150}{V}}\ \text{A.U.}$$

This means that electrons produced at 150 volts will have a wavelength of one A.U. while electrons produced at 40 kilovolts will have a wavelength of 0.062 A.U.

MINING AND PROSPECTING

Probably the first application of ultraviolet light, on a commercial scale, in the field of mining, was made at the Franklin, New Jersey zinc mines. One of the important zinc minerals, willemite, fluoresces a strong green; while the gangue mineral calcite, associated with the zinc ore fluoresces a strong red. The ore from the mine workings is passed under ultraviolet light units, where the waste material is separated from the milling ore by hand picking. The Franklin, New Jersey zinc mines also use the principal of fluorescence in the milling of the ore. The tailings from the jigging and flotation operations may be quickly tested to observe if the proper recovery of ore is being made. In the mine workings, portable ultraviolet light units are used in exploration work to gain some general idea of the character of the mineral bearing strata.

One of the most recent and valuable applications of ultraviolet radiations in the field of mining, is the prospecting, mining, and milling of the important tungsten mineral scheelite. Practically all the scheelite found at various localities in the United States fluoresces a strong and characteristic blue color. By the use of portable ultraviolet light units, numerous deposits of scheelite have been discovered in the southwestern part of the country. Prospecting for scheelite is carried on at night; when outcroppings may be quickly and accurately traced, old ore dumps sorted, and placer sands examined for tungsten.

Scheelite is frequently intergrown with other ore minerals and gangue material, which renders it difficult to detect the tungsten by visual examination. By placing the sample under the proper ultraviolet radiations, even small amounts of scheelite can be easily noted. Scheelite is also traced in mine workings by the aid of portable ultraviolet units. After some experience, and comparison with samples where the tungsten content has been determined by assay methods, the mine operator will be enabled to judge specimens with surprising accuracy under ultraviolet light. Sampling a mine working by the ordinary chemical assay methods is slow and costly. A portable ultraviolet light unit in the hands of an experienced operator will yield accurate data upon which to base mining operations. Wherever scheelite is mined, ultraviolet units are freely used.

In the recovery of scheelite from the ore, various mechanical means are used to separate the tungsten from the waste material. The crushed ore tailings are frequently tested to note if proper recovery is being made. The test of the tailings made under ultraviolet is accurate and enables the mill operator to watch the process closely. Minute fragments of scheelite, mixed with waste material, will stand out in glaring contrast under ultraviolet radiations.

All tungsten minerals do not fluoresce, but scheelite, a calcium tungstate, is one of the most important tungsten minerals. Scheelite fluoresces only under radiations shorter than 2900 A.U., hence cold quartz tube types of ultraviolet light units must be used. Scheelite fluoresces a pale blue color under the open cold quartz tube, but if the unit is fitted with Corning filter number 986, the characteristic strong blue will appear. Cupro-scheelite and powellite are tungsten ores which show marked fluorescence, but are of minor commercial importance. In testing ores for the possible presence of some fluorescing tungsten mineral, a freshly broken surface should be examined.

Pitchblonde (uraninite), the commercial source of radium does not fluoresce, but the mineral may be coated with alteration products (secondary uraninites), which may fluoresce a strong yellow-green or blue-green. Hence any sample of suspected pitchblende which fluoresces in this manner should be examined by other methods for radioactivity. Some secondary uraninites fail to fluoresce.

The primary uraninite ores found at depth in the well known pitchblende mines of Great Bear Lake, Canada, are beyond the zone of oxidation and fail to show the presence of any fluorescent alteration products. The ores which are found nearer the surface and the ores on the storage dumps all develop coatings of some fluorescing secondary uraninite. The reader is referred to a separate chapter on The Radioactive Minerals for a list of secondary uraninites which show fluorescence under ultraviolet light.

W. G. Leighton (1935) has described a method by which small amounts of mercury may be detected in a sample of ore, by an indirect fluorescent means. The sample to be tested is powdered and heated strong over a Bunsen burner or similar source of heat. During heating of sample an ultraviolet light source is placed close to sample, and a willemite coated screen is placed on opposite side of sample. The mercury in sample is volatilized and causes a dense shadow to appear on the willemite screen. Without the presence of volatilized mercury the willemite screen will fluoresce a uniform strong green over the entire surface. Ordinary smoke has little. effect upon the willemite screen, but mercury vapor appears as a dense black cloud of smoke against the screen.

It is stated that the willemite screen test for mercury will detect quantities as small as .001% of mercury in an ore. The method also finds applications in testing the atmosphere of a room for the possible presence of mercury vapor. Willemite coated screens are available from supply houses, listed elsewhere. An anthracene coated screen appears to be as effective as willemite.

In the petroleum industry fluorescence analysis may be applied to crude petroleum and its refined products to determine grade and purity or to identify the specific zones or horizons from which the well are producing. In one unique case, that of the mercury deposits at Skaggs Springs, California, the ore consists mainly of meta cinnabarite disseminated through a matrix of porous sandstone. The mercury mineral is intimately associated with curtisite, a highly fluorescent hydrocarbon; the curtisite appears to vary in percentage in proportion to the amount of mercury present. Hence, the curtisite is followed in the mine workings by the use of ultraviolet light, and rich ore may be separated from the lean and waste material.

As an aid in correlating oil bearing sands, fluorescence analysis is finding numerous applications. John Melhase (1935) was one of the first to call attention to the possibilities of fluorescence analysis in the petroleum industry. According to Melhase the fluorescent properties of crude petroleum may serve as a means of correlating oil sands in certain of the California oil fields. It is believed that the new technique will augment, if not replace, the old methods of correlation now in use, such as the study of micro-fossils and mineral fragments present in the oil-bearing formations. Royer states that it is possible to distinguish anthracite and graphitic rocks from bituminous and carboniferous rocks by means of fluorescence.

All natural petroleum oils fluoresce when subjected to ultraviolet radiations ranging between 2,000 and 3,800 A.U. Melhase (1935) tested petroleum oils from numerous California fields, and found a marked difference in the fluorescence of oils from different fields and different horizons in the same fields. No two oils fluoresced in an identical manner unless derived from the same oil-bearing sands.

It follows, therefore, that when a well is drilled in any particular field and samples from each of the oil-bearing sands penetrated and subsequently tested and classified, the record becomes an index for that field. The classification, of course, being performed by fluorescence analysis. When subsequent wells are drilled the new samples are compared with the index and correlated accordingly. Neither the gravity of the oil, the percentage of water or mud present, or the manner in which the sample is obtained has any effect upon the fluorescent properties of the oil.

PHARMACEUTICALS

Studies on pharmaceuticals are particularly augmented in many cases if observations are carried out in ultraviolet light. The examination of specimens in ampules may be restricted by the transmission characteristics of the glass when it is impossible to remove the material from its container for more adequate observation. Effervescent salts, mixtures, masses and other solids are studied by the methods used for minerals or chemicals. Cordials, wines, elixirs, fluid extracts, tinctures, waters, and such solutions may be examined as obtained or after heat treatment or separation of components by capillary analysis (see section on Chemical Analysis).

Tablets and masses likely to be composed of several solids are tested by placing in solution and separating the fluorescent components by capillary analysis or by the other procedures possible. Many substances used in medical work do not fluoresce markedly when dry or in the solid state but in aqueous solution, which may be of relatively high pH or relatively low pH, or heated, luminesce.

Ointments composed of petrolatum or other bases, normally fluorescent, may be melted and centrifuged while in the liquid state or separated by the capillary method (when molten) into one or more fluorescent substances other than the vehicle. By dissolving the ointment in solvents which do not fluoresce and examining the residue after evaporation, fluorescent materials are often revealed. Aqueous acid and alkaline fractions of ointments allow detection of certain substances, e.g., quinine in the acid fraction and salicylates and mercurochrome and related substances in the alkaline fraction. The absence of luminescence in either fraction at a specific pH may suggest the presence of certain others (e.g., table of fluorescent indicators, the color of which changes with a change in pH) such as caffeine and theobromine. Studies on waxes, petrolatum, oils, and other substances used as ointment bases aids in detection and assay of unknown specimens. The application of reagents, directly to the various zones on a capillary strip, allows studies otherwise prevented by interference of substances which quench or mask fluorescence.

Since many alkaloids and organic poisons are prepared in tablet form for therapeutic use and hence contain a vehicle such as milk sugar and/ or a binding agent caution must be used in examining these materials unless they are known with certainty to be as represented. Characterization of alkaloid specimens is sometimes possible by the fluorescence from binding agents, vehicles, or solvents, and impurities in the active substance itself. Also, due regard should be given the possibility of admixture with the same drug but from a different source or of different processing.

LUMINESCENCE OF DRUGS

(*R. Heller*) .

Weak	*Moderate*	*Strong*
Caffeine	Atropine	Brucine
Berberine	Emetine	Codeine
Aconitine	Hydrastine	Cantharidine
Cocaine	Strychnine	Heroin
Theobromine	Quinine	Morphine
Solanine	Apomorphine	Narcotine
Colchicine	Apoquinine	Pilocarpine

FLUORESCENCE OF HYPNOTICS

(long wavelengths)

Hypnotic	*Fluorescence*
Phenobarbital	Whitish
Nembutal	Blue-violet
Sodium amytal	Bluish
Sodium phenobarbital	Violet tinged
Diallylbarbituric acid	Violet tinged
Luminol .	Bluish
Diethylmalonylurea-aminopyrine	Strong violet
Aminopyrine-diallylbarbituric acid	Bluish on violet
Paraldehyde	Bluish
Chloral hydrate	Bluish to yellowish
Chloral alcoholate, soln	Strong yellow-green
Paregoric	Strong yellow-green

Alkaloids were studied by R. Heller (1916) with the aid of a luminescence microscope. The results of some of his studies are given in the table. Later observations by Danckwortt and Pfau using the capillary strip method of analysis were similar to those of Heller. In examinations of pure members of the isoquinoline and tetrahydro-isoquinoline groups shades of blue were noted in veratric acid, opianic acid, potassium opianate, papaverine, and hydrastinine hydrochloride while no luminescence could be observed in cotarnine and hydrastinine. The fluorescence of alkaloids is generally increased by the introduction of methyl or methoxy groups.

Synthetic *hypnotics* and others may often be distinguished from each other from natural products by fluorescence (see table). The addition of various groups to malonyl-urea hypnotics alters the luminescence. In examinations of synthetic products such as phenobarbital, as well as others, the manufacturer and process should be taken into consideration.

THEATRICAL APPLICATIONS

Fluorescence finds many uses in the theatrical field and commercial lighting effects. Although many thousands have gazed with wonder and amazement at some of the spectacular lighting effects on the modern stage there are few who know the secret. Numerous chemicals, pigments, paints, and dyes which fluoresce and phosphoresce brilliantly are available for theatrical uses. Most of these substances fluoresce best under long wavelengths of ultraviolet, hence units of this kind are utilized in theatrical work. The carbon arc, fitted with a special heat resisting filter, is being replaced in stage and commercial lighting, by recently developed spot-light types of high intensity mercury vapor lamps. The latter units are less cumbersome, easier to operate, and generate less heat.

Suitably painted or dyed scenery and costumes, produce a gorgeously beutiful and sometime weird effect on a stage. A trio of acrobats, painted with fluorescing paints, may be joined by a fourth whose unpainted black costume makes him invisible to the audience. The presence of the invisible fourth acrobat enables the quartette to perform mystifying tricks. An entire ensemble on a stage may suddenly change costumes by simply changing ordinary illumination to ultraviolet. Many mystical stage effects can be explained by fluorescence.

Walking on "red hot rocks", the much discussed performance of the South Sea Islanders, can be readily duplicated on the theatre stage by the modern Houdini. Ordinary rocks, painted with red fluorescing paint, or red fluorescing calcite is placed in a narrow pit. Small fire with much smoke is built below the pit of rocks. Concealed ultraviolet lights cause the rocks to appear red hot, and this illusion accompanied by actual smoke and fire, brings about a realistic appearing performance. Fluorescent grease paints applied to the face of the barefooted performer bring out ghastly effects as the pit of glowing rocks is crossed.

"The magic flag" is another spectacular performance sometimes seen on the stage or in night clubs. A section of white cloth is treated with invisible chemical paints, which when placed under invisible ultraviolet light develops into an American flag. Cadmium borate is applied to the white cloth to represent the strips, calcium tungstate for the blue field and magnesium tungstate for the white stars and bars. The chemicals are activated especially for producing fluorescence.

Special carpets or linoleum in the aisle of a darkened theatre enable patrons to find their way without the aid of aisle lights or flashlights. The carpets or linoleum are printed with fluorescent dyes, which fluoresce from the invisible radiations of ultraviolet light units placed above.

Fluorescent paints are also finding wide use in commercial window displays. Murals can be painted with fluorescent paints invisible in ordinary light. Ornaments, fluorescent fabrics, and other objects may be arranged in exhibits to produce startling contrasts as the lighting is automatically changed from ordinary to ultraviolet. Various plastics dyed or charged with fluorescent pigments find use in commercial exhibits. At the recent New York and San Francisco expositions, fluorescent lighting effects were conspicuous.

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A few of the enormous number of papers on luminescence are included in the following list. The papers which have been used in compiling data for the various chapters are usually listed together with those of more general interest. While it is difficult to include all papers published in the field the reader is referred to the literature references in the respective papers as well as works in which bibliography is treated to a larger extent.

An attempt has been made to list the more readily available papers which will aid the reader in pursuing further studies on the subject. The professional student who desires a very complete index to the technical literature on the luminescence of minerals and fluorescence analysis is directed to Hintze's *Handbuch der Mineralogie* and Radley and Grant's *Fluorescence Analysis in Ultraviolet Light.* The former book is frequently used as a reference for the section on specific minerals.

***Note:** **Books mentioned in the following pages may be obtained from the publishers, Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y.**

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ELEMENTS AND THEIR SYMBOLS *

Aluminum	Al
Antimony	Sb
Argon	A
Arsenic	As
Barium	Ba
Beryllium	Be
Bismuth	Bi
Boron	B
Bromine	Br
Cadmium	Cd
Calcium	Ca
Carbon	C
Cerium	Ce
Cesium	Cs
Chlorine	Cl
Chromium	Cr
Cobalt	Co
Columbium	Cb
Copper	Cu
Dysprosium	Dy
Erbium	Er
Europium	Eu
Fluorine	F
Gadolinium	Gd
Gallium	Ga
Germanium	Ge
Gold	Au
Hafnium	Hf
Helium	He
Holmium	Ho
Hydrogen	H
Indium	In
Iodine	I
Iridium	Ir
Iron	Fe
Krypton	Kr
Lanthanum	La
Lead	Pb
Lithium	Li
Lutecium	Lu
Magnesium	Mg
Manganese	Mn
Mercury	Hg
Molybdenum	Mo
Neodymium	Nd
Neon	Ne
Nickel	Ni
Nitrogen	N
Osmium	Os
Oxygen	O
Palladium	Pd
Phosphorus	P
Platinum	Pt
Potassium	K
Praseodymium	Pr
Protactinium	Pa
Radium	Ra
Radon	Rn

*** Elements not adopted by the Committee On Atomic Weights: Actinium (Ac), Alabamine (Ab), Illinium (Il), Masurium (Ma), Polonium (Po), and, Virginium (Vi).**

ELEMENTS AND THEIR SYMBOLS

Rhenium	Re
Rhodium	Rh
Rubidium	Rb
Ruthenium	Ru
Samarium	Sm
Scandium	Sc
Selenium	Se
Silicon	Si
Silver	Ag
Sodium	Na
Strontium	Sr
Sulfur	S
Tantalum	Ta
Tellurium	Te
Terbium	Tb
Thallium	Tl
Thorium	Th
Thulium	Tm
Tin	Sn
Titanium	Ti
Tungsten	W
Uranium	U
Vanadium	V
Xenon	Xe
Ytterbium	Y
Zinc	Zn
Zirconium	Zr

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