Article: A review of ultra-violet light and examination techniques
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A REVIEW OF ULTRA-VIOLET LIGHT AND EXAMINATION TECHNIQUES

Laramie Hickey-Friedman

1. Introduction

This presentation topic will include a brief history of ultra-violet light technology, fluorescence, and the introduction of UV examination into conservation via museums, concluding with a discussion of current research involving UV examination and possibilities for qualitative analysis. During a review of technical reports numerous notations appeared which identified restoration materials by the color of the fluorescent reflectance. Only in a handful of the reports were the materials analyzed for definitive identification. The remainder relied on visual identification. It is the author's desire to re-address this common, non-destructive technique and evaluate its usefulness and limitations in comparison to similar analytical techniques and review specifications for both qualitative and quantitative examination studies.

2. History

Fluorescence is named from the mineral fluorite, which has a faint, yet visible blue glow in response to the ultraviolet in sunlight. Possibly the earliest recorded case of fluorescence dates to the early 17th century. An alchemist, Vincenzio Cascariola, prepared a compound of phosphorescent barium sulphide (known as Bologna Phosphorus) by burning barite. An account of Cascariola's compound was published by a Professor La Galla, who had learned of the substance from Galileo (Marfunin 1979:143).

It was not until the mid 1800's that methodical scientific studies of fluorescence were undertaken. In 1810 The German romanticist Goethe noted that some minerals fluoresced. Early scientific experimenters including Sir David Brewster and Sir John Herschel identified the fluorescent phenomena as variations on known properties of light such as diffusion and dispersion (Robbins 1983: 3-13).

Repeating Goethe's work, Sir George Stokes, recognized as the discoverer of fluorescence, observed fluorite glowing from the middle of the violet region into the apparently dark space beyond (i.e. the ultraviolet band) when exposed to a spectrum created by natural sunlight. Stokes called this new physical property fluorescence after the mineral he had examined (Dake and De Ment 1941: 1-7; Radley and Grant 1954: 4-10).

2.1 Lamps

Early development of fluorescent lamps included the iron arc lamp, in 1903, which was capable of producing abundant short-wave light (Radley and Grant 1954:11-13). That year the British Museum of Natural History created in London the first public display of fluorescent minerals, the precedent for the use of ultra-violet examination in museums.

In the 1920s and 1930s, new sources of ultra-violet light were developed. One, the argon bulb, was only able to produce low intensities. Another, known as the Nico lamp, was more effective, but very costly to manufacture. Dr. Robert Wood developed a glass filter capable of passing only ultraviolet, leading to the development of the first mercury vapor lamps. This type of lamp, known as a Wood's light, is the hand-held ultraviolet light typically found in conservation laboratories. The nickel-plated glass filter allows the emission of UV-A long wave from 320-380nm, with a peak at 365nm. Other lamps commonly used for the non-destructive examination of artwork are short wave lamps. The short wave band or UV-C runs from 180 to 280nm with a peak at 254nm.

2.2 Museums

Art historians and museum curators have long relied on differential fluorescence and the occurrence of fluorescent glues, varnishes, plasters, and plastic resins to help them detect signs of hidden repairs and forgery. The invention of the Wood's light at the end of the 1920's led to the eventual widespread use of UV in the examination of works of art. The technique was embraced by curators and later conservators for its non-destructive diagnostic capabilities.

In 1931 the Metropolitan Museum of Art published a book by James Rorimer, "Ultra-violet Rays and Their Use in the Examination of Works of Art". This is one of the earliest published examples of the widespread use of UV examination in museums. Rorimer sought to establish this technique as a valuable analytical tool for museums. It is worthwhile to note that he recommended UV photography as a means of recording the fluorescence, and for reproducibility, but made little mention of standards.

The other hallmark publication, "Fluorescence Analysis in Ultra-Violet Light", by Radley and Grant (1933), devotes an entire chapter to UV examination of museum artifacts. It cites uses of UV illumination to distinguish between genuine objects and fakes, and for the enhancement of surfaces.

3. Mechanics

To begin to understand UV examination it is useful to appreciate the mechanics of fluorescence. Simply, fluorescence is luminescence in which light of a visible color is emitted from a substance under stimulation or excitation by ultra-violet radiation. The light is given off only while the stimulation continues; in this the phenomenon differs from phosphorescence, in which light continues to be emitted after the excitation by other radiation has ceased.

The theory of molecular luminescence (fluorescence and phosphorescence) is fairly well understood. When light (or energy) hits a substance, the incoming energy will either pass through or be temporarily absorbed. This is dependent on the molecular structure of the substance and the wavelength of the energy. The energy that is absorbed by a molecule is stored as increased electron vibrational or even rotational motion, and, if there is sufficient energy, as an elevation in the molecule energy states (molecular excitation). The absorbed energy is released in the visible spectrum as the molecule relaxes. The slight shift in wavelength from the UV to the visible range is a result of prior vibrational relaxation.

Photons of visible light, and especially those of ultraviolet light wavelengths, typically have sufficient energy to cause a transition into one of the excited states. The energy must be of a type that is appropriate to the molecular structure; excitation energy that is at less ideal wavelengths may still produce fluorescence, but at a lower intensity. This explains why fluorescence occurs or is perceived differently during the examination of non-similar materials.

4. Uses

Today, ultra-violet lights are primarily used as a diagnostic tool for identifying surface inconsistencies on the object, such as inpainting or fills. UV illumination has proven to be an important non-destructive technique for initial diagnostic examination. By taking advantage of the scientific properties, surface variations can be identified and noted. Some examples of this are: sizing in paper and textiles; varnishes on paintings, and furniture; and fills and repairs on ceramics.

It is very useful during cleaning to observe the success of a treatment, or to examine a group of several similar objects looking for inconsistencies or matching qualities. The UV light is an immediate tool, easy to use, low in cost, needing only a dark room and protective glasses. Virtually anyone can see surface inconsistencies with UV light.

5. Limitations

5.1 Standards

The limitations of UV examination become immediately apparent when the technique is applied for qualitative analysis. While early scientific publications stressed the use of standards and reproducibility, this is no longer customary practice. An informal survey of conservation labs will show that there are a variety of lamps with differing emission, the UV emission is not routinely measured, and comparable standards are not utilized. While photographers tend to have a more standardized methodology, the energy sources used for UV photography tend to vary.

5.2 Detector Reliability

A recent review of 20th century conservation records and published articles yielded a number of references for material identification by visible fluorescence using UV examination. The most common of these materials is shellac, which fluoresces a strong orange color. This can become a great concern for accuracy since the detector is essentially the human eye and there can be no repeatable recording of the results.

A number of researchers from other fields, primarily petrology, have addressed procedural concerns. Of these, the classification of fluorescent color is typically foremost. It is generally agreed that a standardized system is needed, but to date a number of schemes have been used, including generalized color groups, the Pantone Color System (which is a standard in the printing industry), and the AdMark system.

5.3 Misidentification

Ambient conditions and exposure to certain rays and chemicals can have an effect on fluorescence. Previous exposure to heat may alter color and intensity, but this effect has not been studied in detail. At the outset, and increase in pressure will amplify fluorescent intensity, up to a threshold, after which the intensity will decline. Prior exposure to x-ray radiation may make non-fluorescing substances fluoresce. A similar phenomenon may occur due to exposure to some certain acids and alkalis.

In the case of resins and adhesives, there is strong evidence to suggest mixtures were often employed when restoring works of art. The shellac molecule fluoresces so strongly that in small amounts it can overpower the fluorescence of other molecules.

6. Discussion

All of the preceding information is readily available and accepted. However, what does not seem to have been addressed is whether the conservation community should look to new methods and technology to increase the knowledge gained from UV examination, and if there is a justification for improving the technique. Can conservators can improve UV examination with reproducible and qualitative results through standard examination techniques?

To answer this question it is important to examine the whole picture. Most people would still agree with James Rorimer: it is a great diagnostic tool. However, to standardize the technique we must look at the equipment and the methods employed. A variety of UV light sources are commercially available, and even lamps of the same type do not necessarily produce the same output as their filaments may emit somewhat different wavelengths. To block the visible light which is a side effect in the production of ultraviolet, manufacturers use a variety of filters which also have dissimilar properties.

The spectra emitted by different types of lamp are even more varied. Shortwave and longwave lights produce different results in some materials. Since the shortwave light has a shorter wavelength than the long wave, the resulting fluorescence will also tend to have a shorter wavelength (Stoke's Law).

Additionally, these lamps are not very efficient when compared to the energy sources for analytical equipment. After the addition of filters, the long wavelengths are reduced to as little as 11% of the original output, while the shortwave is about 43%. In addition, both lamps and filters become more opaque over time, due to interaction of their materials with the light source (Fig. 1).

Since the brain is highly subjective with regard to color, various devices have been developed over the years to measure the intensity and color of fluorescence, such as fluorimeters, colorimeters, spectrophotometers and Raman spectroscopy. Other simpler devices may also be used, such as handheld photographic light meters. Some of these devices operate by comparing the sample to artificial light. Others use photo-cells and actually measure the wavelength of the emitted light. Another instrument to measure fluorescence is not needed. What could be useful is a way to standardize the examination of artwork with UV, a method that can be repeated and recorded.

It is not unusual for conservation to look towards other fields for adapting technology. Mineralogy, forensics, holography, and the biological sciences continue to use fluorescence. What conservation needs is a hand-held, easily portable and inexpensive method to roughly measure the visible emission of energy from the irradiated object. An analytical technique widely used in medical and forensic applications may be the answer. This is a liquid crystal tunable filter and charge-coupled device, based on visible reflectance hyperspectral imaging.

6.1 Standards

As mentioned previously, different wavelengths of excitation light may all produce some degree of fluorescence, but the intensity of fluorescence may vary significantly. Since changes in any of the fluorescent light intensities will alter the overall color, it is advisable to use the same source throughout a study.

Certain details should be recorded during examination, including the type of UV source, the distance between the source and the object, and the distance between the object and the observer (or camera). For consistency, these distances should be kept constant, and recorded. Since irradiation and other chemical alteration can influence fluorescence, it is important to know the past history of the object.

For descriptive purposes, conservators could look into adapting an existing system (such as Munsell) using the three visual descriptors of color: brightness (the fluorescent intensity), saturation (how much white is mixed with the basic color, ranked pale, medium, deep), and hue (primary and secondary colors). In any case, exotic and potentially confusing terms (such as hazel or turquoise) should be avoided.

7. Conclusion

It is the desire of the author that this presentation promote more discussions about the use of ultra-violet examination. This technique is still a viable diagnostic tool for evaluating surface and coating inconsistencies. It is immediate, and in many institutions one of the few available, affordable techniques. With this in mind a method for recording reproducible results is important.

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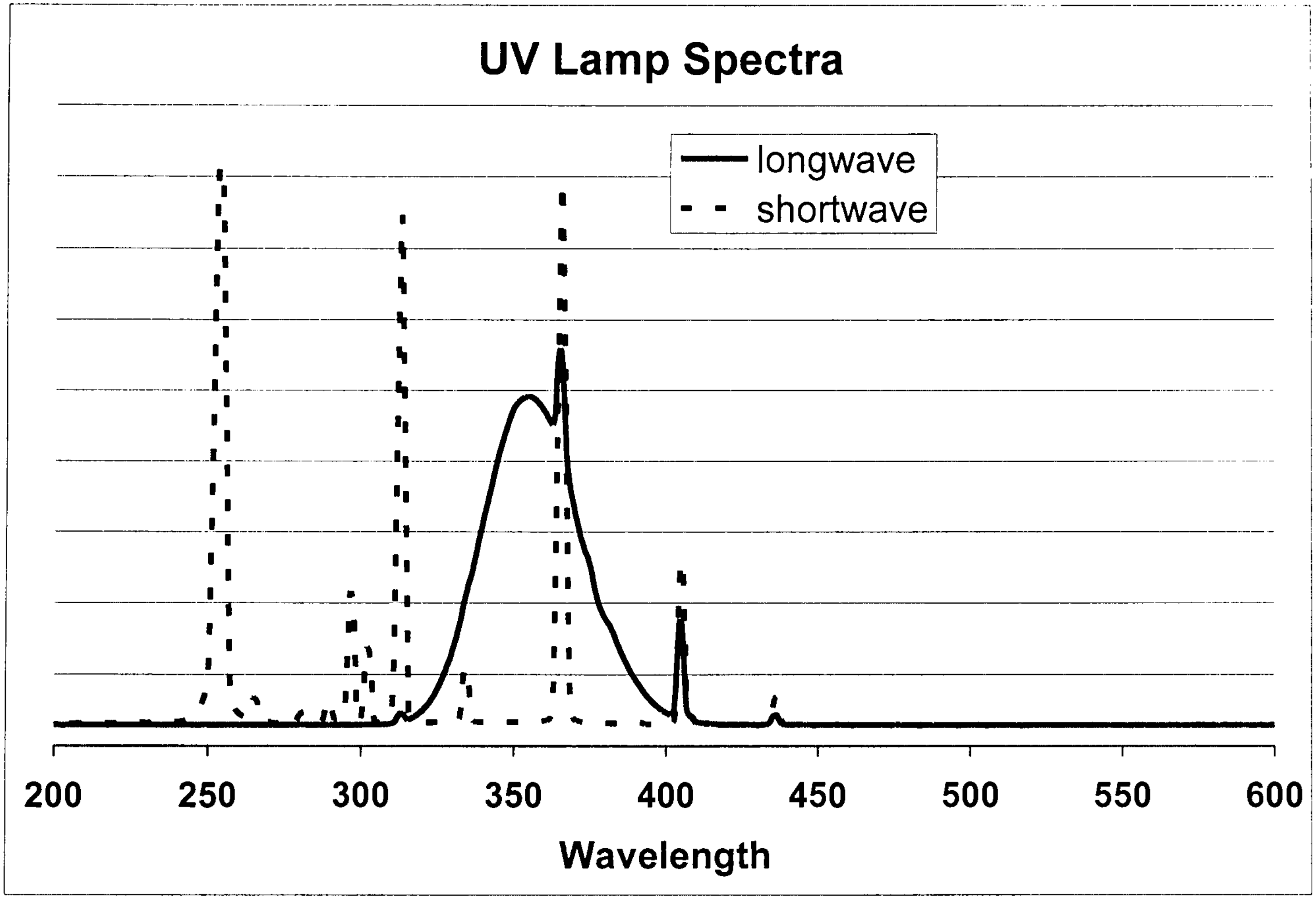

Figure 1. This graph shows the different spectra emitted by long-wave and short-wave lamps. Notice that both have a peak in the visible range, but the filtering on the long-wave is much more exclusive. Spectra taken directly from ultra-violet lamps at the Los Angeles County Museum of Art using a spectrophotometer.