ANTHONY D. MCGRATH, S. MORI VAEZI-NEJAD

Communications Technology Group
London Metropolitan University
North Campus, Holloway Road, London N7 8DB
e-mail: m.vaezinejad@londonmet.ac.uk

MEASUREMENT OF LUMINESCENCE IN COLOURED PRINTED MATERIALS

While fluorescent pigments have been used for many years, the formulation and quality control of coloured printed materials containing them, has been a challenge, primarily due to lack of appropriate instrumentation at a cost that is economically viable to make the necessary measurements. This paper deals with the economical instrumentation and measurement of fluorescent properties of coloured printed material under investigation. Significance of the correct method of excitation and detection are discussed. Characteristics of desirable commercially available light sources and detectors are also described. Application of one of such a detector for our investigation is considered in some detail.

Keywords: Colour detection, Fluorescent pigmentation, Printed materials, Spectrometer

1. INTRODUCTION

Luminescence can be defined as being the radiation emitted by an atom or molecule after it has absorbed energy in order to go to an excited state. Luminescence is generally considered of two categories, fluorescence and phosphorescence depending on the nature of the state. In short, fluorescence is the emission of light by a material that ceases as soon as the source is removed. In comparison, phosphorescence is mostly evident by an after-glow which can vary from a few milliseconds to hours [1, 2]. Our investigation focused on development of two types of Ultra Violet (UV) fluorescent materials and their properties were fully analysed using a high-resolution laboratory spectrometer.

2. SELECTION OF THE LIGHT SOURCE

In order to improve experimentation and capability of luminescent work, it is highly desirable to understand the performance and limitation of the light sources suitable for this investigation. Our past experience in this area was found very useful in selecting the most suitable economical light source [3, 4].

2.1. Xenon lamps

One of the most commonly available and used light sources for most steady-state spectrometers is the Xenon (Xe) arc lamp [4]. These lamps provide a relatively continuous output in the visible spectrum from 250nm to 700nm, although their Infra Red (IR) characteristics are extremely useful they are not uniform.

2.2. Semiconductor laser diode

Lasers have many good attributes for use in spectroscopy due to their construction and operating principles. Laser light is monochromatic due to the single wavelength that is emitted and coherent (in-phase) due to the stimulated emission of radiation. These devices offer good optical power and are flexible for use due to reducing size [5].

2.3. Light Emitting Diodes

Light Emitting Diodes (LEDs) emit individual photons in a quite random or spontaneous way, compared to the laser that emits photons in a stimulated manner. The LED's photon wavelength (nm) is dictated by the bandgap energy (eV) of the LED's semiconductor material. These two parameters are related by $\lambda = 1240/eV$, and serves as an important issue for a low cost excitation source [2, 6].

Table 1. Comparison of some important properties of LEDs and Lasers.

LED	**LASER DIODE**
Wide beam	Narrow beam
Current control	Current and temperature control
Frequency modulation up to 100MHz	Frequency modulation in excess of 1GHz
Spectral width typically > 5nm	Spectral Width typically <5nm
Optical power up to 10mW	Optical power obtainable to 500mW
Low cost	High cost

LEDs and laser diodes are the most common type of semiconductor light sources. Relevant properties of these devices are shown in Table 1. LEDs are extensively used as indicators and displays combining advantages such as small size, long-life, low operating temperature and compatibility with silicon integrated circuits. They are widely available in the visible and infrared regions of the emission spectrum, but only recently became commercially available in the UV region due to successful fabrication using gallium nitride (GaN) on sapphire [6, 7].

For the reason described above, and the fact that the cost is relatively low, a UV LED formed an integral part of this experiment. The UV LED used for this experiment is a relatively new product available from Nichia Corporation, model NSHU590A [8].

A Nichia LED emitting 373nm was chosen for evaluating the UV to green and UV to red samples. Figure 1 confirms the spectral peak is at 373nm with a Full Width Half Maximum (FWHM) of 7.3nm. A second LED selected from the same supplier was measured for demonstrating the typical variation in LED peak wavelength. The manufacturers' data sheet quoted the peak wavelength as 375 ±5nm.

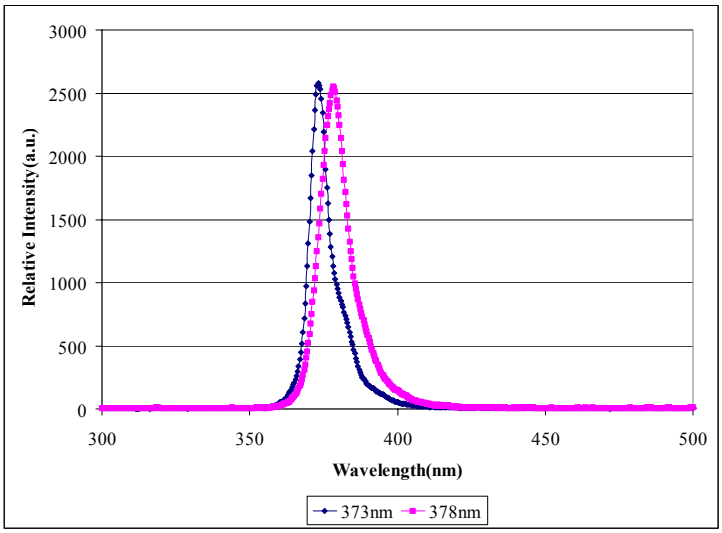

Fig. 1. UV LED output characteristics.

3. SELECTION OF THE DETECTOR

There has been a significant progress in optical devices as sensors and detectors for a variety of applications [9, 10]. For the purpose of this investigation, three different types of detectors were considered for experimental work; Photomultiplier tubes (PMT), Photodiodes and linear Charge Coupled Devices (CCD).

PMTs are light detectors that are useful in low intensity applications such as fluorescence spectroscopy. Due to high internal gain, PMTs are very sensitive detectors. Almost all equipment utilised for laboratory spectroscopy analysis incorporates a PMT as a means of detecting electromagnetic radiation, in particular, the UV/VIS and IR regions. Although silicon photodiodes poses a very good response time, of the order of 10^{-9} seconds, they are somewhat limited on sensitivity when compared to the PMT.

An alternative to the conventional photodiode is the avalanche photodiode, which provides some internal amplification, but not to the level of the PMT. A photodiode array (PDA) is a linear array of discrete photodiodes on an integrated circuit (IC) chip. For spectroscopy it is placed at the image plane of a spectrometer to allow a range of wavelengths to be detected simultaneously. PDA devices can be used in conjunction with a spectrograph for monitoring multiple wavelengths simultaneously. They can also be used for measuring decay of intensity of certain materials that fall within the response time.

A CCD is an integrated-circuit chip that contains an array of capacitors that store charge when light creates electron-hole pairs. The charge accumulates and is read in a fixed time interval. CCDs are used in similar applications to other array detectors such as PDAs although the CCD is much more sensitive for measurement of low light levels.

CCDs are being employed heavily in the multi-channel instrumentation systems due to their good performance at affordable prices. PDAs cannot match the performance of PMTs with respect to signal-to-noise ratio, sensitivity, and dynamic range. In contrast, the performance characteristics of CCDs approach those of PMTs. For this experiment, the Sony IXL511 linear image sensor will be evaluated for low to medium cost sensory systems for the use in analysing both fluorescent and phosphorescence materials. This device consists of 2048 pixels (14µm x 200µm) built in a 22 pin DIP package.

4. CALIBRATION AND MATERIAL ANALYSIS

Host calibration was undertaken using Double Monochromator Spectrometer (DMS).

The set-up configuration is shown in Fig. 2. The spectrometer consists of two monochromators, one for the excitation path and one for the emission path. The excitation monochromator incorporates a diffraction grating of 600 lines per millimetre (l/mm), compared to the emission monochromator that has a resolution of 0.05nm due to a diffraction grating of 1800 l/mm. A xenon arc lamp was used for the excitation source in combination with filters to ensure no second or third order effects are entered into the emission monochromator. The sample cell is the location for the material to be analysed. Two detectors are shown, the PMT for capturing the low level emission from the sample that is being irradiated by the selected wavelength of the Xenon source, and secondly a reference detector. This reference detector provides a check that the system is functioning correctly.

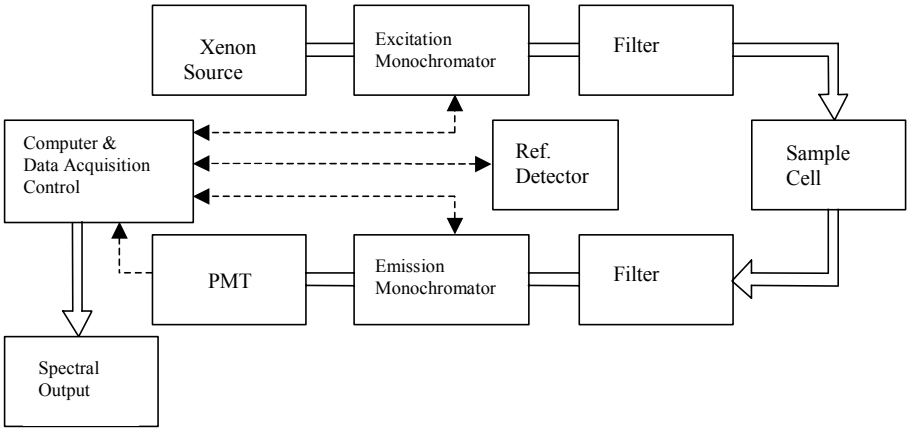

Fig. 2. Double monochromator spectrometer.

The user interfaces with the spectrometer through a computer that in turn positions the gratings to the parameters entered by the user. The computer is configured with a dedicated data acquisition system for handling data transfer and commands. The resultant spectrum is computed and presented graphically to the user.

Two products are under investigation, both of which undergo a chemical reaction when irradiated with UV radiation. It was observed that when both samples were examined under a UV lamp that one product emits a green glow and the second product emits a red glow. Using the laboratory spectrometer both products were examined in detail to establish their primarily absorption (excitation) wavelength, and their fluorescent emission.

Most commercially available UV lamps typically emit radiation at 365nm, although due to their construction a visible blue colour is present. The green and red products were best excited at different wavelengths of the UVA region (380-315nm) and their fluorescent emissions were captured. Figure 3 shows the emission curve for the red product and Figure 4 confirms the spectral response for the green product. For the material emitting in the red region the peak excitation was shared between both the 365nm and 373nm as illustrated above. The red emitting material whilst being irradiated by either of the four excitation wavelengths show a much differing response to that of the green emission in terms of its spectral properties. The FWHM is approximately one-tenth of the emission curve for the green material.

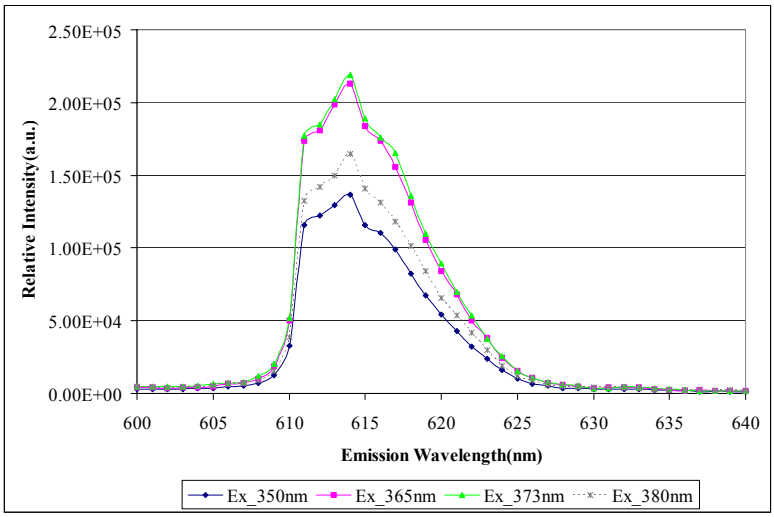

Fig. 3. Material irradiated with UV radiation resulting in red narrow-band emission.

Variations in colour print has an effect that can be noticeable to the human eye, such as changes in print weight (density), but measuring variations in fluorescent ink vehicles requires detectors with sensitivity that far exceeds the human eye response. To demonstrate detector sensitivity for fluorescent materials, a number of samples with different print weight have been constructed for evaluation.

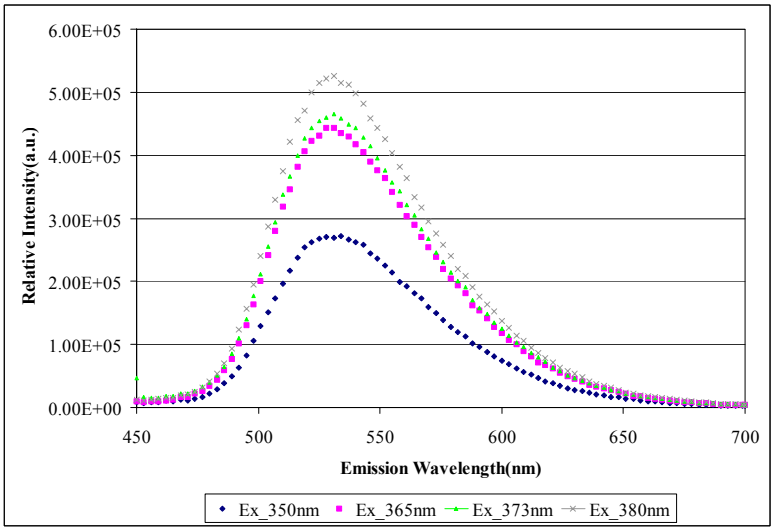

Fig. 4. Material irradiated with UV radiation resulting in broad-band green emission.

4.1. Green and red emissions for different print density

For the evaluation of print weight versus green emission, the chosen excitation was 373nm as this was previously confirmed to be commercially available as a low cost LED solution. Four samples of different print weight form the measurement evaluation: *Control; Sample 1; Sample 2; Sample 3.* The resultant emission curves for the four materials are plotted graphically in Fig. 5. By observation it is clear that the detector performance distinguishes between changes in print weight. The spectral characteristics have remained consistent, both in terms of the peak emission and the FWHM.

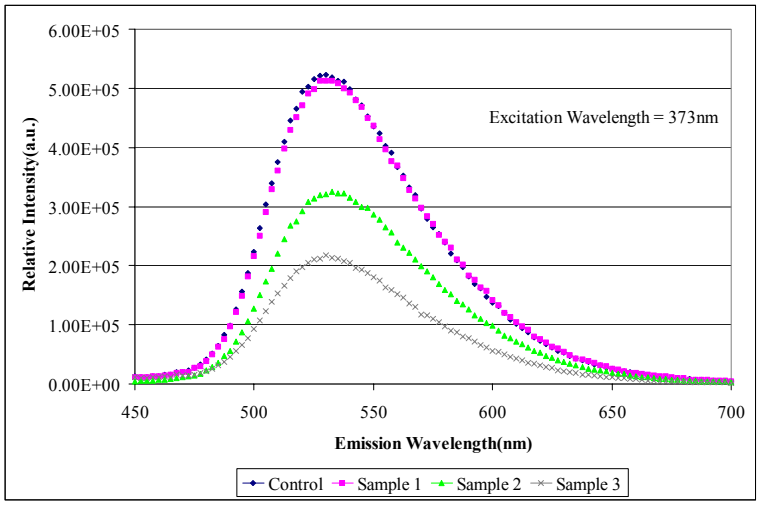

Fig. 5. Fluorescent green emissions of different print weights irradiated at 373nm.

The same procedure was performed for the red emission materials using an excitation of 373nm, although the emission spectrum was measured in 0.5nm steps compared to the previous measurements of 1nm step intervals. The resultant emission curves are shown in Fig. 6. Note that the emission of the red material appears to have two minor spikes instead of a singular peak. The reason for this is due to the improvement of the measurement resolution from 1nm to 0.5nm, hence the output as shown.

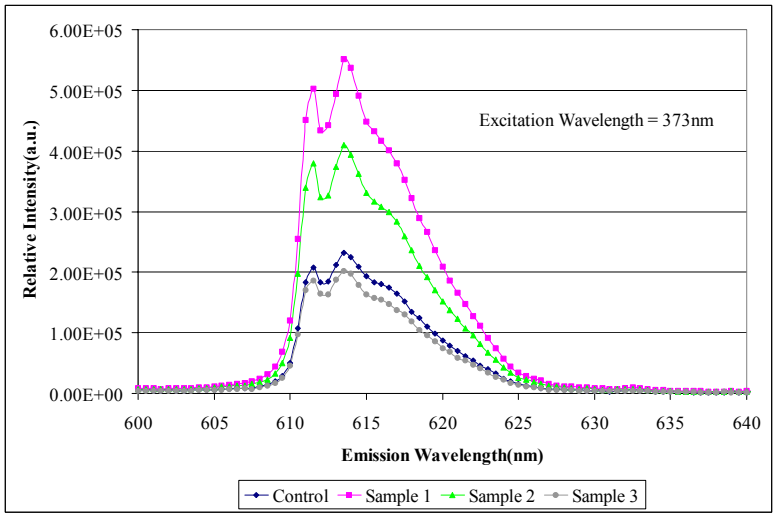

Fig. 6. Fluorescent red emissions of different print weights irradiated at 373nm.

4.2. CCD Measurements

The configuration for this experiment is much simpler, robust and cost effective for most applications of luminescent analysis. The system block diagram, as shown in Fig. 7, confirms the individual components required and the order in which they are configured.

The light source in this case is a LED with an output peak of 373nm when driven from a constant current supply of 10mA. The material under investigation is located in the sample cell of which the fluorescent emission is scattered from the sample being irradiated, and optically guided through a filter to the fixed-position grating. The grating is located on an

optical bench that incorporates the CCD detector and mirrors to form the optical path. The particular arrangement is known as the Czerny-Turner layout [11].

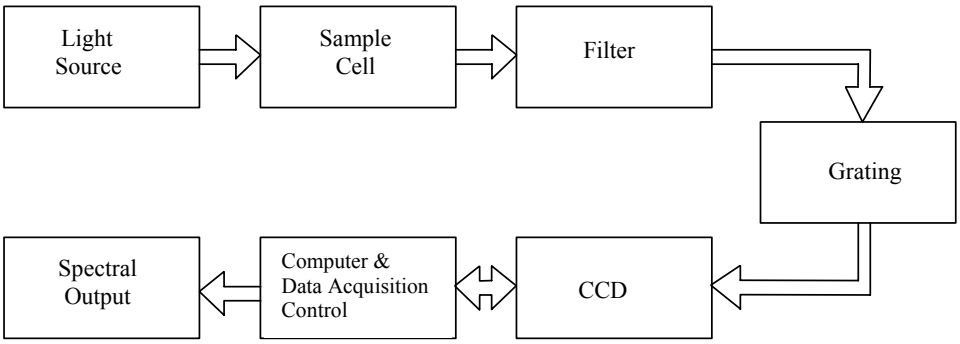

Fig. 7 Block diagram of CCD spectrometer with fixed position grating.

The CCD detector consists of 2048 pixel configured in a linear array; the output of each pixel is converted to an electrical unit which is representative of the amount of energy that has fallen on each pixel. With the aid of dedicated electronics and software, these signals are converted and sent to a personal computer (PC) for post processing. This task computes the relative intensity against wavelength (nm) by utilising Universal Serial Bus (USB) connectivity.

The print density exercise was repeated to obtain the emissions for the UV to green materials, at four different print weights. Using appropriate software, the raw data was captured, processed and stored to a file for each of the four samples, which provided confirmation of system functionality and the first spectral measurements of the CCD detector for the UV to green emissions.

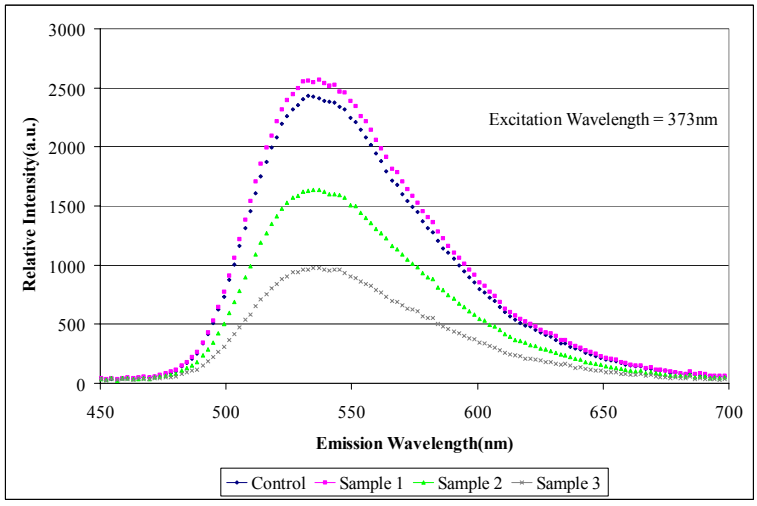

Fig. 8. Green fluorescent emission of four printed ink samples irradiated with UV LED.

It can be observed in Fig. 8 that a trend in the variations is similar to that witnessed by the DMS measurements recorded earlier, in Fig. 5. The exercise was repeated to obtain the emissions for the UV to red materials, at four different print weights. Once again the results show in Figs. 9 and 6 respectively, confirm that the variation in print density can be discriminated using the CCD detection method.

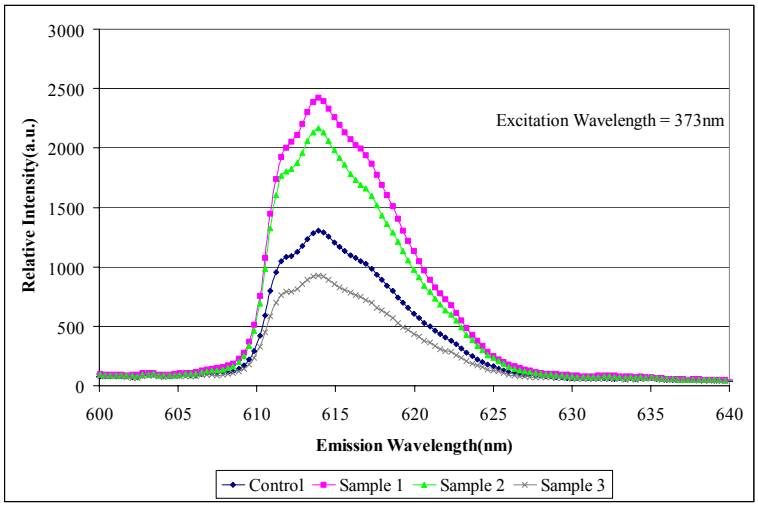

Fig. 9. Red fluorescent emission of four printed ink samples irradiated with UV LED.

5. SUMMARY

Measurement results corresponding to two alternative method of detecting luminescence from printed samples irradiated by UV radiation were reported in this paper. Experimental data show that the DMS offer superiority in analysis of materials in terms of resolution, PMT sensitivity and excellent signal to noise ratio. In comparison, the low cost CCD spectrometer can achieve merits in resolution, sensitivity and signal to noise, albeit not to the level of the DMS, but good enough to be considered for batch to batch measurement of ink formations and quality control measurements. The final outcome of the above investigation resulted in the prototype development of a fully integrated CCD spectrometer, tested, and evaluated for the use of UV fluorescent materials.

REFERENCES

1. Lakowicz J. R.: *Principles of Fluorescence Spectroscopy*, 2nd Ed, Kluwer academic/ Plenum, New York, 1999, Chapter 1: Introduction to fluorescence.
2. Hawkes J., Wilson J.: *Optoelectronics an Introduction*, 3rd Ed, Prentice Hall, Europe, 1998, Chapter 7: Photodetectors.
3. Jenner R. P., Vaezi-Nejad S. M.: *Development of novel light source for investigation of amorphous semiconductors as sensors for process tomography*, Measurement + Control Journal of Institute of Measurement and Control, vol. 32, no. 3, pp.75, April 1999.
4. Vaezi-Nejad S. M.: *Instrumentation aspects and application of charge transport measurement techniques*, Measurement journal of the international measurement confederation (IMEKO), 17(4) (1996) 267.
5. Schubet E. F.: *Light Emitting Diodes*, Cambridge University press, 2003, p59.
6. Vicic M., Sobotka L. G., Williamson J. F., Charity R. J., Elson J. M.: *Fast Pulsed UV light source and calibration of non-linear photomultiplier response*, Nuclear Instruments and Methods in Physics Resrearch A, 507 (2003), p.636-642.
7. Fitzpatrick C., O'Donoghue C., Lewis E.: *A novel multi-point ultraviolet optical fibre sensor based on cladding luminescence,* Measurement Science and Technology, 14 (2003), p.1477-1483.
8. See Nichia Corporation, Specification for Nichia UV LED, 2002.
9. Vaezi-Nejad S. M.: *Selected Topics in Advanced Solid State and Fibre-Optics Sensors,* published by the IEE in 2000.
10. Vaezi-Nejad S. M.: *A Random Walk in Sensors: Recent Advances and Market Opportunities*, Measurement and Control Journal of Institute of Measurement Control, vol. 31, pp.80, April 1998.
11. Palmer C.: *Diffraction Grating Handbook*, 4th Ed, Richardson Grating Laboratory, New York, 2000, See Chapter 6 on Plane gratings and their mounts.

POMIAR LUMINESCENCJI DRUKOWANYCH MATERIAŁÓW BARWNYCH

Streszczenie

Pigmenty fluorescencyjne były w użyciu od wielu lat, lecz forma użytkowa i kontrola jakości barwnych drukowanych materiałów zawierających te pigmenty stanowiło wyzwanie, głównie z powodu braku odpowiedniego oprzyrządowania na tyle taniego, że koszt niezbędnych pomiarów byłby do przyjęcia. Niniejszy artykuł omawia oszczędne oprzyrządowanie oraz pomiar własności fluorescencyjnych badanego zadrukowanego kolorowo materiału. Zostało omówione znaczenie właściwej metody pobudzenia i detekcji. Opisane są również potrzebne, dostępne w handlu źródła i detektory światła. Zastosowanie jednego z takich detektorów do badań zostało omówione w szczegółach.