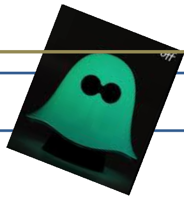

Studying photoluminescent samples emissions

Part #1

Phosphorescent Materials

Co-funded by the Erasmus+ Programme of the European Union

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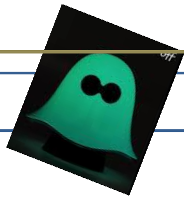

Characterization of the decay curve of a phosphorescent materials

Version: 29/10/2017

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Short description of the topic

We present the Teacher-Guide to an experiment finalized to characterize the decay curve of light emitted by a phosphorescent materials

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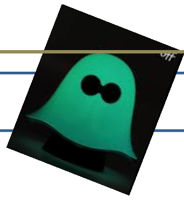

The Phosphorescent “Ghost-Lamp”

Experimental Goal

The aim of this experiment is the characterization of the decay curve of a ***Phosphorescent*** object (Emitted Light Intensity VS Time).

We choose to study a design object available “off the shelf” in order to highlight the fact that the use of Phosphorescent materials is not restricted to a niche in Materials Science research but is already widely

Fig1-Photoluminescent night lamp by lucedentro www.lucedentro.com - lukemodel -

employed in industrial and commercial applications. Our study object is a night lamp [*Lucedentro “luke” lamp http://shop.lucedentro.com/collections/catalogo/products/luke, see fig.1*] whose lampshade is made of plastic with embedded phosphorescent pigments. Such pigments are excited by the light radiation emitted by the bulb once it is turned. The phosphorescent effect lasts even when the bulb is turned off, thus creating an “emotional” night light.

However the same experimental setup may be easily adapted to the study of any other phosphorescent object or sample.

Considering the theoretical background we expect to record an exponential decay of the light intensity emitted by the sample on UV/Visible excitation. No major changes with varying excitation time accordingly with quantum theory of electron bands and quantized energy in matter

See background reading for a more in depth description of photoluminescence phenomena and related decay times.

The light sensor

Fig 2 - Light Dependant Resistance

We used an LDR (Light Dependant Resistance) as light sensor. This is an electronic device with a strongly light sensitive electrical resistance. (Buy it in any electronic stuff shop, less than 1 euro).

Previously to connecting the LDR into the final circuit, students should understand how it works. Using a tester in Ohmmeter modality they will study how the LDR resistance varies with the incident light: they will move the LDR back and forth in the surroundings of light sources of different intensity/luminance, rotate it, shadow it with their hands, etc.…)

From these early observations, one may evince the following characteristics of the LDR. This will be valuable knowledge to use in the experiment.

- The LDR resistance is extremely sensitive to light conditions, varying greatly even upon tiny variations.

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- The LDR resistance varies promptly as light varies, even if a small retard in response (approx. 1 sec) is detectable even at naked eye.
- The variability range of the LDR resistance is broad, covering from 6 to 7 magnitude orders. It can actually range from a few Ohms at minimum illuminance threshold (darkness) to more than 10-20 MegaOhm at the maximum illuminance level.
- Although not very easy, it is possible to bring the resistance down to “zero”(this actually means below the Ohmmeter sensitiveness). This can be achieved in many ways, such as by wrapping it up tightly inside your fist.
- On the other hand by bringing the LDR close enough to an intense light source (in our case we just brought it a few centimetres away from a 100W light bulb) the Resistance rises up to infinity (actually goes beyond the measuring range of the instrument). In such condition of “maximum illuminance” the LDR works as an open switch.
- Although the LDR seems to have a clearly definite photosensitive surface (and the Resistance greatly varies even for slight inclinations of the light incidence plane) when you totally shadow such surface (covering it with your finger) the Resistance doesn’t completely drop down to zero thus showing that the device is light sensitive also to the diffused and reflected light coming from the sides and even partially from the back.

The circuit

The LDR is connected into the electrical circuit. See scheme in Fig.3.

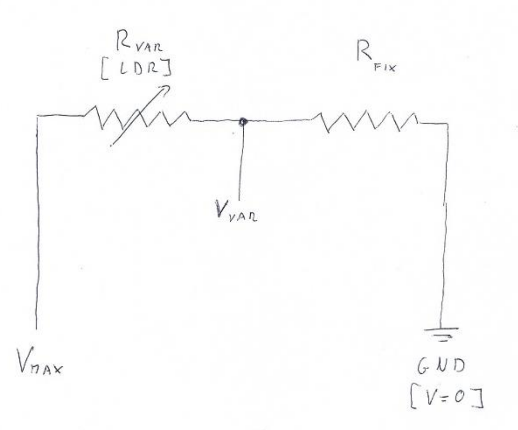

Fig. 3- The experimental circuit

In the scheme GRD means the connection to the ground. We arbitrarily choose zero for the value of the potential voltage at this spot. This allows us to work with Voltage rather than Voltage Differences between the specific spot and the ground and simplifies the subsequent theoretical analysis of the circuit.

Vmax stands for the Voltage input of the apparatus (5V).

Rvar is the variable resistance of the LDR, and Rfix is a fixed resistance connected in series with the LDR. Its main role is to limit the maximum current circulating within the circuit (in the maximum illuminance case with Rvar becoming zero). This helps preserve both the interface (Arduino) and the power source (PC). The value of Rfix has no direct influence on the measures, provided that it doesn’t change its value during the whole experiment.

However the value of Rfix actually has a relevant influence on the sensibility of the measuring apparatus, particularly at low illuminance level. This calls for a very careful calibration and the resistance value may be changed in case we are interested to study in detail this kind of situation like in our specific case (see final discussion).

In such a configuration the LDR works as a voltage divider: the variable voltage Vvar between the two resistances depends on the value of Rvar (and therefore on the light intensity of the incident light on the LDR) ranging from the maximum value Vmax when Rvar = 0 (“maximum illuminance: LDR as a perfect conductor and Vvar directly connected to the power source) to

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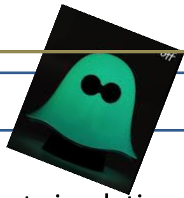

zero when Rvar goes to “infinity”(total darkness: Rvar as an open switch, no current circulating in the circuit and Vvar equal to ground)

Vvar is the physical quantity that we will actually measure and from which we will calculate the value of illuminance which ultimately is what we are looking for.

Theoretical Analysis

The analysis of the circuit (Fig.3) reveals that the current circulating through the two resistances in series is

$$i = \frac{V_{Max}}{R_{Fix}+R_{Var}} \qquad \text{EQ1}$$

And the voltage at the junction of the two resistances is

$$V_{Var} = i \cdot R_{Fix} \qquad \text{EQ2}$$

Inserting in Eq.2 the current value from Eq.1

$$V_{Var} = V_{Max}\frac{R_{Fix}}{R_{Fix}+R_{Var}} \qquad \text{EQ3}$$

and this may be finally written as :

$$\frac{V_{Var}}{V_{Max}} = \frac{1}{1+\frac{R_{Var}}{R_{Fix}}} \qquad \text{EQ4}$$

The above expression may be inverted in order to obtain Rvar (of the LDR) as a function of the Voltage at the junction of the two resistances

$$R_{Var} = R_{Fix} \cdot \left(\frac{V_{Max}}{V_{var}} - 1\right) \qquad \text{EQ5}$$

Taking into consideration the observations on the LDR behaviour, our hypothesis is of inverse proportionality between light intensity of the light incident on the LDR [L_{Var}] and the corresponding value of the LDR Resistance [R_{Var}]:

$$L_{Var} = \frac{k}{R_{Var}} \qquad \text{EQ6}$$

Combining the last two equations leads from the measured voltage to the value of the Light intensity provided that the proportionality constant is known.

The constant *k* may be determined by calibrating the instrument comparing a known level of light (obtained with a light sensor) with what is obtained by Eq. 5 and 6 from the corresponding voltage.

This is not an easy task due to the strong influence of position and angle of the sensor on the sensor output. Ideally the light sensor should replace the LDR exactly in the same spot and position,

However what we are mostly interested in is monitoring the intensity of the light emitted by the sample versus time.

We especially want to study the trend of light intensity relative to its initial value. [L_0]. From eq.6, we have:

$$L_{Rel} = \frac{L_{Var}}{L_0} = \frac{R_0}{R_{Var}} \qquad \text{EQ7}$$

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where R_0 and V_0 respectively, express Rvar and Vvar matching the initial illuminance condition [1].

.

As we put the two Resistances (initial and variable) vs. the measured voltage from eq.5 after a few algebra passages we obtain

$$L_{Rel} = \frac{V_{Var}/V_{Max}}{V_0/V_{Max}} \cdot \frac{1-V_0/V_{Max}}{1-V_{Var}/V_{Max}} \qquad \text{EQ8}$$

Such a formula allows us to calculate the relative light intensity from [V_{Var}], [V_0] and the apparatus input voltage [V_{Max}].

The measuring interface.

We used Arduino as electronic interface for recording measures.

An additional advantage of using Arduino is that he directly gives out the input voltage Vmax and the connection to ground. V= 0

Here's the sketch:

```
//Choose the values of parameters
const int Lapse=1000;  //Choose time lapse between 2 measures (in millisec)
const int Nmis=1800;   //Choose the number of measures to do
const int VvarPin=A0;  //Choose the pin to which connect the potential
                       //(Vvar) to be measured

// Initialize the values of the variables
int Vvar=-1; //"-1"  and "-2" are unphysical value: getting -1 as an output
             //means that the measures are started;
             //"-2" means that the measures are ended
int Cont=1;  //"Cont" is the variable that counts the measure's number
             //Arduino is doing (it starts from 1)

// Initial set up (It will be done just once)
void setup ()
  {
  Serial.begin (115200);   //Initialisation of the serial monitor of Arduino
                           //(where the measures will be written on)
  Serial.println (Vvar);   //Write on serial monitor the unphysical value
                           //(start to measure)
  }

// Cycle (It will be repeated until Arduino is connected)
void loop ()
  {

    if (Cont<=Nmis)   //measuring
      {
      Vvar=analogRead (VvarPin); //Reading the value of Vvar
      Cont=Cont+1;               //Increasing the number of measure Arduino
                                 //will do next time it will repeat the
```

[1]What we mean by "initial" will be clarified below.

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```
                              //cycle
    Serial.println (Vvar);     //Write on serial monitor the value of Vvar
    }

  else              //The measures are finished
    {if (Cont<=(Nmis+1))
       {
       Vvar=-2;
       Serial.println (Vvar);     //Write on serial monitor the unphysical
                                  //value
       }
     else   // Do nothing for the rest of time Arduino is connected,
            // just "wait"!!
       {
       }
       Cont=Cont+1;               //Increasing the counter
     }

   delay(Lapse);        //Wait the chosen time lapse before next measure

}
```

Lapse in the sketch is the time interval between two adjacent measures (in milliseconds), while Nmis is the settled total number of measures that have to be taken.

Arduino is able to collect data each millisecond, however it's not the best option in our case, due to the extreme variability of the phenomena. By trial and error we found out that the most convenient Lapse between two measures should last 1 second.

On the contrary the Nmis should be quite high in order to allow a complete scan of the phenomena even if data analysis issues may occur when the emitted light level goes to zero (and Vvar goes to zero too since Rvar is quite big).Therefore it may be a better choice, instead of a fixed Nmis, to leave Arduino loop indefinitely until Vvar recorded values will turn zero.

As Vvar has been declared as analogic it must be connected to an analogic door (n° …in the sketch) in reading modality. Arduino reads Vvar and gives back an integer between 0 and 1023 corresponding to 0V and 5V respectively.

To convert this value to Volt it should be multiplied by a factor 5/1023.

However it's not strictly necessary since in all the previous equations voltages appear only in ratios. It's therefore possible to measure all voltages in "Arduino units"(numbers only) gaining in simplicity in the data analysis by putting Vmax=1023 and Vground=0

The Experimental setup

As previously mentioned the LDR is very sensitive to the surrounding environment light level and it's also impossible to put it into direct contact to the surface of which you want to study the photoluminescence. This is why we built a "black box" containing both the light sensor LDR and the photoluminescent sample.

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Our box was made of wood (see pictures) but you can also opt for a cardboard one. What's really important in both cases is 1) to avoid any external light seeping into the box (just seal any crevices) and 2) to reduce the contribution to the LDR signal of any reflected light (just paint the inside of the box with opaque black paint or coat the internal walls with black opaque light cardboard.

Fig.4 – The experimental setup

On the upper side of the box drill a hole for the LDR wires. A second hole at the bottom will be necessary for the lamp cable (in case the sample is something different, the hole will be used for the wires of the light source used to excite the photoluminescent material.

It's possible (however not necessary) to put a videocamera inside too through which to monitor the level of emitted photoluminescence of the sample without opening the box. This is particularly useful when the illumination level will drop below the LDR sensitivity.

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In case you decide to use such device you must check whether the photocamera gives off some light of its own either in the visible or in the IR (for instance to adjust the focus). This in fact may

Figura4 - Left: the experimental setup. "The black box" with Arduino on the top. You can notice the photocamera fixed to the front side. Right: detail of the photocamera working .the label reads "you are watching live the photoluminescent lamp inside the box).

actually interfere with the measurements altering the results.

Once all the wires have been inserted, seal any remaining hole with either plastilin or black electrician tape. To test that no light is filtering in run the first measurement WITHOUT the sample. If everything is OK you should read Vvar=0.

Never change the relative orientation and the distance between the sample and the LDR or it will be impossible to correctly compare results as initial excitement conditions or the experiment duration are changed. In order to achieve this design specific and fixed sustains for LDR and sample or just sign the exact position with adhesive tape and paste both sample and LDR down.

Put the LDR as far away as possible from the sample and its sensing surface perpendicular to the incident light coming from the sample.

Take care to make the LDR cables long enough and insulate the two ends of the photoresistance either with electrical tape or thermo shrinking tubes.

To facilitate the setup of the apparatus, make the terminal part of the LDR more strong, roll some tape around it and a metal rod. Put a sign in the point at which it touches the wall of the box in which is inserted so as to reposition the sensor each time in the following session. Picture missing

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The LDR cables will be respectively connected to the power source (5V pin on Arduino) and to Rfix (the fixed resistance) which is ultimately connected to the ground (GRD pin on Arduino) See Fig.1.

Last but not least connect the analog pin chosen on Arduino (see Sketch) to the junction of Rvar e la Rfix. The experimental setup is ready to work.

Data collection

Put the photoluminescent object/sample together with the light source needed to initially charge it. (in our case as we used a night lamp both source and object are the same thing). Switch on the light for the chosen time interval, then start data collection upon switching off the lamp.

In our first measurements the time interval was 30' but we repeated the experiment varying such slot.

In case data collection is not perfectly synchronized with the switching off of the light source, this is not an issue since the data will show a noticeable drop in the value of V (which means a drop in the emitted light) .

However some preliminary tests without the sample (empty box, showed that V value is dropping instantaneously with the switching off of the light but still takes 3-4 seconds before reaching zero (complete dark)

We don't know whether this is caused by a residual light emitted by the light source even after current is no more flowing (like in fluorescent or LED bulbs) or rather a retard in the LDR response. In any case we consider those 3-4 seconds as "response time" of the whole apparatus. This is why in the data analysis we start reading from the 5th experimental point (corresponding to a 5 seconds retard) after the drop in V signalling the switching off of the light. We will consider such point as the initial value for the voltage [V_0].

We will stick to this choice of the first value for V in each of the measurement sessions.

Data collection is run till the voltage values will stabilize on zero. The trend is definitively a downward one although many fluctuations are visible, mainly when the voltage is near zero (sensibility range of the apparatus)

Since the fluctuations near zero go on for a long time, we consider as end of measurements when a series of more than 10 zero values in a row appear. Typically this happens in half an hour or more.

In any case, once the measurement is over, observation of the photoluminescent sample with the naked eye (either opening the box or watching through the camera) actually shows that a residual illumination is still there although the instruments reads zero.

Data analysis

N.B. We used an Excel sheet for data analysis although from a scientific point of view this may not be the best option the software is easy to manage, well known to the students who have it or a similar one (Open office)at home. This is the Excel data sheet:

	A	B	C	D	E	F
1	t	V_{Var}	Lrel (see eq.8)*		Vmax =	1023

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2	sec	mV			V0=	**
3						
4						

- * in Lrel (see eq.8) we put Vmax =1023 in "Arduino units"
- ** V0 is the 5th point immediately after the brusque drop of Vvar registered as the lamp is switched off.

You can see the resulting plot of relative light intensity VS time. (see graph in fig.6)we plotted also the best fitting curve (exponential)

The best fitting curve exhibits a correlation coefficient which is definitively < 1. However its observation brings to some useful considerations about the graph: the light intensity drops quite fast, actually faster than any exponential curve and then slows down. In this last area of the curve the exponential fits the data perfectly

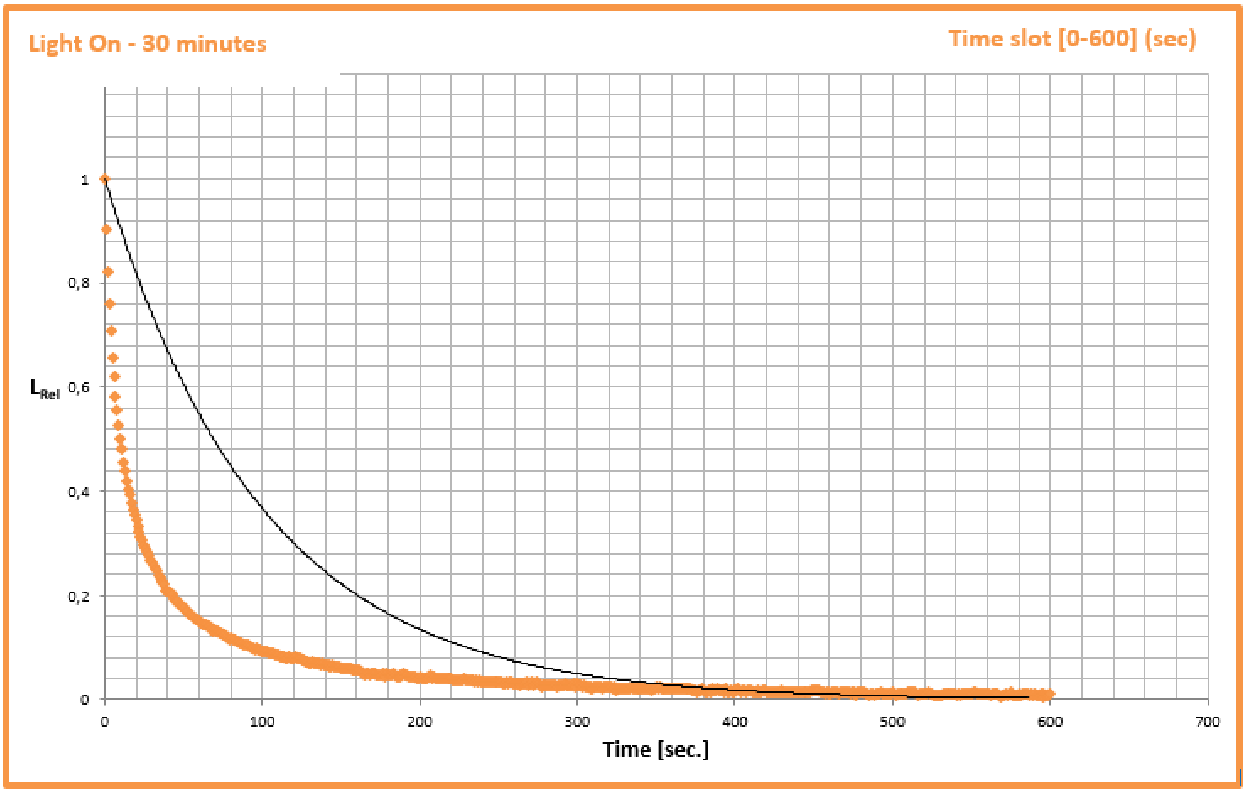

Fig.5 - Graph 1

We decided to delve a bit deeper into this and we proceeded further with the analysis of the data divided into groups of 50 consecutive experimental points. We then plotted each subgroup of 50 data in a graph of their own. The new decreasing exponential best fit curve calculated on each subgroup data was fitting perfectly! (correlation coefficient > 0,95). We did this analysis for a total period of some hundred of seconds. See graphs 2 and 3

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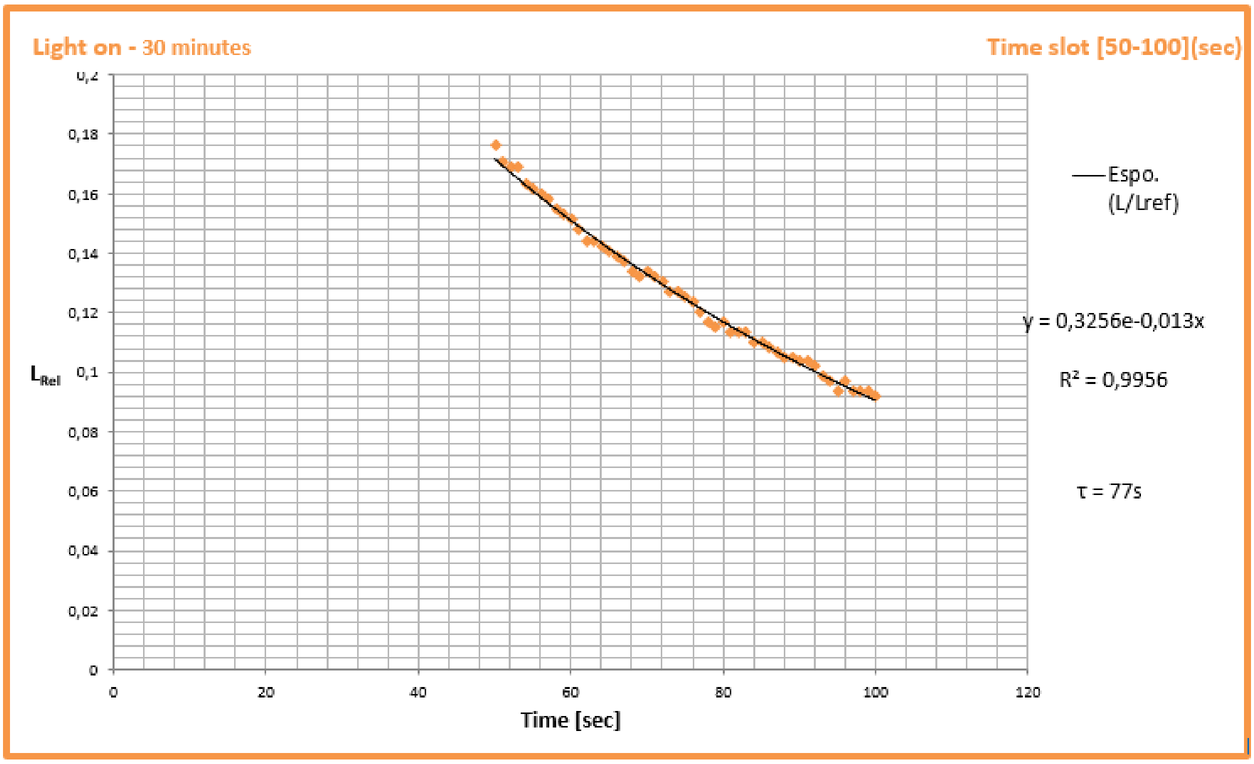

Fig.6 - Graph 2

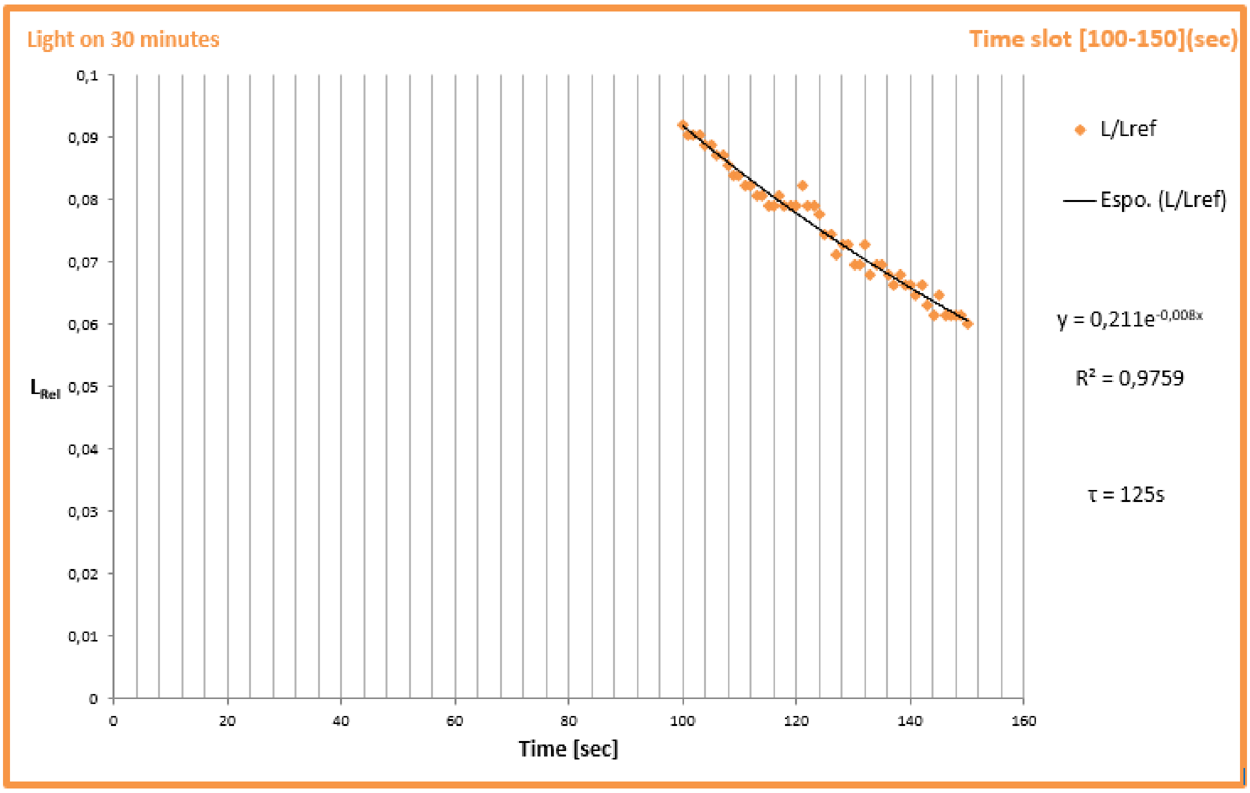

Fig. 7 - Graph 3

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If we extract the time constants[9] from the different interpolating curves, we notice that their trend is an increasing one[10], therefore confirming the initial observation of diminishing decay speed rate in the light intensity. See the time constant (τ) in graph 2 and 3.

If the time is beyond 5-600 seconds the fluctuations become so relevant (relative to the very low values, almost zero) that it becomes impossible to go on with the analysis of data subgroups, since the best fit curves are no more reliable (low interpolation coefficient[11]).

To overcome this issue we have smoothed the data series by substituting each of the measured voltages the average obtained by the following nine data: the 4 previous ones, the data itself and the 4 following ones. With this approach the new curve appears far more regular even at 1000 sec and beyond. If we analyze the 50 points subgroups in this new curve we still see all the previously described aspects.

Conclusions

The experiment confirms what we expected from theoretical knowledge: the light emission from the photoluminescent sample diminishes initially very fast and then slows down and goes to zero quite slowly.

We have repeated the experiment many times varying the time interval during which the recharging light source is on. We went from 5 to 8 minutes and beyond. Each time the trend was as described above.

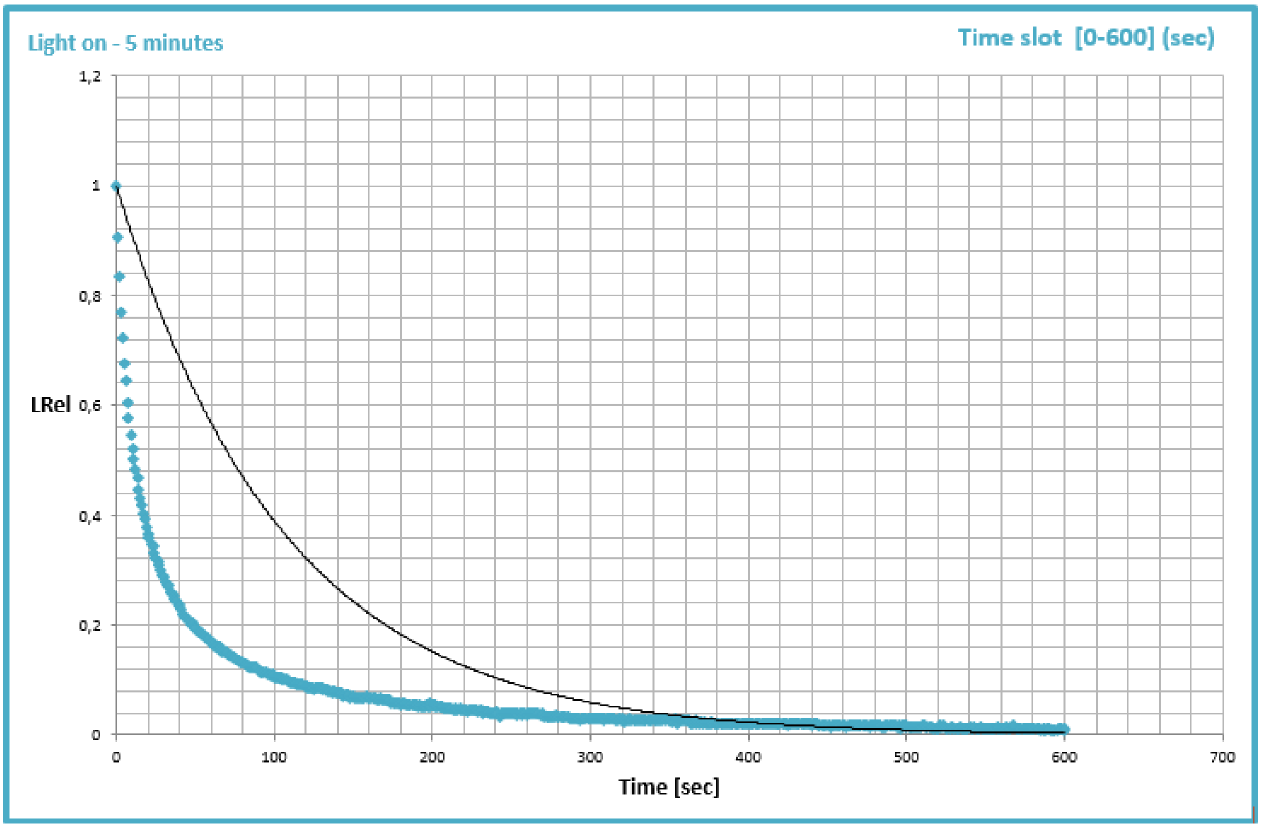

Fig. 8 – Graph 4

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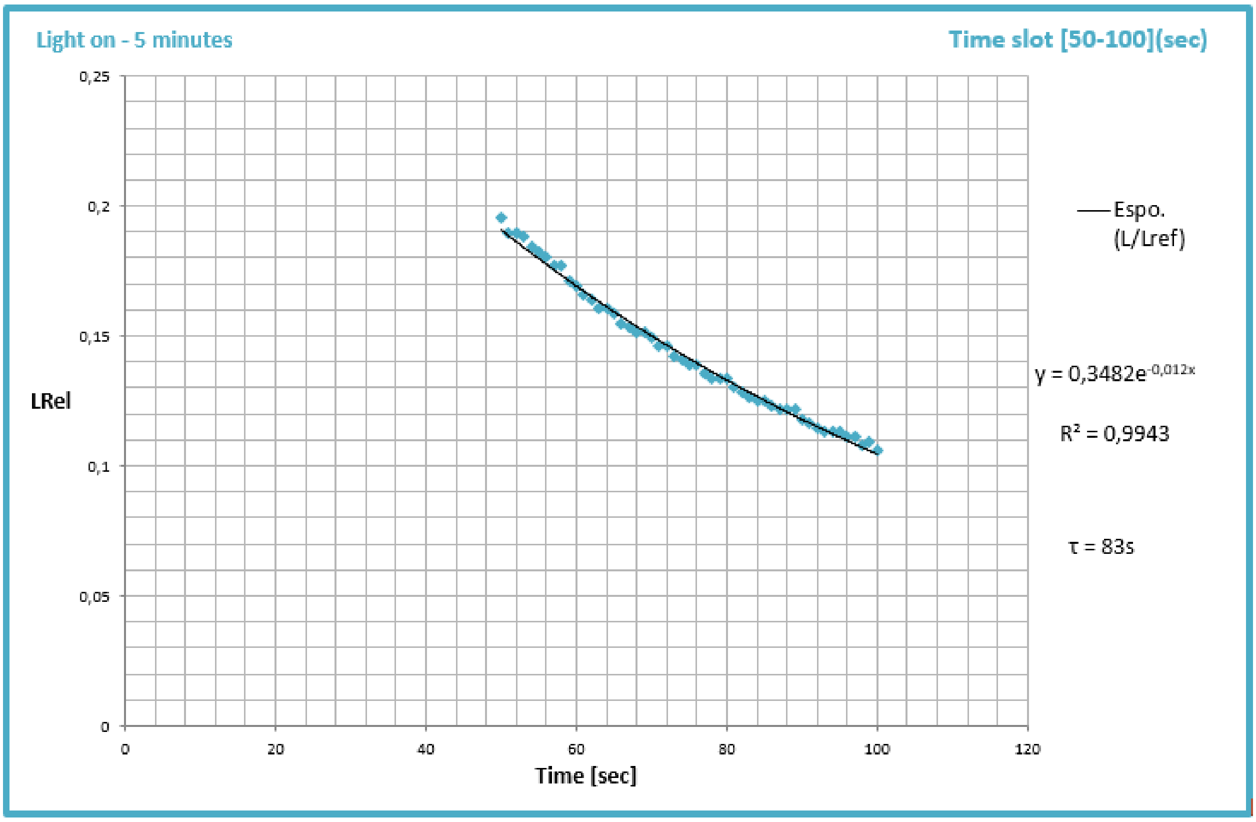

Fig. 9 - Graph 5

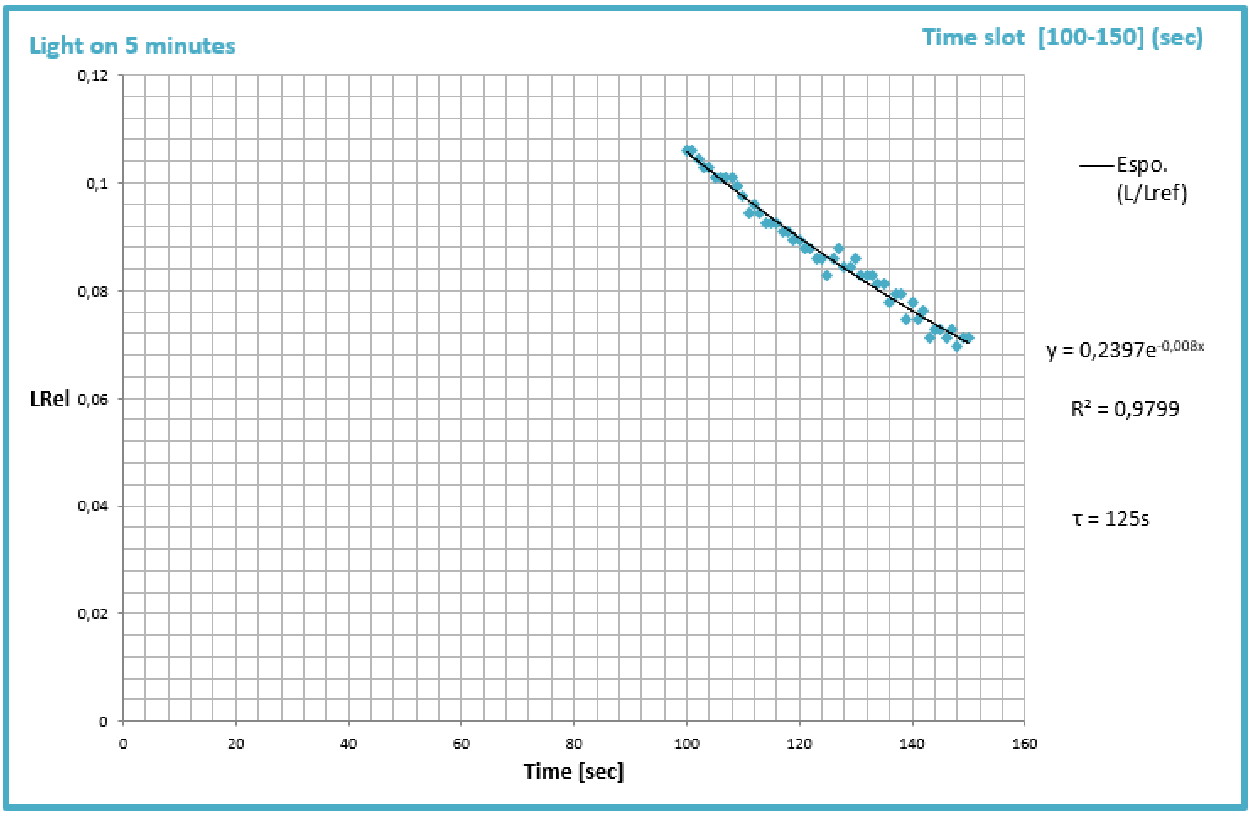

Fig. 10 - Graph 6

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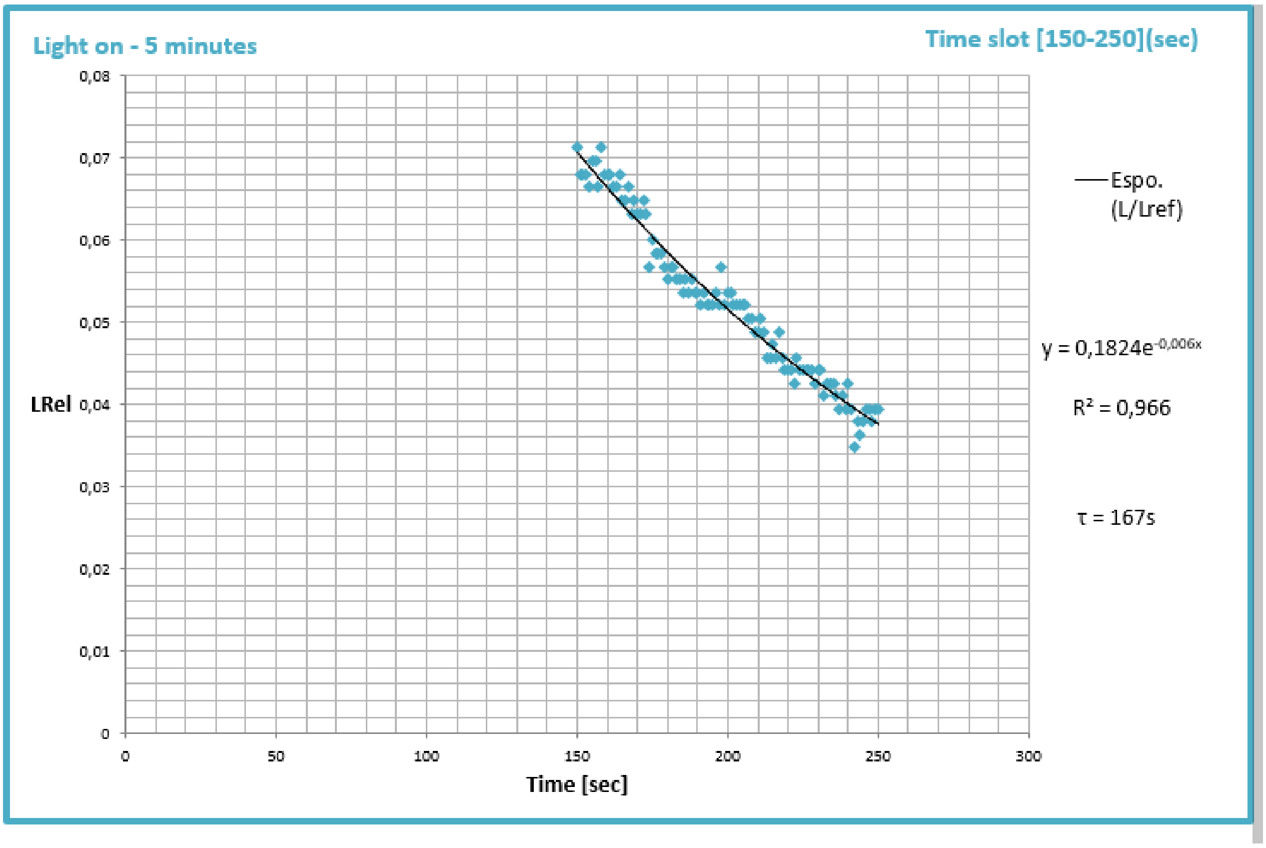

Fig. 11 . Graph 7

Quite surprisingly the time constant doesn't not vary that much. They slightly increase along with the length of the time interval during which the bulb is on. However their increase is much less impressive than the time slot one (one hundred time increase)See the time constants(τ) in the above graphs 2-3 and 5-6 respectively

Such a behaviour may be a clue to the fact that the excitation of the electron levels, which ultimately causes the photoluminescence, saturates very quickly and therefore such an effect is substantially independent, once a minimum level has been reached, of the photoluminescent material "charging time"

References

See Background reading.

Where to get the materials

- Online or @lucedentro

Acknowledgements

[1] Lucedentro – Luca Beltrame – who generously offered samples and a lamp for our tests http://www.lucedentro.com/

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