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HYPERSPECTRAL CHARACTERIZATION OF FLUORESCENT ORGANIC CONTAMINANTS ON OPTICAL PAYLOADS

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I. INTRODUCTION

The increase of performance of new optical instruments for science and Earth observation always leads to higher requirements in terms of contamination due to particle sedimentation in cleanrooms and deposition of chemical species in vacuum environment. Specific cleanliness control procedures are implemented in order to mitigate the risks of contamination on optical sensors and sensitive diopters, especially when used for UV applications. Such procedures are commonly carried out in cleanrooms and are described in both European ECSS-Q-ST-70-50C and NASA SN-C-0005D standards. UV light at 365 nm is often used for the inspection of optical sensitive surfaces to localize and to evaluate the amount of fluorescent particles, essentially coming from textile fibers. But other groups of compounds can be observed with a different spectral response and distribution, like adhesives and resins or even organic residues. Therefore, we could take advantage of this spectral information closely linked to specific molecules for partial identification of these materials before further investigation involving wipe on flight model and measurement in a laboratory.

II. FLUORESCENCE OF SOLID STATE MATERIALS

A. Definitions and background

According to the IUPAC (International Union of Pure and Applied Chemistry) definition, the luminescence is a “spontaneous emission of radiation from an electronically or vibrationally excited species not in thermal equilibrium with its environment”. Fluorescence is a luminescence generated by photons.

“…not in thermal equilibrium with its environment…” means that we have to provide the energy to the sample with an excitation source in the absorption spectrum of the sample. After interaction with the studied material, the energy is going to be released in different ways. Among several conversions in the material, some photons can be generated by the atom de-excitation. We can collect them and characterize their energy which is directly linked to the energy levels in the material (vibrations, rotations…). This is the fluorescence emission spectrum.
Part of the energy of the exciting photon is lost before the emission and there is an energy shift, called the Stokes shift, from short to higher wavelengths between absorption and emission. The Jablonsky diagram and Morse curves [1] [2] [3] both describe the possible quantified energy levels that can be reached in order to excite each species in the material spectrum. In addition, it describes the energy of the photons that can be emitted and therefore the shape of the emission spectrum. For molecules (organic contaminants in our application), there are not only electronic but also vibrational and rotational levels which strongly influence the shape of the spectral bands. The X-ray fluorescence principle means high excitation energy of the electrons (50KeV) localized in the highest energetic levels of the atoms close to the nucleus (K, L, M levels) whereas only the valence electrons are excited in the UV/vis fluorescence of molecules (1 to 5eV). Only covalent and coordinate bond can fluoresce in the UV/vis range of the electromagnetic spectrum. On the contrary, ionized molecules do not fluoresce. There is also a fluorescence behavior in crystals including impurities like ruby and its specific red color, and in some nanoparticles. The emission spectrum of these two examples shows quite narrow bands compared to huge molecules which have numerous complex vibrational and rotational levels. In the UV/vis range (1 to 5eV), luminescence is related to the band gap of the semi-conductors and to the HOMO-LUMO [1] transition in molecules as described in Fig 1.

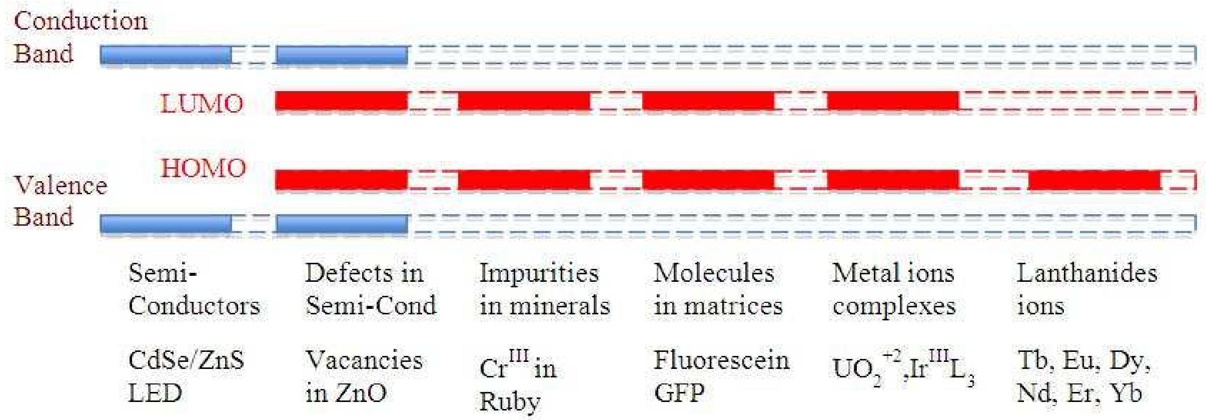


Fig. 1. The luminescence is associated to the transition of an electron from the Conduction to the Valence band in semiconductors[3], from the LUMO to the HOMO levels in small emitters [2] and between magnetic sub-levels of the LUMO for Lanthanides[4]

A good example in space applications is the alumina a of CCD detectors package used for Earth observation that fluoresces in a quite narrow red line when irradiated with 450 nm excitation wavelength and the adhesive of the protection window which shows a wide and smooth spectrum at around 550 nm.

The absorption of diluted emitters follows the Beer-Lambert law. In case of fluorescent molecules in solution, the fluorescent flux increases with the density of bright molecules but at high absorbance most of the excitation is absorbed in the first layer (see Fig 2). On the contrary, if fluorescent particles are isolated, they can be discriminated and even counted as it can be seen in Fig 3.

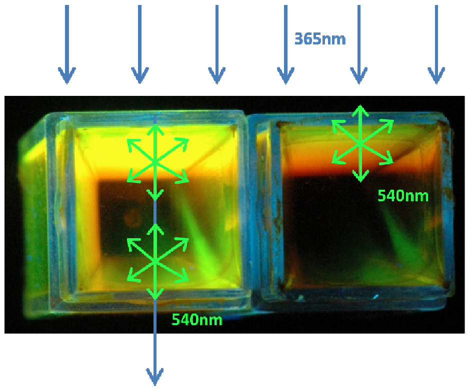


Fig. 2. Transmission of fluorescein in aqueous solution for high concentration (right) and low concentration (left). On the right cell, the absorption due to the fluorescein is strong and there is a saturation of the fluorescence. On the left cell, the concentration is optimized to balance absorption through the overall cell. The yield is better for this lower concentration.

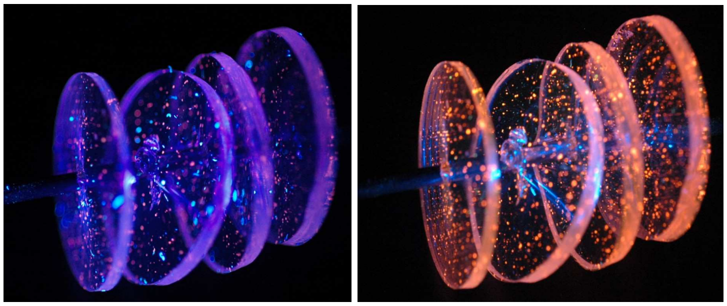
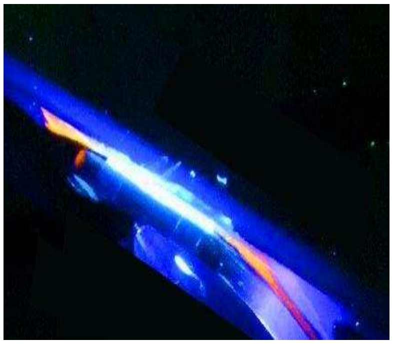


Fig. 3. Nanoparticles in MAPSIL213 irradiated respectively from left to right with 365 nm and 450 nm excitation sources. On the left, nanoparticles have a low emission due to their weak absorbance at 365 nm. On the right the excitation is optimum. We can also see the emission of textile particles due to the brightener included in washing powders.

Organic contaminants and particles involve a significant decrease on detectors sensitivity and optical diopters transmission. These contaminants can be due to the outgassing of polymers in vacuum conditions. If these materials have a specific fluorescent behavior, it is obvious that it can be useful for inspection. Furthermore, the fluorescence of the alumina used for CCD package and some doped glasses in dioptric systems can generate an unexpected background in the detection as shown in Fig 4. This phenomenon should be considered in very low flux instruments design.



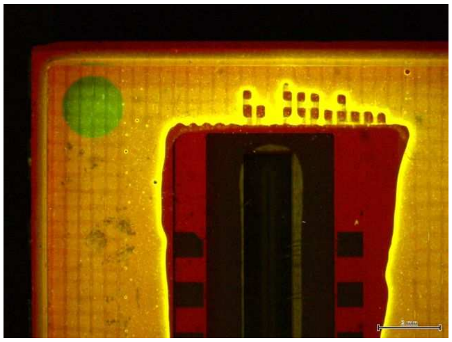


Fig. 4a. Picture of the rear side of a mirror taken with a classic reflex camera in visible light (excitation 365 nm). The red fluorescence corresponds to the primer and the blue color to the adhesive.
Fig. 4b. fluorescence of particles in the bulk of a glass. **Fig. 4c.** SPOT3 detector (glass fiber preform highlighted)

A first research activity on the fluorescence of materials was carried out in 2010 and the results presented at the ISMSE symposium in 2012 [6]. The goal of this study was to synthetize the theory on fluorescence of solid state materials in particular and also to measure the response under irradiation of several common polymer materials found on payloads, generally close to sensitive optics : adhesives: Scotchweld EC2216, Scotchweld DP490, Dynaloy 325; rosin flux; white paints: MAP SG120FD, MAP SG121FD; and varnishes: Solithane 113, MAPSIL213B.
The absorption and the emission spectrum measurement for each excitation wavelength from 200 to 800 nm showed a specific spectral signature for each of them indicating that it is possible to identify at least these 8 materials only with their fluorescence behavior even though a full identification with conventional techniques such as EDS, X-ray fluorescence or FTIR spectroscopy is necessary to go deeper. But standard laboratory techniques cannot really be carried out on satellites without any contact. That is why we are developing a new device to acquire the fluorescence signal, in situ and contactless.

B. The fluorescence yield

The quantum fluorescence yield is defined as the ratio between the number of emitted photons and the number of absorbed ones (1). It can be related to some fundamental properties of the material. k_f, k_{ci} and k_{cis} are respectively the fluorescence rate, the internal conversion and intersystem conversion rate constants.

$$\Phi_f = \frac{k_f}{\mathrm{k_f} + \mathrm{k_{ci}} + \mathrm{k_{ics}}} = k_f \tau_{s1} \tag{1}$$

Fluorescence yield goes from 1E-4 (considered as non-fluorescent species) to 5E-1 (which is considered as a good fluorescence yield). To measure the fluorescence flux, it is important that the molecule have a very low interaction with the others in the bulk . In medicine and forensic science, the fluorescence molecules are chosen for their very good yield and in solution in a particular solvent. For our materials (resins, paints and adhesives…), the yield is strongly affected and can be inhibited by the link between the different molecules in the formulation of the polymers. So, it is really impossible to quantify the fluorescence yield in solid state materials containing a great amount of chemical species which all interact with each other. Moreover, it is difficult to know exactly the nature of the additive products the manufacturers use. Previously and according to the literature [2] we thought that the fluorescence of the materials we use for space applications was due to the conjugated bonds in the polymer itself but the study [6] showed that it is probably the additive molecules that are mainly responsible for the fluorescence of the 8 tested materials. In addition, the non-fluorescent molecules in the bulk can also absorb.
Thanks to our first study [6], we know, that 257 nm is the common excitation wavelength. But the better compromise to cover all the needs with a good yield is to use at least 3 exciting wavelengths from 250 nm to 450 nm. We also have defined the interesting reemission spectrum limits from 300 nm up to 700 nm for the

materials we use for space applications. The UV range is the most interesting one and needs a higher resolution that the visible range.

C. Examples of fluorescent materials used for space applications

The following Fig 5 show the excitation and emission spectra of eight samples measured during the previous study [6]. The UV emission from 300 to 450 nm is significant. Different fluorescent molecules can be identified in EC2216 and Solithane 113. We can notice a spectral width of the two fluorescent molecules in MAP SG121 at 390 nm and 510 nm and the inhibition of the oxygen vacancy in MAP SG120 compared to the next generation MAP SG121. We do not notice modulations due to aromatic bonds in relation to bibliography [2] (these modulations can be inhibited or blurred by interaction between molecules).

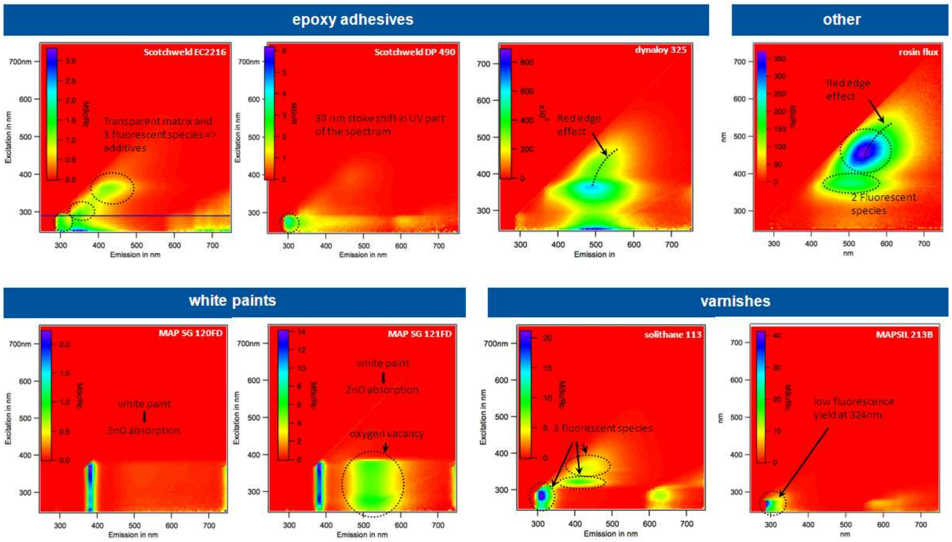


Fig. 5. Absorption and emission spectra of common organic materials for space applications

D. Needs for contamination inspection in cleanrooms

When an organic deposit is suspected on a sensitive surface of a flight model, any contact is forbidden and no representative samples are available for characterization in a laboratory. A very convenient solution would be to irradiate the area of interest with excitation wavelengths and then to acquire the spectrum from UV to visible wavelengths. It is also important to get information about the location of the organic residues. Therefore a hyperspectral instrument is the solution.

Our ambition was first to build a UV/vis sensitive camera with a catoptric objective, a filter wheel and three excitation sources. This is a quite easy set up for high resolution imaging and location in a reasonable period of time for a preliminary investigation. Then, a long exposure measurement could be carried out to acquire a lower imaging resolution but a continuous spectrum simultaneously. The two following chapters will describe the development on progress for this purpose.

III. FLUORESCENT IMAGING TELESCOPE

In our laboratory, we designed a small Cassegrain spherical telescope with the following specifications:

- 50 cm to infinite working distance
- Standard high resolution CCD for astronomical applications (no IR filters, cooling system, long exposure etc…)
- 8 filters: 340, 360, 400, 450, 500, 550, 600, 650 nm
- A motorization to focus and to correct the variation of optical path through the filters, especially for short wavelengths
- 3 coaxial excitation sources at 257, 370 and 450 nm

The following pictures, Fig 6, show an example on a PLEIADES detector. We can notice the fluorescence of the window adhesive at 550 nm and the aluminum nitride of the substrate at 650 nm. Some few fibers can also be seen. But the spectral information in too limited with 8 filters to go further in the interpretation. To increase the spectral resolution, we need to see the shape of the fluorescence spectrum to isolate the narrow line of the alumina from the adhesive on the third picture.

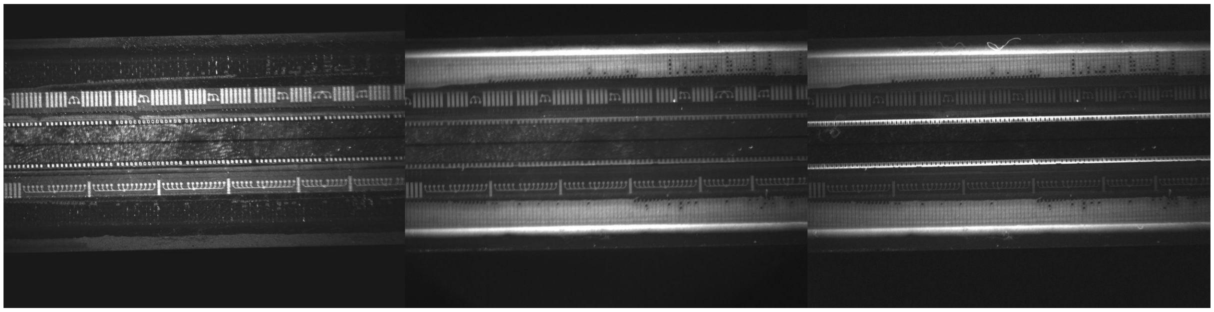


Fig. 6. PLEIADES detector from left to right: 450 nm excitation wavelength filter (1s), 550 nm filter (20s) and 650 nm filter (45s). Dark subtracted but no Flat correction.

IV. DEFINITION OF A HYPERSPECTRAL INSTRUMENT

According to the characterization of some materials (Fig5) and first images with the telescope, we defined the following performances for a hyperspectral instrument:

- 50 cm to infinite working distance
- 200 x 200 pixels spatial resolution in a 20 x 20 mm field
- At least 80 wavelengths from 300 to 700 nm. 5 nm resolution from 300 to 450 nm, 10 to 20 nm in the visible part of the spectrum to fit with Fig 4 measurements

Fourier transform spectrometers are very high resolution and bright instruments but very difficult to build for UV and very sensitive to vibration. It would be a complex solution. Gratings spectrometers are not optimized for wide spectral bandwidth. Finally the dispersion of a prism seems to be very adapted to our needs with higher dispersion under 400 nm than in the visible part of the spectrum.

The needs in terms of image quality and spectral requirements lead us to the configuration, as shown in Fig 7. To avoid problem of chromatism and transmission in a wide spectral band (300-700 nm), the best solution is to design a full catoptric instrument. Obviously, the dispersion of the prism involves the use of a slit which limits the field in one dimension. Then a scan is necessary to rebuild the two dimensions for each wavelength. Off-axis solutions are good for one dimension detectors but not so much for imaging (except with at least 3 mirrors). So, only the mirror M6 is off-axis parabola shaped.

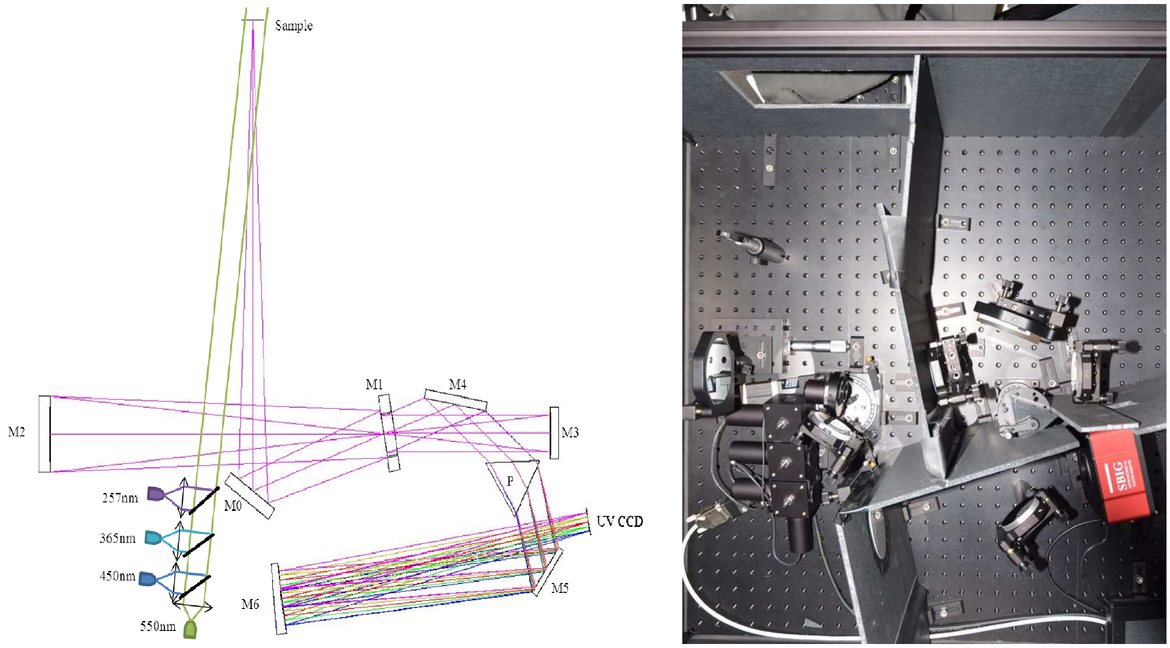
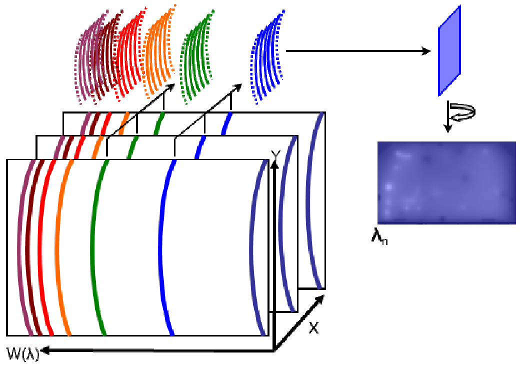


Fig. 7. Spectrometer: Ray tracing and bench in development at CNES

The limitation of this design is the crossing of the glass through M1 slit mirror. The axial chromatism is insignificant but this element introduces also astigmatism. The depth of glass crossed by marginal rays through

M1 is not the same for both directions. This is the reason why M1 tilt is reduced to a minimum of 10° (Fig 7 and Fig8). The reduction of this angle is also an opportunity to introduce the scanning mirror M0 and to optimize the working distance.



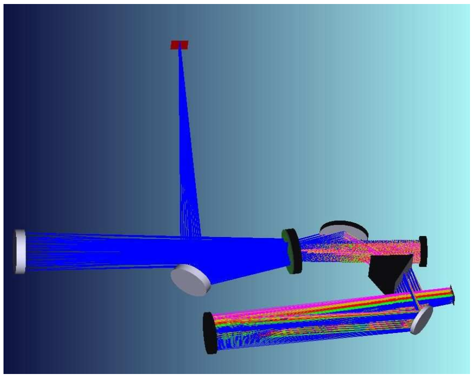
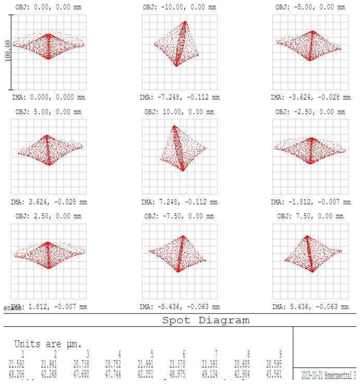


Fig. 8a. Image reconstruction. **Fig. 8b.** 3D view of the beams for 5 points in the vertical field of view and their corresponding projections for 5 different wavelengths

An example of a single raw image acquisition on a reference low pressure calibration lamp (Hg and Ne) can be seen in Fig 9.



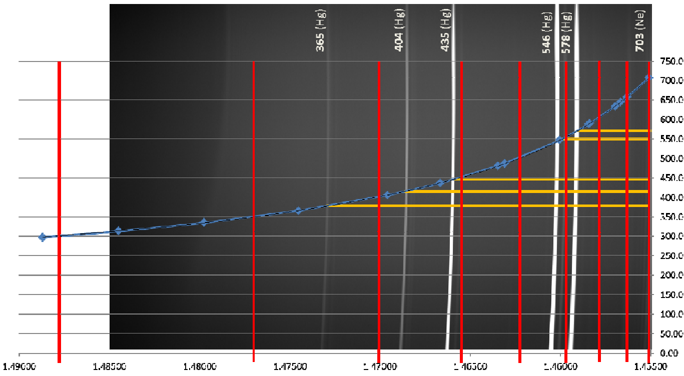


Fig. 9 a. Spot diagram for all fields, one wavelength. **Fig. 9 b.** Real spectral calibration image

The smile is more important for a higher aperture and has to be corrected in order to reconstruct the cube image. The slit is narrow and constant along the vertical field of view. The image quality is preserved in the field. Residual optical aberrations can be seen in the simulation (Fig 9) with parabolas version and off-axis imaging (M3 and M6 in Fig 7).

The first raw hyperspectral image at 550 nm, extracted from the cube data composed of 70 pictures can be seen on Fig 10. In the field (20 x 20 mm => 211 x 211pixels), the two white paints MAP SG120 and SG 121 (new generation) can be seen and their spectrum can be extracted. Darks have been subtracted. The uniformity due to the optical system and illumination source has not been corrected yet.
The camera is a front side illuminated CCD at that time : that explains the limitation at 340 nm. The two spectra are raw spectra, not corrected regarding the spectral sensitivity of the detector. Therefore, the excitation wavelength is very low on the graph. We can see the two emission wavelengths in accordance to Fig 4 characterization: a narrow fluorescent emission wavelength at 390 nm and a smooth large band around 550 nm with different Stokes shift and yield between the two generations of white paints.

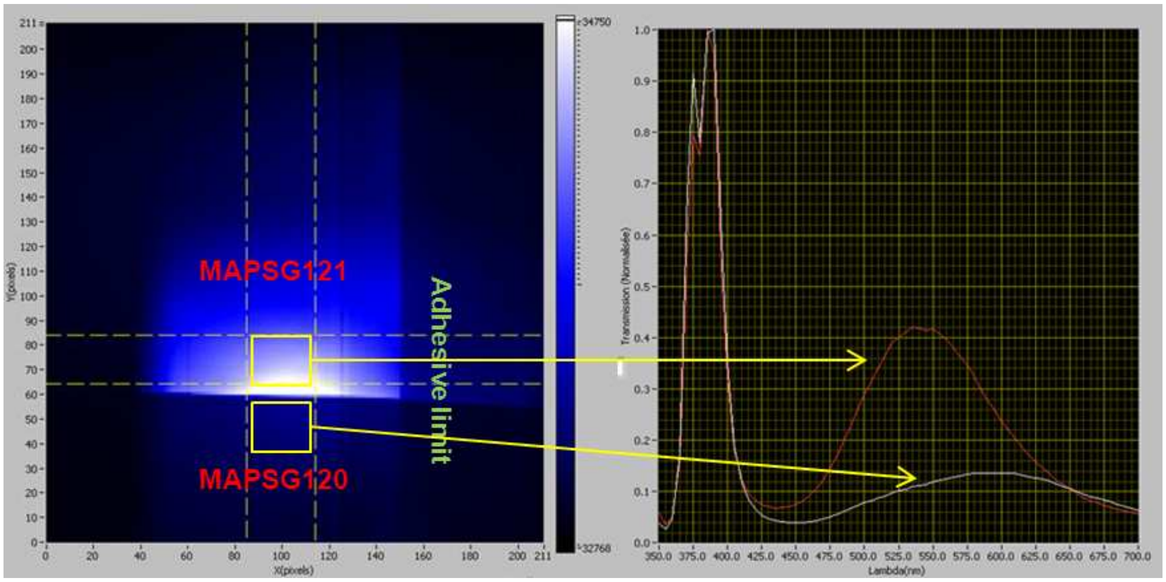


Fig. 10 a. Picture at 550 nm extracted from the hyperspectral cube. **Fig. 10 b.** Spectrum extracted in the other direction from the two yellow rectangles

V CONCLUSION

The raw acquisition with the first bench of a hyperspectral instrument presented in this paper shows that it is possible and interesting to acquire, in a wide range spectrum (from 300 nm to 700 nm) a rather good image resolution in the direction of the slit, to build up a cube image composed of 80 wavelengths and 200 x 200 pixels at least. Calibrations, corrections and radiometry measurements have to be carried out, but this first hyperspectral image acquired with spherical optics "on the shelf" validate the optimum design composed of aspheric and lower radius of curvature mirrors for an application compliant to the characterization of the fluorescence of organic materials, on flight models.

The main limitation in terms of image quality is due to the astigmatism induced by crossing the glass of the slit mirror. However, this design is a good balance between a medium resolution imaging and an instrument bright enough (no central obscuration) to identify and locate some organic in flight model. A version with a hole in the slit mirror can be used if the central obscuration and the working distance are compliant with the integration time. The solution with the hole in the slit mirror is best for long working distances.

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