

TIE-36: Fluorescence of optical glass

1. Introduction

Fluorescence is a phenomenon in which a substance absorbs light of a certain wavelength and almost instantaneously radiates light at longer wavelength (lower energy). These processes are known as excitation and emission. Many substances, organic as well as inorganic, can exhibit fluorescence.

Other designations of fluorescence are “primary fluorescence”, or “autofluorescence”, which is usually used by optical designers and microscopists. In certain optical applications using active lighting, like e.g. lamps or lasers, the usage of fluorescing optical materials may decrease the contrast. Especially in applications, where the fluorescence of fluorophores or dyes is detected, the fluorescence of optical components is generally not desirable, as it falsifies the detected signal (fluorescence of optical components as major source of unwanted light in an image).

Fluorescence in optical glass is for instance generated by point defects like color centers, which are known to be originated by rare earth elements, and certain impurities [1,2,3]. The fluorescence behavior of a glass can be influenced by either process technology or use of higher purified raw materials.

Usually, standard optical qualification takes into account initial absorption (also named internal transmission), the induced absorption (laser resistivity, solarization) [4], and fluorescence [5], for example. Typical light sources applied for these kinds of measurements are UV-lasers and high power Mercury, Xenon- or Deuterium-lamps. As the last two strongly depend on measurement setup and parameters, our metrology has been enhanced to allow customized measurements, e.g. to provide fluorescence spectroscopy with various excitation and detection characteristics.

2. Origin of fluorescence in glass

When optical material is exposed to light, a certain part of it is usually absorbed by the glass or impurities. Most of the absorbed is transformed into vibrational energy, generating heat, but a part of it can be re-emitted as light of different wavelength. As mentioned above, the emitted light typically either originates from color or defect centers in the glass matrix or from certain impurities.

In typical non-radiative energy relaxation, the excited electron relaxes via generation of phonons (solid state vibrations), appearing as heat. In contrast to non-radiative decay, in fluorescence the excited electron decays to the ground vibrational level of the electronically excited state and then returns to the ground electronic state by emission of light of lower energy (longer wavelength) than the absorbed light.

There are two major types of luminescence, which can be distinguished by the lifetime or decay of the excited state, which is e.g. typically several ns to μ s for fluorescence or in the ms to s range for phosphorescence.

The efficiency of energy transfer of absorbed light to emitted light, known as quantum efficiency, strongly depends on the excitation wavelength. It usually has a maximum close to absorption bands, at direct absorption bands of the emitting species.

In case of glass, e.g. the observed UV excited fluorescence correlates strongly with the content of UV absorbing ions in the material like rare earth elements, Iron, Zinc or Vanadium [6].

There are two independent origins of fluorescence:

The so-called elementary fluorescence displays the optical absorption and emission of impurity ions, e.g. rare earth elements and lead Pb^{2+} . These elements absorb and emit nearly independent from the glass matrix.

Optical transitions from the ns^2 -levels ($n=1,2,3,..$), related to structural units of the glass matrix, like e.g. SbO_3 , AsO_3 or ZnO , behave in a different way. Here the glass matrix and the processing (oxidation and reduction) have a strong influence on the absorption and emission characteristics.

3. Methods of Characterization

The typical measurement procedure at SCHOTT is shown in figure 1: For excitation a 450 Watt Osram type lamp delivers a broad band radiation spectrum from 200 to 1500 nm with maximum intensity between 250 and 650 nm. The same wavelength range is mainly used for excitation in typical fluorescence applications. For excitation, typically a narrow part of this wavelength range is selected and guided to the sample box by a double monochromator system. The monochromator further enables a high noise reduction and thus a signal to noise ratio better than 4000. The spectral linewidth of the excitation is 5nm FWHM (full width half maximum). The modular setup of this equipment allows an easy change of the excitation source. On request, excitation via LED lamp is possible having typical linewidths of 20-30 nm FWHM.

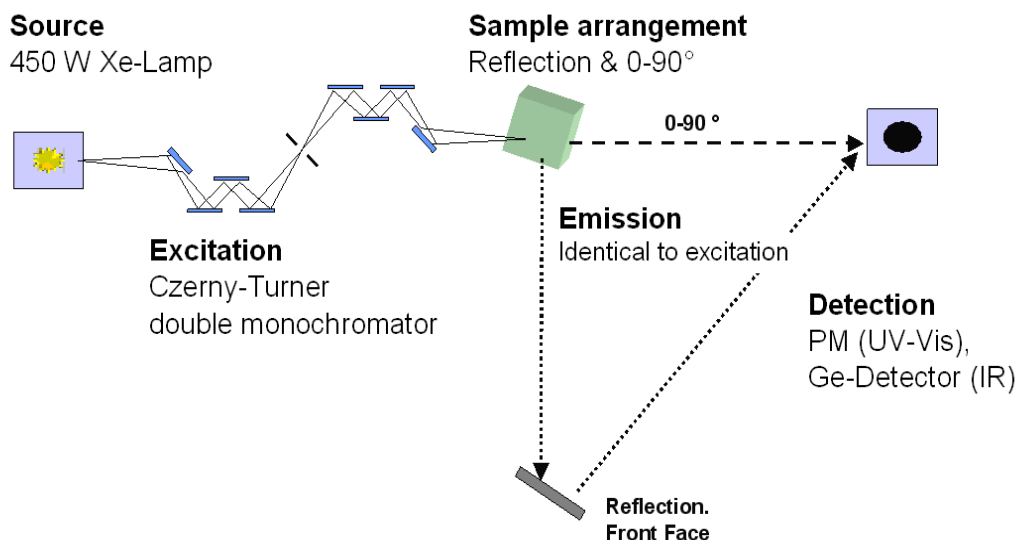


Figure 1: Setup of the fluorescence spectrometer Jobin Yvon Fluorolog 3. The arrangement allows flexibility in geometry and excitation source. Due to the double monochromator concept no filters are required

For emission detection, one can choose between UV/VIS and IR-channel. At SCHOTT, the typical spectral range for fluorescence emission is 300 nm to 850 nm. For UV/VIS detection a photo multiplier is used, whereas the IR-detection is based on a germanium detector. Alternatively, pulsed excitation and a corresponding detection are also possible.

The detection efficiency not only depends on the excitation, but also on the proper choice of sample geometry as well as cut-off filter settings. The latter are required to cut off the excitation wavelengths.

4. Accuracy of method

For quantitative measurements the grating efficiency has to be evaluated using different types of calibrated standards from Starna (Starna Company (Essex, UK) and BAM (Bundesanstalt für Materialforschung und -prüfung [Berlin, Germany])). The grating consists of 1200 lines/mm and has its maximum reflection efficiency at 420 nm due to blazing of the grooves (fig. 2). For further measurements the spectrometer software allows us to correct the original spectrum with a flat line spectrum simultaneously. One has to consider that the numerical correction is most accurate in the range of the maximum sensitivity and decreases with the loss in sensitivity. The sensitivity range defines the detectable wavelength range. This means that emission between 300 and ~850 nm can be investigated.

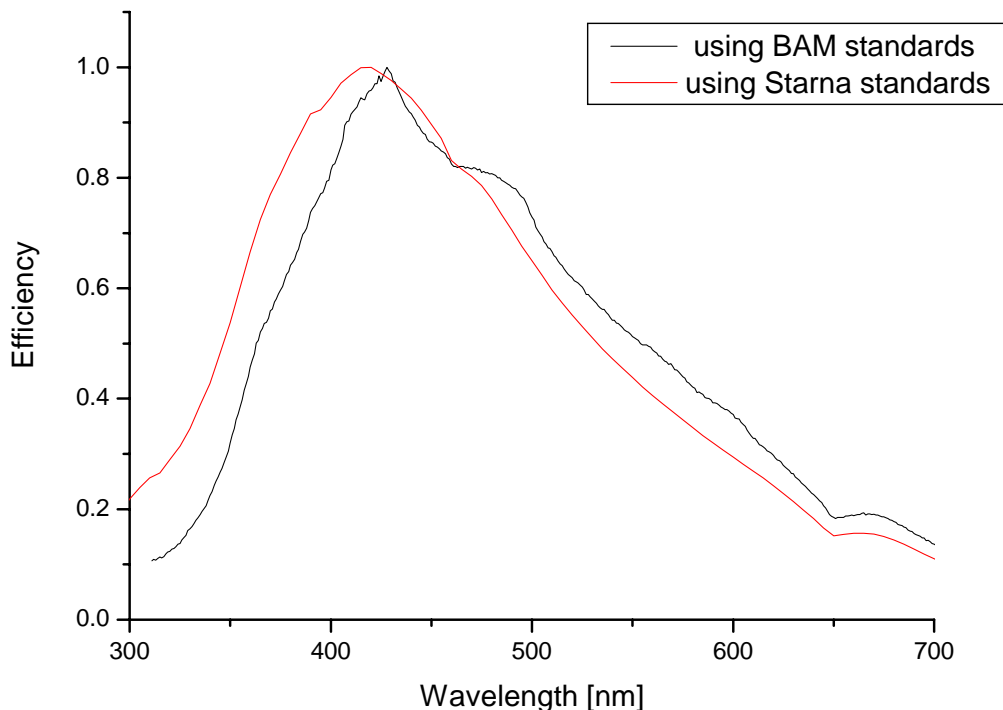


Figure 2: Efficiency for 1200 lines/nm grating and the PM detector. The maximum efficiency is observed for appr. 420 nm.

With this setup emission spectra, as well as excitation spectra can be obtained. The [emission spectra](#) are recorded by keeping the excitation wavelength constant and detecting the spectrally resolved fluorescence signal. In contrast, for [excitation spectra](#) the detected emission wavelength is kept constant but the excitation wavelength spectrally tuned.

For wavelength calibration and determination of the wavelength accuracy, e.g. emission, excitation and absorption spectra of certain doped samples, exhibiting narrow band absorption or emission can be used. In figure 3 these spectra are visualized for a CaF₂ crystal doped with 485 ppm TmF₃. Doped CaF₂ is used because it exhibits a higher light yield compared to optical glass and can therefore be used even for less sensitive fluorescence spectrometers.

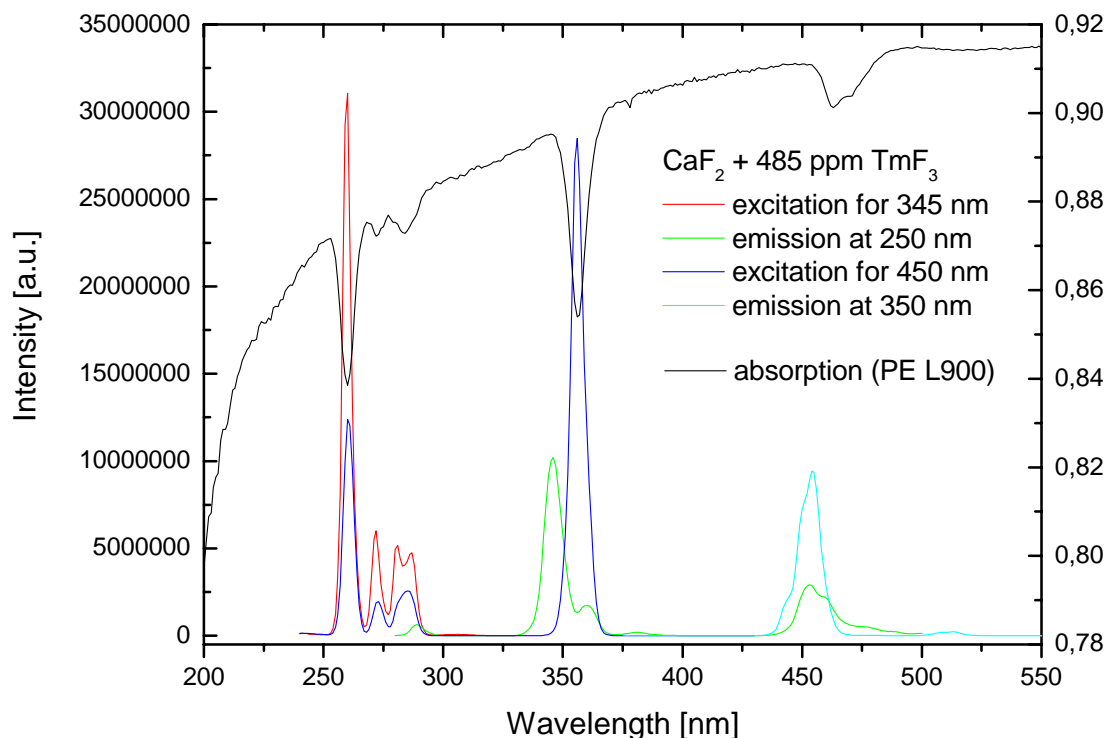


Figure 3: Absorption, excitation and emission spectra of TmF₃ doped CaF₂.

The results of our measurements have been compared with theoretical and analytical data from literature [1-4,6]:

In this example, the peaks of absorption (or transmittance) and excitation spectra are exactly at the same spectral position, proving that the observed absorption bands are responsible for the fluorescence at 345nm or 450nm. Therefore the consistency of absorption and excitation spectrum becomes visible. The emission peaks at 350 and 450 nm are situated at the same position as expected from the literature and known from optical glass when excited with 250 and 350 nm respectively.

The accuracy of the spectrometer has been evaluated using certified standards. In figure 4 the emission spectra of Quinine Sulphate certified by NIST is shown. We observed accuracy better than five percent for the FLUOROLOG 3 spectrometer.

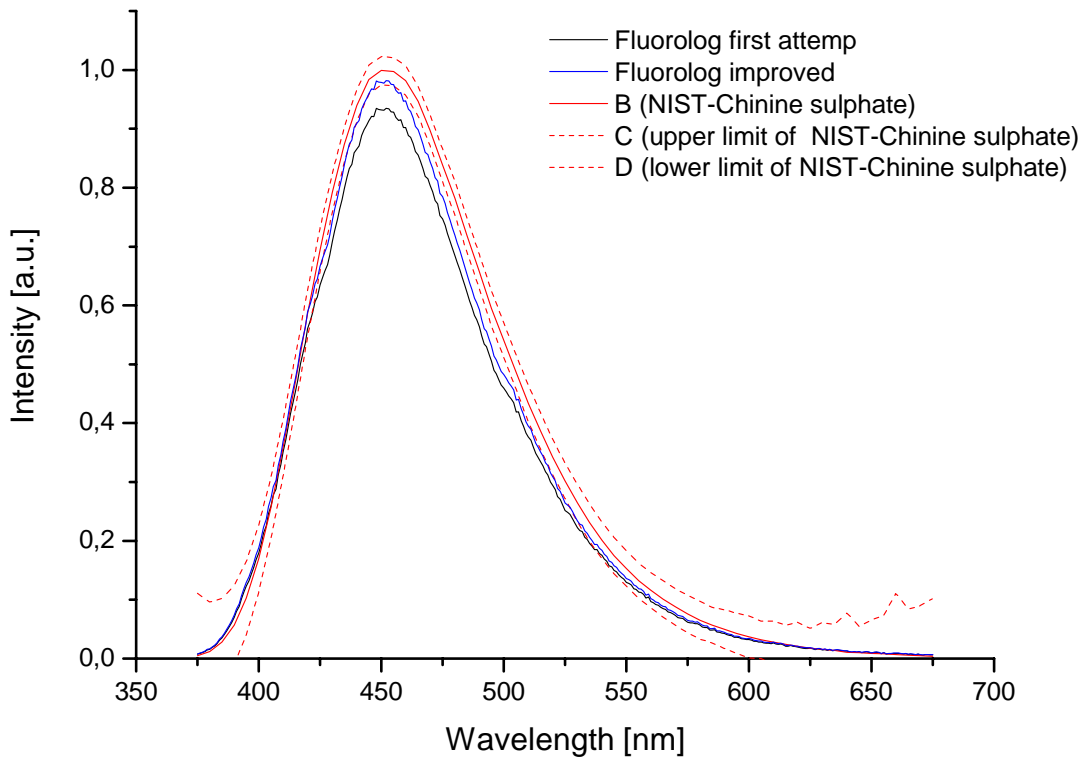


Figure 4: Emission spectrum of NIST certificates fluorophore Quinine Sulphate.

5. Fluorescence results for optical glass

5.1 UV excited fluorescence @365 nm

To classify optical glasses regarding fluorescence, emission spectra of samples excited by the mercury excitation line at 365 nm have been investigated. The results are shown in figure 5a for different glasses using identical setup parameters (slit widths, integration time, detection regime). The emission spectra have typical maxima at e.g. 435 and 525 nm depending on the material composition of each glass type. The differences in features for N-type glasses are arising by the elimination of PbO and As₂O₃, which is substituted by Sb₂O₃, or ZnO as reported in [3,4,6].

The most common method to compare the fluorescence of different optical glasses is to integrate the spectrum of each glass and compare the results with a reference glass.

For many N-type glasses, the typical values as evaluated from emission curves in figure 5– shown in figure 5b – are ranging from 1 to 5 percent using the PbO containing glass SF1 as standard.

In principle, characteristic fluorescence data were calculated by integrating intensity values of the measured spectrum between 400 nm and 700 nm first. The obtained result is divided by a reference value (SF1 or SF6), which was calculated in the same way.

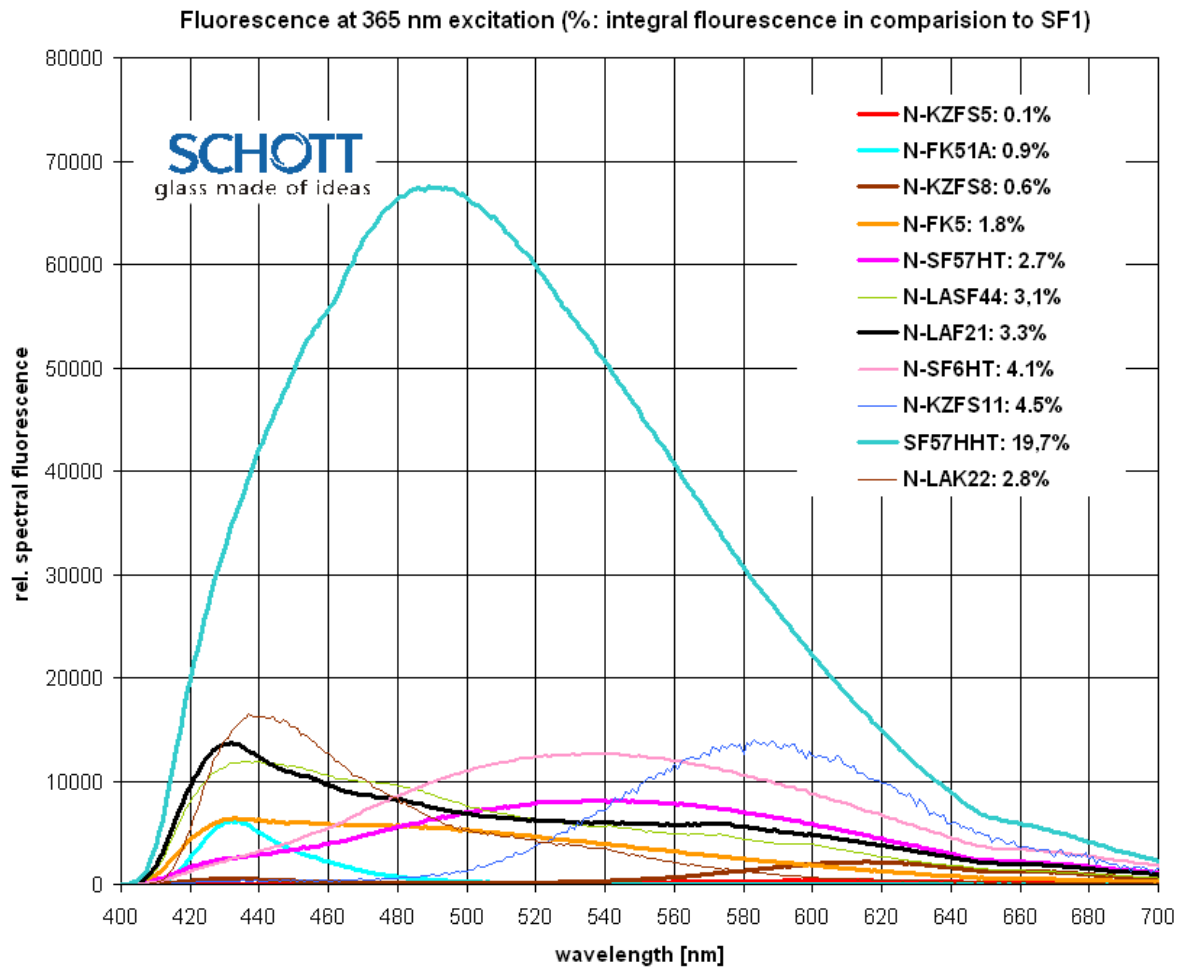


Figure 5a: Emission spectra of low fluorescent optical glasses using 365 nm excitation wavelength and a cut off filter (KV 418)

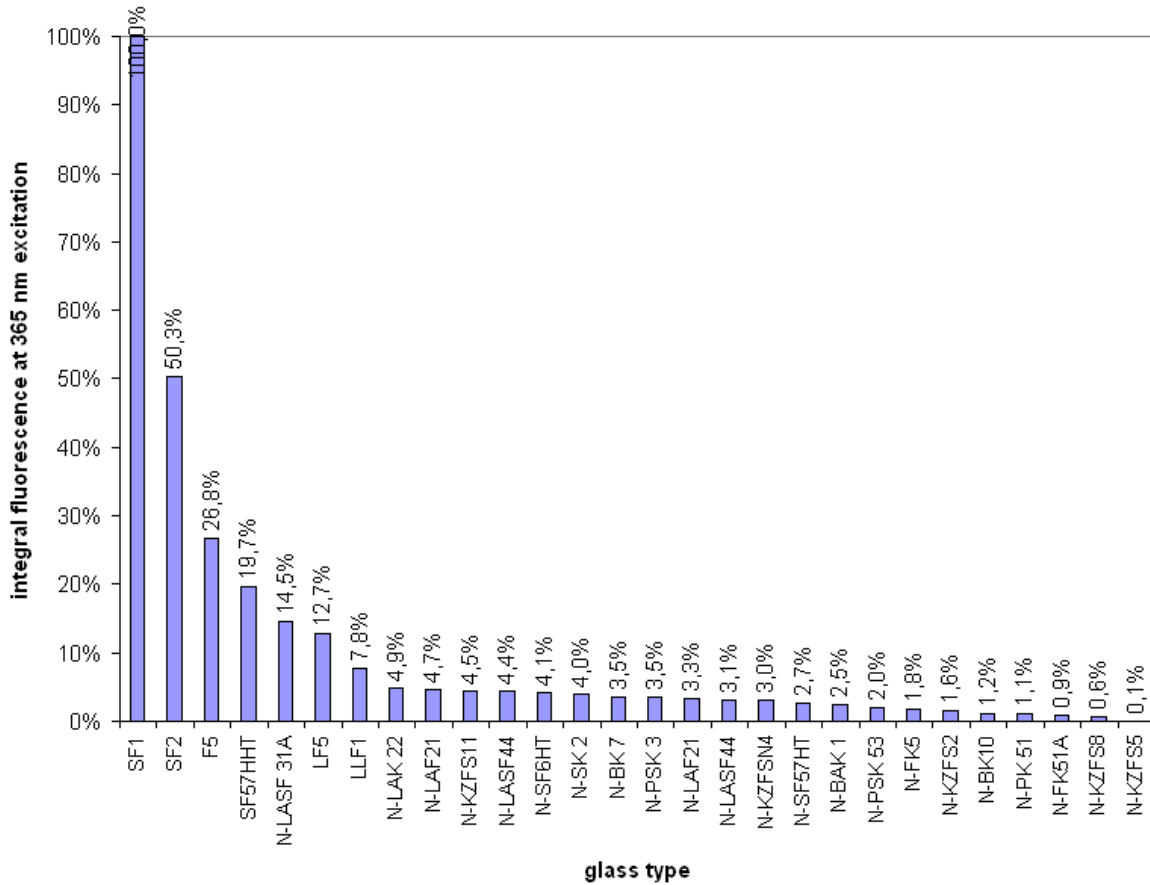


Figure 5b: Typical integral fluorescence data using 365 nm excitation

A similar type of quantitative evaluation for 365 nm excitation is performed within the Japanese Optical Glass Industrial Standard JOGIS procedure, which is used by Japanese companies [7]. Even for the low fluorescent material, typically used for I-line lithography or fluorescence microscopy, the analytical emission intensity level is still significantly above the detection limit of the spectrometer and offers potential for the characterization of high quality material of the next generation.

The long term reproducibility and batch-to-batch variation is shown in figure 6 using different samples of N-LASF type glass. The measurement reproducibility is $\pm 10\%$ of the rel. fluorescence. The variation from batch to batch is in the same range. In principle, the error can be further reduced by working with optimized experimental setup for each glass type, but then the comparison between different glasses is becoming less accurate.

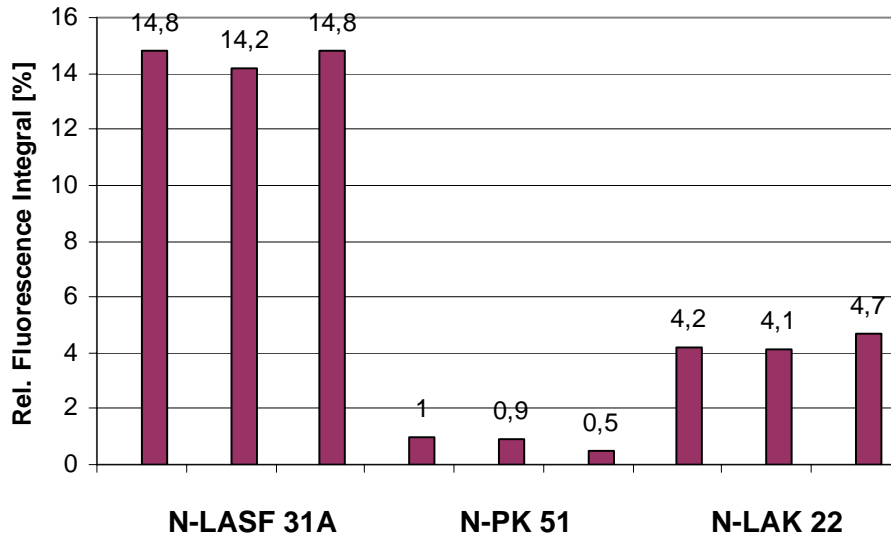


Figure 6a: Fluorescence data using 365 nm excitation obtained from one melt

N-LASF-type error indicator 10 %

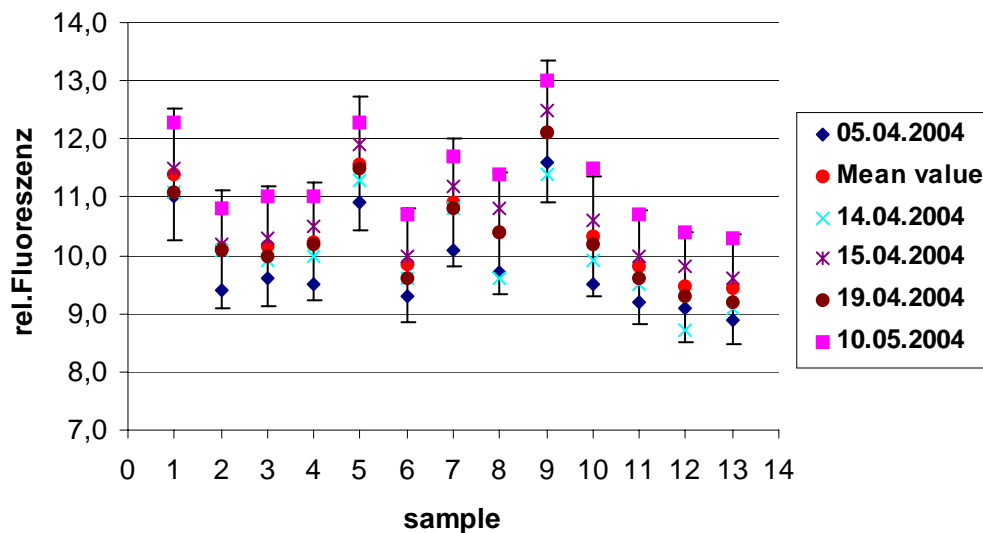


Figure 6b: Typical fluorescence data using 365 nm excitation for various samples of N-LASF type.

5.2 Fluorescence for excitation at higher wavelengths

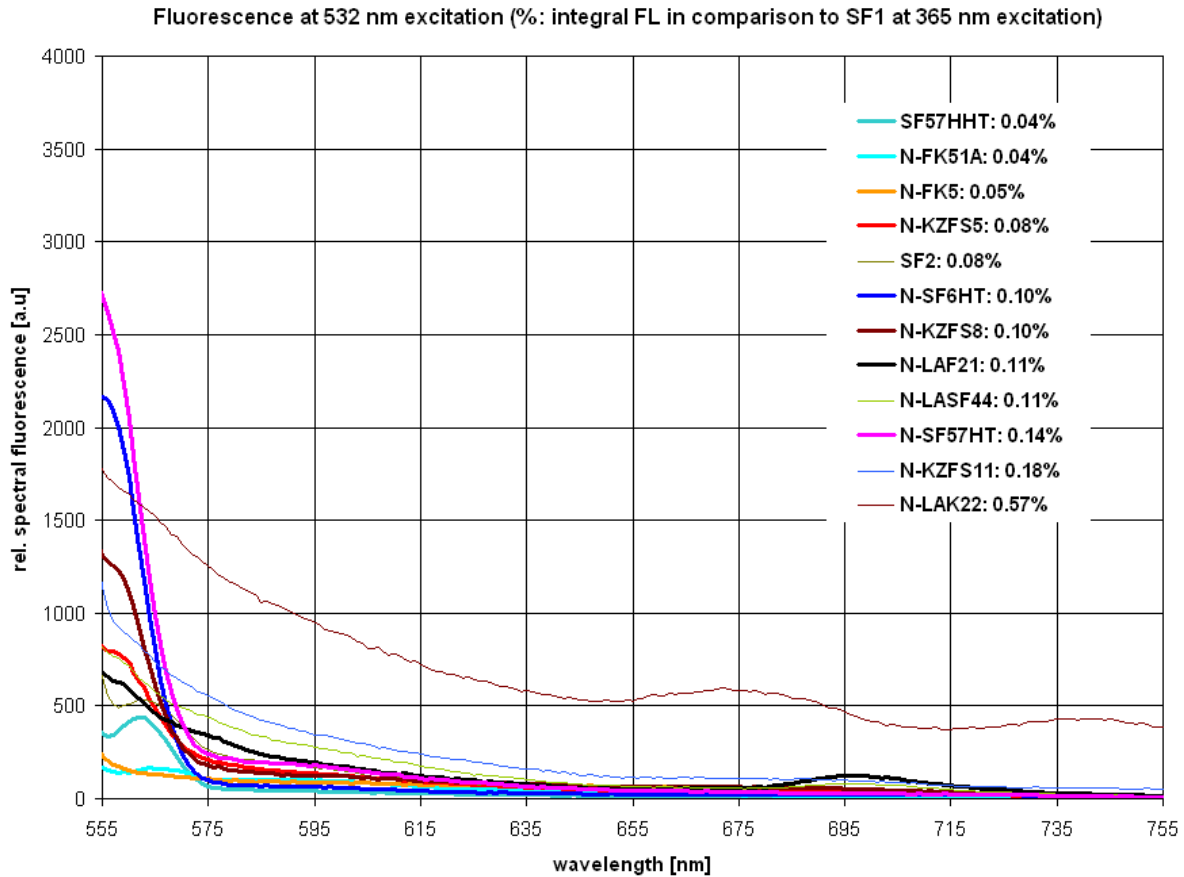


Figure 7: Emission spectra of optical glasses using 532 nm excitation wavelength and without cut off filter.

Typical fluorescence applications not only use 365 nm excitation, but also excitation at longer wavelengths, e.g. for bioanalytical use where excitation wavelengths longer than 400 nm required to excite certain organic fluorophors [8]. In figure 7 typical emission spectra using 532 nm excitation wavelength are shown for several optical glasses. Using the identical experimental setup, the general shape of the emission profiles is similar, but the measured intensities are different, as can be seen from the integral fluorescence data in the figure caption (532 nm excitation in comparison to SF1 at 365 nm excitation).

It has to be pointed out, that there is no correlation between the fluorescence at 365 nm and fluorescence at excitation wavelengths longer than 400 nm. The reason is that the absorption bands of different types of structural units, defects, or impurities are responsible for the observed signal [5].

Figure 8 shows a comparison of the integral fluorescence of some optical glasses at different excitation wavelengths using the integral fluorescence of SF1 at 365 nm excitation as standard. It can be seen that the absolute level of fluorescence light decreases in most cases with increasing excitation wavelength.

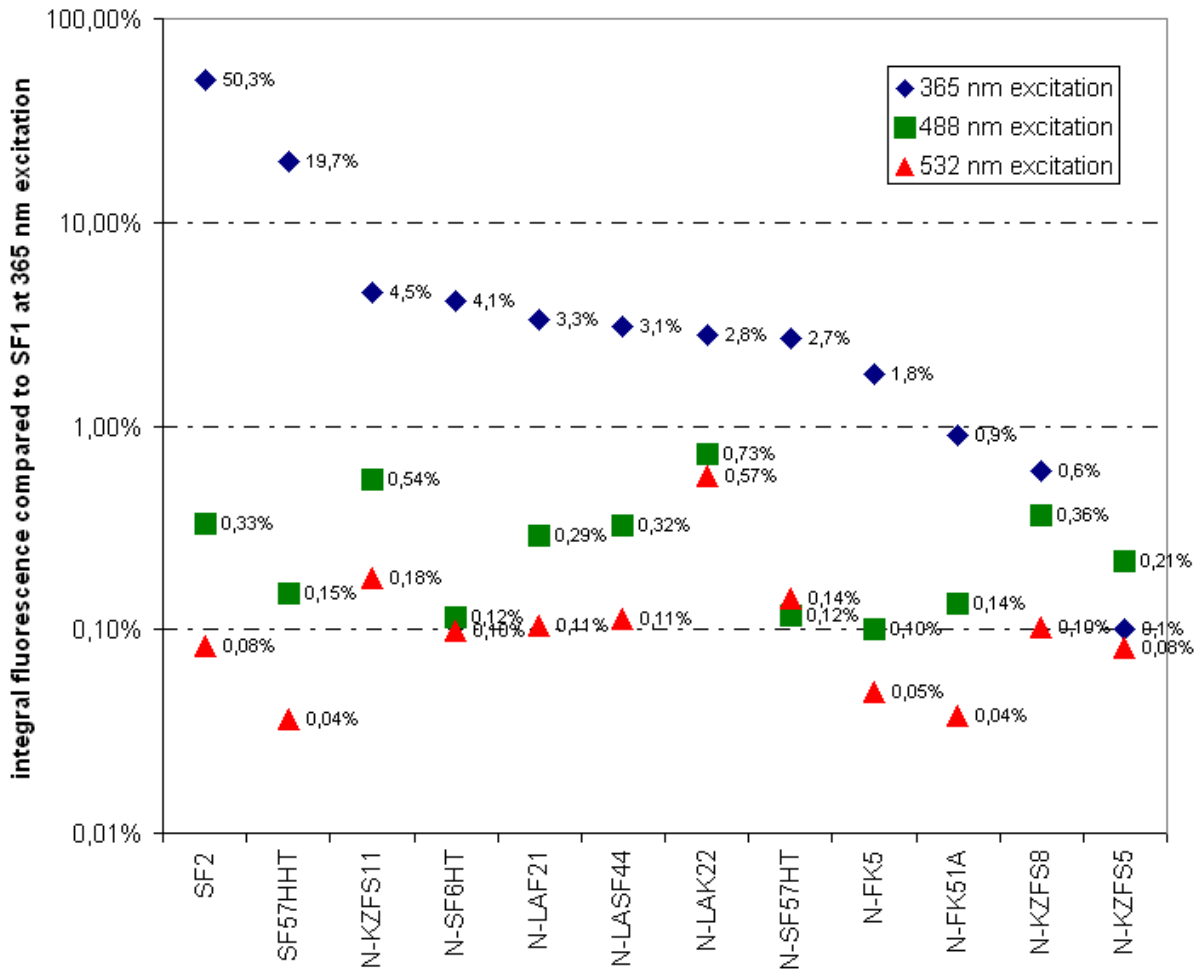


Figure 8: Integral fluorescence of UV-, 488 nm and 532 nm excited optical glass compared to the integral fluorescence of SF1 at 365 nm.

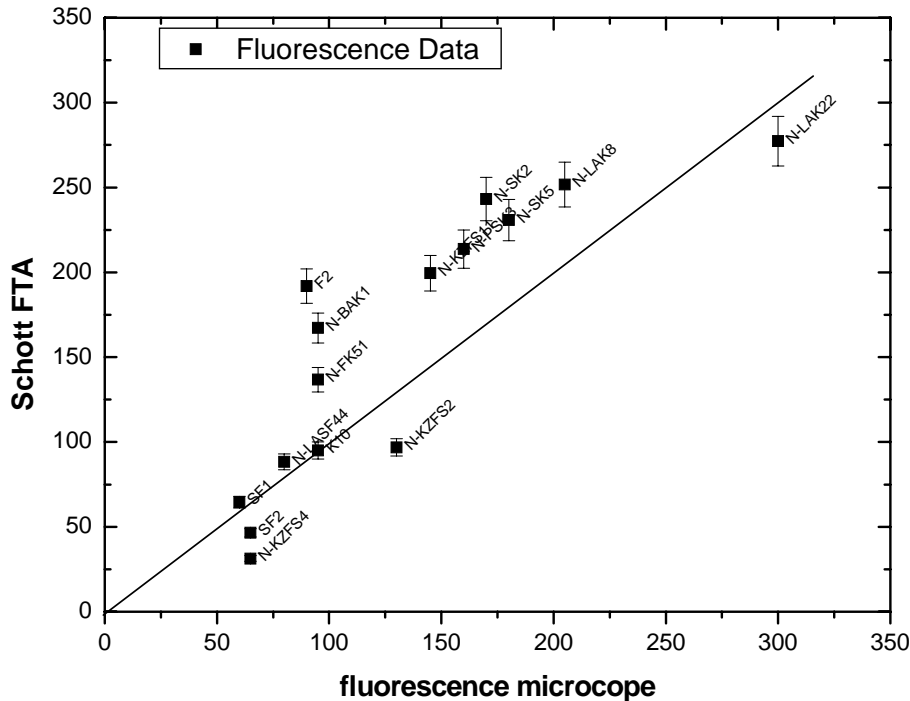


Figure 9: Correlation of spectroscopic and microscopic fluorescence for the red excitation

For certain applications of optical glass, where low fluorescence of the optical system is required, e.g. in microscopy and lithography, effective ways of quantification of fluorescence have to be found, to be able to cross compare the fluorescence of glasses, obtained with different setups. Optimally, this spectroscopic setup is very similar to the projected optical design. In figure 9 the correlation of fluorescence data in the red wavelength range determined by a fluorescence microscope and the Fluorolog 3 spectrometer are shown. It is clearly seen that a correlation of both detection methods is very feasible.

6. Summary

At SCHOTT, the characterization of fluorescence of optical glass is possible for excitation between 250 and 650 nm and detection of emission between 300 and 850 nm. SCHOTT is providing data and additional measurements for optical and colored glass exhibiting low and high intensity levels with an accuracy and reproducibility better than 10 percent. Additionally fluorescence evaluation for specific applications using various set-ups (applications wavelengths, geometries) can be done on demand.

7. Literature

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