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Photoluminescence of the integrating sphere walls, its influence on the absolute quantum yield measurements and correction methods

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Determination of the absolute quantum yield (QY) of photoluminescence (PL) or electroluminescence is commonly performed using an integrating sphere (IS) – versatile device for radiometry applications. The key feature of IS is very high diffused reflectance of its internal surface. Two materials are commonly used: (a) the sintered high-density polytetrafluoroethylene (Spectralon) and (b) materials based on barium sulphate (Spectraflect). Using PL-micro-spectroscopy we show that both materials reveal PL from localized centers excitable by UV, blue and green light emitting broad PL spectrum extending up to the red spectral region. The main effect of PL from IS-walls is introduction of non-constant parasitic background which is mixed with PL from a tested sample during the QY measurements. We develop theoretical description of QY determination which includes effects of PL from IS walls. This allows us to propose and test a reliable and universal correction for the IS-related PL background. Finally, a method of “black sample” is proposed and applied to estimate PL QY of Spectraflect which is shown to decrease from 0.09 to 0.015% for excitation shift from 320 to 440 nm. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5052601

I. INTRODUCTION

Absolute quantum yield (QY) determination using an integrating sphere (IS) is well established method whose main advantage is independence on the use of a QY-standard, sample scattering and emission polarization. An integrating sphere is a spherical cavity with highly-reflective (diffusive) surfaces that enable spatial integration of incoming light flux. It is widely applied in radiometry, photometry and other optical experiments. Internal walls of IS are made of materials with the highest possible diffused reflectance. The most common materials are Spectralon® (SL) and Spectraflect® (SF), the first one being sintered high-density polytetrafluoroethylene (PTFE) similar to Teflon® and the second one is based on barium sulphate and applied by spraying. Both these materials have diffused reflectance distributed nearly according the Lambert law and the total value of reflectance is between 92 and 99 % for wavelengths from UV-B to near IR. This means that during each reflection a few % of light flux is lost. In principle, these losses have negligible influence on the precision of the determined QY value. However, it was shown that materials forming IS walls transform part of the absorbed energy into a broad band photoluminescence (PL) under excitation in UV and blue light. PL QY of Spectralon under middle-UV excitation (205-268 nm) was shown to be between ~1.5% to 0.25% rapidly decreasing for longer excitation wavelengths. PL of PTFE materials was attributed to organic contamination and some procedures (sanding and baking) were proposed to reduce PL intensity.
Surprisingly, the effects of IS PL on the measurements of QY were not elaborated and described in literature, to our best knowledge. This is the motivation of the present paper where we first study micro-PL images and spectra of both SL and SF materials. Then we develop theoretical description of IS PL and its influence on the QY measurements. The proposed correction procedure is demonstrated on two practical examples and finally the original method to determine the yield of IS PL is presented.

II. MATERIALS AND METHODS

A. Samples of diffused reflectors and integrating sphere

Samples of reflecting materials studied by micro-spectroscopy were: The Spectraflex® reflectance standard from LabSphere (type USRS-99-010 AS-01158-060) and the Spectralect®-coated lid for the 10-cm IS from SphereOptics (type PP-100-O, as received).

The studied integrating sphere is SF-coated 4-inch (10 cm) universal integrating sphere (SPH-4-5) from SphereOptics GmbH with fiber coupling of input and output signals.

B. Optical spectroscopy set-ups

The PL QY set-up is based on the above mentioned SF-coated 10-cm diameter IS (SphereOptics GmbH). The tunable excitation source consists of the laser-driven light source (LDLS, EQ-99X from Energetiq) coupled to the 15-cm monochromator (Acton SP 2150i, Princeton Instruments). The selected band of light spectrum is coupled to a silica fiber bundle and guided to IS. Output signal is collected by another fiber bundle placed in the direction perpendicular to the excitation axis and shielded by baffles against the direct visibility of both the excitation port and a sample. The end of the fiber bundle with the stripe-like shape is imaged to the input slit of a spectrometer. The detection system is formed by the 30-cm imaging spectrograph (Acton SP2300i, Princeton Instruments) and the liquid-nitrogen-cooled back-illuminated deep-depletion CCD camera (Spec-10:400BR, Princeton Instruments). The set-up is calibrated using the standard of spectral irradiance (Oriel model No. 63358, calibrated between 250 - 2400 nm). The lamp was placed at the distance of 50 cm from the entrance port of an IS because the absolute calibration data are given for this distance. Consequently, we can perform the absolute calibration of a set-up in radiometric units. By dividing the measured spectral signal (expressed in count/s/pixel) by the calibrated spectral irradiance of the standard (W/nm/m²) multiplied by the area of an entrance port (in m²) we obtain the sensitivity spectrum of the apparatus \(C(\lambda)\) in (count/s/pixel)/(W/nm). This sensitivity curve is then used to convert experimental spectra (count/s/pixel) into the spectral radiance (W/nm). We have to note, that for a correct calibration of boundary spectral regions, where the response of an apparatus rapidly drops down, special care must be given to effects like stray light of a spectrometer. Useful recommendations for characterization of a PL apparatus were recently published by Resch-Genger and DeRose.

Micro-PL/reflectance imaging and spectroscopy is performed with the same detection system as described above coupled to the inverted optical microscope (Olympus IX-71). The 405-nm excitation laser beam (Omicron, LDM405.120.CW) and light from a halogen lamp are coupled via the back-port and appropriate filter cubes (epifluorescence configuration). All spectra are corrected for the spectral sensitivity of the detection system.

III. LUMINESCENCE SPECTROSCOPY OF IS MATERIALS

Micro-reflectance images show that SF surface is more structured and heterogeneous than the fairly homogeneous SL surface. Micro-PL images and spectra of both SL and SF surfaces reveal that PL is mostly coming from isolated emitting spots and sometimes from a weakly emitting background (especially for SF), see Fig. 1b, e. The diffused emission background can possibly come from emitting centers inside the coating whose emission is scattered and guided through the partially porous SF layer before escaping to free space. The local PL spectra are broad and may vary in the
FIG. 1. Micro-reflectance (a, d) and luminescence (b, c) of Spectralon® (a, b, c) and Spectraflect® (d, e, f) surfaces under low magnification (objective 4x/0.13). The yellow dashed rectangles indicate area of the spectrometer slit used to detect micro-PL spectra shown on the right side (c, f).

Peak position and band width, especially for SF (Fig. 1f). However, the PL spectra integrated over larger area (Fig. 2) are very similar for both SL and SF, while the intensity is significantly stronger for SF.

FIG. 2. (a) Micro-PL spectra integrated over the whole slit area under 405 nm excitation. Note the different intensity scale for the SF (left) and SL (right) surfaces. (b) Excitation power dependence of the spectrally integrated signal over six orders of magnitude of power density.
FIG. 3. PL spectra emitted by the whole IS (d = 10 cm, SF-coated surface) under weak tunable excitation between 320 and 440 nm. The panel (a) shows spectra corrected for the system response but unscaled, while the panel (b) contains spectra scaled to the relative number of absorbed photons.

Then we studied PL power dependence over a broad range of excitation density between ∼1 µW/cm² and 1 W/cm² (using laser emitting at 405 nm as for all micro-PL experiments). The power dependence of PL is well linear except for slightly superlinear dependence of SF PL at very low excitation power densities below ∼10 µW/cm². Such low power is obtained by application of several neutral density filters and cannot be confirmed by a power-meter, therefore we cannot be sure whether observed deviation from linearity is real. Anyway, this effect is out of the scope of this paper and it will be studied separately.

Then, we measured PL spectra of the empty SF-coated IS under excitation by the tunable excitation source based on LDLS. The spectra shown in Fig. 3a contain some structure when excited below 350 nm, for longer excitation wavelengths we observe one broad band which is shifting to longer wavelength following the shift of excitation wavelength until it stops at around 500 nm (peak). These characteristics agree quite well with previously reported SL spectra that were proposed to originate from organic contamination. From dividing the spectra from Fig. 3a by the relative number of absorbed photons, we can see (Fig. 3b) that overall PL intensity continuously decreases with shifting excitation to longer wavelengths – this is mostly due to cutting off part of the broad spectrum which cannot be excited.

IV. INTEGRATING SPHERE THEORY INCLUDING THE PARASITIC FLUORESCENCE FROM IS WALLS

An IS has the inner surface area $S_{is}$ mostly formed by highly reflecting material with reflectance $\rho_{is}$. The remaining area is occupied by ports and, eventually, a sample with reduced reflectance $\rho < \rho_{is}$. Size of each from $n$ ports is characterized by the fill factor $f_k$ ($k = 1$ to $n$) which is a ratio of the port area to the area of IS $f_k = S_k/S_{is}$. An ideal IS distributes the input radiant flux $\Phi_{in}$ evenly...
over the whole inner surface. Then the output flux $\Phi_{\text{out}}$ through a port with the fill factor $f_{\text{out}}$ is equal to

$$\Phi_{\text{out}}(\lambda) = \Phi_{\text{in}}(\lambda) \cdot \frac{f_{\text{out}} \cdot \rho_0(\lambda)}{1 - \rho_0(\lambda)(1 - \sum_{k=1}^{n} f_k) - \sum_{k=1}^{n} f_k \cdot \rho_k(\lambda)}$$

(1)

where $\rho_0$ is reflectance of the first surface encountered by incoming radiation (strictly speaking the above equation is valid only for the ideal output port with zero reflectance and numerical aperture 1, compare Eq. (5) below). The ratio of output and input fluxes $\Phi_{\text{out}}/\Phi_{\text{in}}$ is called the integrating sphere efficiency $\chi$. Dividing $\chi$ by the output port fill factor $f_{\text{out}}$ we get the sphere multiplier $M$

$$M(\lambda) = \frac{\rho_0(\lambda)}{1 - \rho_0(\lambda)(1 - \sum_{k=1}^{n} f_k) - \sum_{k=1}^{n} f_k \cdot \rho_k(\lambda)}$$

(2)

which characterizes how much the IS surface radiance increases compared to a single reflection.$^{12}$

In the typical experimental configuration (inset of Fig. 4) we have just two ports – the input ($\text{in}$) and the output ($\text{out}$) ports with fill factors and reflectances of $f_{\text{in}}, f_{\text{out}}$ and $\rho_{\text{in}}, \rho_{\text{out}}$, respectively.

![Diagram](image-url)

**FIG. 4.** (a) The sphere multiplier as function of IS-wall reflectance for the case of input and output ports with overall fill factor of $5.73 \cdot 10^{-5}$ and reflectivity 5% (blue line) and the hypothetic IS without any ports (dashed yellow line) – both cases are indistinguishable. The inset shows the IS cross-section with sample in the direct and indirect excitation. (b) The log-log plot of sample absorptance inside IS as function of its single-pass absorptance (the inset shows the same plot in linear scales) for the case of direct (red) and indirect (light blue) excitation. The sample has form of thin flat layer (area $12 \times 12 \text{ mm}^2$) placed on the IS wall with reflectance 97% (IS diameter is 10 cm and port arrangement like in the panel (a) above). The yellow circles indicate absorptance for which the measured difference of excitation signals (with and without sample) exceeds the common uncertainty (i.e. this is kind of a sensitivity limit).
Then the sphere multiplier $M$, takes form

$$M(\lambda) = \frac{\rho_0(\lambda)}{1 - \rho_{ts}(\lambda)(1 - f_{in} - f_{out}) - f_{in} \cdot \rho_{in}(\lambda) - f_{out} \cdot \rho_{out}(\lambda)} \approx \frac{\rho_0(\lambda)}{1 - \rho_{ts}(\lambda)(1 - f_{in} - f_{out})}, \quad (3)$$

where we can neglect the last two terms of the denominator as both reflectance and fill factors of input and output ports are small. The multiplier will be maximized in case when the first reflection is from the IS wall and the fill factor of ports is negligible (which is often the case), then $M = \rho_{ts}/(1 - \rho_{ts}) \sim 100$ for the IS reflectance $\sim 99\%$ (see Fig. 4a). For a typical IS the reflectance $\rho_{ts}$ and the total port fill fraction $f$ are in the range of 0.94 – 0.99 and 0.02 – 0.05, respectively, and then the multiplier is between 10 and 50.\(^4\) Note that in the above equations we explicitly marked which quantities are spectrally dependent ($\lambda$) – namely, photon flux, reflectance and sphere multiplier – as it will be important in the following description.

Radiance of the IS surface $L_{ts}$ is equal to

$$L_{ts}(\lambda) = \frac{\Phi_{in}(\lambda)}{\pi S_{ts}(\lambda)} M(\lambda). \quad (4)$$

An output port with fill factor $f_{out}$, reflectivity $\rho_{out}$ and numerical aperture $NA$ collects light reflected from a baffle (which is part of the IS internal surface). Then the output flux is given by

$$\Phi_{out}(\lambda) = \Phi_{in}(\lambda) M(\lambda) f_{out} [1 - \rho_{out}(\lambda)] NA^2(\lambda), \quad (5)$$

where the last two terms are in addition compared to the ideal output port described by Eq. (1) and these coupling factors are spectrally dependent.

The calibration procedure is usually performed by measuring a known radiation source (standard) giving specific input flux to the IS (see Section II B). The measured signal (e.g. in counts per second and pixel in case of a CCD detector) is then divided by the input signal (usually given as spectral irradiance in W/m\(^2\)/nm) and the resulting sensitivity curve is used to correct measurements performed with that instrument. Thus the sensitivity spectrum includes effects of the multiplier and output coupling characteristics given by Eq. (5).

When we introduce a tested sample (TS) into IS it decreases the output flux via reduction of the multiplier $M$. In fact it plays two roles which are easily understandable in case of a flat solid sample (e.g. a layer of luminescing material deposited on transparent substrate) placed on the IS wall:

(a) Semitransparent port – The sample with area $S_{TS}$ and absorptance $a_{TS}$ (fraction of incident light which is absorbed during the single passage through a sample, i.e. the probability to absorb a passing photon) placed anywhere on the IS wall influences the sphere multiplier $M$ as a port with reflectance $\rho_{ts}(1 - a_{TS})^2$ (where we considered the first passage, reflection from a wall and the second passage).

(b) Input filter – When a sample is placed on the IS wall illuminated directly by the incoming excitation beam, it reduces the first reflectance $\rho_0$ from $\rho_{ts}$ to $\rho_{ts}(1 - a_{TS})^2$, which has nearly the same effect on the IS surface radiance as the double-passage filtering of incoming photon flux. In general, only fraction of the incoming flux may pass through a sample which we characterize by the factor $F$ ($F=1$ is direct excitation while $F=0$ is purely indirect excitation). In our previous study we have shown that the value of $F$ does not influence the correct determination of QY.\(^13\)

The direct excitation gives stronger reduction of $M$ (i.e. larger difference between input and output flux) but the purely indirect excitation is the simplest case for theoretical description.

It is instructive to express the absorptance in the sphere ($\Phi_{out,R}(\lambda_{ex}) - \Phi_{out,S}(\lambda_{ex})/\Phi_{out,R}(\lambda_{ex})$, i.e. relative reduction of the output signal due to a sample, as function of the sample single pass absorptance for the case of directly ($F=1$) and indirectly ($F=0$) excited sample (size 12 $\times$ 12 mm\(^2\), laying on the wall $\rho_{ts} = 97\%$). By combining Eqs. (3) and (5) we obtain

$$\frac{\Phi_{out,R}(\lambda_{ex}) - \Phi_{out,S}(\lambda_{ex})}{\Phi_{out,R}(\lambda_{ex})} = \frac{M_R(\lambda_{ex}) - M_S^{dir,indir}(\lambda_{ex})}{M_R(\lambda_{ex})}. \quad (6)$$
This relation is plotted in Fig. 4(b) for the IS parameters considered before. We can see that the direct excitation provides stronger absorbance and consequently better sensitivity. In a typical experiment the standard deviation of the IS output measurement is about 1% or more, therefore the absorbance of sample inside IS must be at least \~2.5% (our detailed statistical treatment of QY determination and uncertainty will be published separately) which is achieved for single pass absorbance of slightly above 1% and \~9% for direct and indirect excitation, respectively (obviously, it depends on the sample size and the IS-wall reflectivity).

The QY determination can be based on just two measurements, one for the IS with sample (S) and one for the reference sample or empty IS (R), both covering the whole excitation and emission spectral ranges. These spectra are subtracted, corrected, transferred to photon fluxes and spectrally integrated over the emission (em) and excitation (ex) bands. The overall calculation is described by the following equation:

\[
\eta = \frac{\int \frac{I_{em}^S(\lambda_{em}) - I_{em}^R(\lambda_{em})}{C(\lambda_{em}) \cdot T_{emF} \cdot (hc/\lambda_{em})} d\lambda_{em}}{\int \frac{I_{ex}^S(\lambda_{ex}) - I_{ex}^R(\lambda_{ex})}{C(\lambda_{ex}) \cdot T_{emF} \cdot (hc/\lambda_{ex})}} d\lambda_{ex},
\]

where the nominator represents PL emission rate (photons/s), while denominator stands for absorption rate. The functions \(T_{exF}\) and \(T_{emF}\) represent transmittance spectra of filters used during acquisition of excitation and emission signals (e.g. a long-pass filter cutting off excitation photons or neutral-density filters), \(C\) is the spectral sensitivity of the set-up and \(hc/\lambda\) is energy of photon.

Now, we can turn to the description of IS luminescence. As the IS system is in a steady state, the difference between input and output fluxes \(\Phi_{in} - \Phi_{out}\) is equal to losses due to the absorption rate by IS walls and, eventually, due to absorption by the tested sample

\[
\Phi_{in}(\lambda) - \Phi_{out}(\lambda) = 1 - f_{out} \cdot M(\lambda) = A_{is}(\lambda) + A_{TS}(\lambda).
\]

PL fluxes emitted by the IS wall and the tested sample are proportional to their absorption rates \(A_{is}\) and \(A_{TS}\) multiplied by quantum efficiency \(\eta_{is}\) and \(\eta_{TS}\), respectively. (Obviously, PL is emitted at longer wavelength relative to the wavelength of absorbed photons - the Stokes shift.) In principle, when the absorption and PL spectra partially overlap, there can be reabsorption, eventually, a cascade of absorption \(\rightarrow\) emission \(\rightarrow\) absorption \(\rightarrow\) emission etc. Later we will show that the efficiency of IS wall luminescence is so low (<10^-3) that the secondary PL can be neglected.

During the measurement of PL QY of a sample inside IS, the PL from IS walls produces basically just an increased background, which is subtracted out when making the difference of sample and reference measurements according to Eq. (7). However, the IS PL-related background is not constant as it decreases due to the sample absorption (which decreases flux available to excite PL from IS walls).

Let us consider the indirect excitation of a flat sample (area \(S_{TS}\) and fill factor \(f_{TS}\)) laying on the IS wall. The ratio of the background fluxes \(B_{R,S}(\lambda_{em})\) due to IS PL observed during reference (R) and sample (S) measurements is simply

\[
\frac{B_{R}(\lambda_{em})}{B_{S}(\lambda_{em})} = \frac{A_{is,R}(\lambda_{ex})\eta_{is}(\lambda_{em})}{A_{is,S}(\lambda_{ex})\eta_{is}(\lambda_{em})} = \frac{\Phi_{in}(\lambda_{ex}) - \Phi_{out,R}(\lambda_{ex})}{\Phi_{in}(\lambda_{ex}) - \Phi_{out,S}(\lambda_{ex}) - A_{TS}(\lambda_{ex})}
= 1 - f_{out} \cdot M_{R}(\lambda_{ex})
= 1 - f_{out} \cdot M_{S}(\lambda_{ex}) - f_{TS} \cdot \rho_{is} \cdot a_{TS}^2(\lambda_{ex}) \cdot M_{S}(\lambda_{ex})
\]

Then, in order to correct for reduction of the luminescence background, the measured \(B_{R}(\lambda_{em})\) must be divided by the left side of Eq. (9), which can be calculated using the known configuration of the IS and the single pass absorbance of a tested sample \(a_{TS}\). Usually, the background signal contains not only the IS PL background but also constant (approximately) background related to thermal noise of the detector etc. This constant background must be subtracted before application of the correction and then added back.
There are several problems with application of the PL background correction according to Eq. (9), the most important one is related to the calculation of multipliers $M_S$, $M_R$ which is very sensitive to exact knowledge of the reflectance spectrum of the IS material (see Eq. 2, Fig. 4). Our attempts to use the correction calculated according to Eq. (9) for various experimental data lead to unsatisfactory results. Moreover it does not describe other experimental configurations, e.g. a liquid sample in a cuvette held in the center of IS or the case of (partially or fully) direct excitation.

Fortunately, very simple and reliable universal correction can be obtained. It is based on the assumption that the IS PL is directly proportional to the wall luminosity at the excitation wavelength and this is actually directly proportional to the excitation output signal. Therefore, the correction factor is simply obtained as ratio of the detected excitation peak intensities of sample and reference (after subtracting constant background $cb$) $(I_{S}^{ex}(\lambda_{ex.peack})-cb)/(I_{R}^{ex}(\lambda_{ex.peack})-cb)$. We can incorporate this correction easily into the QY calculation via Eq. (6)

$$\eta = \frac{\int_{\text{em.band}} I_{S}^{em}(\lambda_{em}) - \left[ I_{R}^{em}(\lambda_{em}) - cb \right] \cdot \frac{I_{S}^{ex.peack} - cb + cb}{C(\lambda_{em}) \cdot T_{emF} \cdot (hc/\lambda_{em})} d\lambda_{em}}{\int_{\text{ex.band}} I_{R}^{ex}(\lambda_{ex}) - I_{S}^{ex}(\lambda_{ex}) C(\lambda_{ex}) \cdot T_{exF} \cdot (hc/\lambda_{ex}) d\lambda_{ex}}. \quad (10)$$

This correction works very well and is universal for any sample configuration.

V. EXAMPLES OF THE COATING PL-RELATED BACKGROUND AND ITS CORRECTION

The first example is a layer of silicon suboxide SiO$_{0.6}$ deposited on a silica slide with area $20 \times 20 \text{ mm}^2$ and annealed at 1000 °C which produces percolated structure of Si-nanoparticles in silica (see Ref. 15 for details). PL of this sample is situated in the NIR spectral region (Fig. 5) and there is almost no overlap with the IS-wall luminescence. The Fig. 5 presents the raw experimental data for both the direct and indirect excitation of this sample by the weak (LDLS) excitation at 400 nm (inset of Fig. 5). The background due to IS-wall PL is observed at wavelengths below 700 nm and it decreases after introduction of a sample – the reduction is much stronger for direct excitation as expected. The background correction based on the excitation peak ratio (as described in Section IV.) works nearly perfectly for both configurations. In fact, this example is quite easy, as we know that this sample has no PL below 600 nm, we can adjust the background correction to reach zero level on the short-wavelength side of the sample PL band. This example was selected in order to
FIG. 6. Measured PL spectra of the small ZnO bulk sample directly excited in the IS at 340 nm (red lines). The excitation peak (left side) is reduced about 20-times by using the neutral density filter. The blue lines are reference measurements with empty IS. The inset presents the final excitation (blue) and emission (red) peaks in the scale of photon rate. Ratio of the peak integrals gives the PL QY of about 5.8%. The black line represent the emission spectrum (like the red line) but without background correction. This gives underestimated QY of 4.3 or 4.9% depending on the range of integration.

clearly show the changes of background without overlap with the sample PL. Here the correction has negligible influence on the calculated QY (the effect is much smaller than the overall experimental uncertainty).

Second example is more complicated as the investigated PL spectrum overlaps with the PL background. The sample is a small bulk crystal of ZnO (single-side polished plate $5 \times 5 \times 0.5 \text{ mm}^3$) under direct excitation at 340 nm. Under this weak excitation the emission from deep-level defect-states dominates the PL spectra producing a broad band ranging from green to red spectral region (Fig. 6). Even in such a case, where the investigated PL is just a shoulder on the PL band due to IS-walls, the proposed correction procedure allows to determine the PL QY of the investigated sample quite precisely (5.8% with estimated uncertainty below 10%, see the inset in Fig. 6). The PL spectrum obtained without the background correction (black line in the inset of Fig. 6) has reduced intensity on the short-wavelength side and even drops below zero on the band edge. This leads to underestimated QY, which is about 4.3% (4.9%) depending on the wavelength where integration starts (422 and 462 nm, respectively). Thus the effect of background is about two times larger than the estimated uncertainty of QY.

VI. DETERMINING THE EFFICIENCY OF PL FROM IS-WALLS

In order to characterize the IS wall luminescence yield we propose to compare IS PL measurements of an empty IS and the IS with additional loss channel which decreases the wall luminosity and consequently PL intensity. The loss channel (port) is a square hole of $12.2 \times 12.2 \text{ mm}^2$ (cut out in one of the lids) with a light trap outside the sphere behind the hole. This is kind of “black hole” or absolutely dark sample with perfect absorption $a_{IS} = 1$ and no luminescence.

The difference of output signal of PL from IS without (R) and with (S) additional hole (dark sample) is due to decrease of both the sphere multiplier (i.e. wall luminosity) and the IS surface area.

$$\Phi_{\text{out},R} (\lambda_{em}) - \Phi_{\text{out},S} (\lambda_{em}) = \eta_{is} (\lambda_{em}) \left( \Phi_{in} (\lambda_{ex}) M_R (\lambda_{ex}) - \Phi_{in} (\lambda_{ex}) \frac{S_{is,S}}{S_{is,R}} M_R (\lambda_{ex}) \right)$$

(11)

where the input flux $\Phi_{in} (\lambda_{ex})$ is obtained by measuring power coming from the input fiber and transforming it into photon flux (i.e. it represents integral excitation flux). The $\Phi_{\text{out},S} (\lambda_{em})$ and $\Phi_{\text{out},R} (\lambda_{em})$ spectra (which represent the output spectral photon rate of IS PL in configuration with and without “dark sample”; respectively) are obtained by correcting and integrating the detected spectra like in the nominator of Eq. (10).
The quantum yield determined using Eq. (11) is shown in Fig. 7 for excitation between 320 and 440 nm. It is rapidly decreasing from 0.09% to 0.04% between 320 and 360 nm and then only slightly decreasing towards 0.025% at 440 nm. We can say that this result is in line with QY reported for shorter wavelengths.

VII. CONCLUSIONS

We have investigated PL from materials used to fabricate integrating spheres – devices that are crucial for many photometric measurements. The micro-PL experiments show that the emission comes mostly from localized spots and the intensity of PL from Spectralon® is roughly an order of magnitude lower than for Spectraflect®. A novel method to measure QY of the IS luminescence is proposed and applied to measure QY of SF-coated IS revealing yield between 0.09 and 0.025% under excitation wavelengths between 320 and 440 nm. These characteristics are in line with previously reported PL from SL materials under even shorter excitation wavelengths.

The origin of such PL was proposed to be contamination of IS walls by organic materials. Our observations agree with such hypothesis. The contamination can be accelerated by working with materials (dyes, quantum dots etc.) in organic solvents that evaporates and may form fluorescent centers under UV-excitation applied during typical experiments. We note that spectral characteristics of IS PL are similar to those observed in so called carbon dots, which is probably related to specific oxidized hydrocarbon groups. This parasitic luminescence of IS-walls can be possibly reduced by some special cleaning procedures like baking of sanding of the SL materials, however, this was not investigated within the present work.

The main goal of this paper was to theoretically describe the effects of IS PL on the measurements of absolute luminescence QY using the IS-based method. The main effect is introduction of non-constant parasitic signal background. We described and tested universal and reliable method to correct for the IS PL background and determine QY even for materials whose PL is weak and largely overlapping with PL from IS walls.

The magnitude of error in determination of PL QY introduced by the changing parasitic background (when not corrected) cannot be described in general, as it depends on number of parameters: spectral position of the emission band, excitation wavelength, sample absorptance inside IS, PL QY of a sample, sphere multiplier etc. We can say that the error can often significantly exceed the usual experimental uncertainty of the QY determination method (which is typically couple of %) as we have shown in Fig. 6.

In the case of manual treatment of measured spectra and performing calculations of QY according to Eq. (7), one can often see clearly the problem of background as the emission spectrum to be integrated (nominator in Eq. (7) may show some negative intensity. However, in case of automatic treatment of data, the background effect may pass unnoticed. Therefore the calculation procedure must be programmed according to Eq. (10) instead of Eq. (7).
Anyway, the best solution will be finding some treatment of the IS wall materials that could reduce their luminescence as much as possible. Users of IS must be aware of the effects of possible contamination of IS walls by organic materials and reduce any evaporation of solvents (minimizing time that a sample spends inside IS). Contamination will also change the optical characteristics of IS, therefore the system must be regularly recalibrated.

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1 C. Würth, M. Grabolle, J. Pauli, M. Spieles, and U. Resch-Genger, Nat. Protocols 8, 1535 (2013).
2 W. R. McCluney, Introduction to Radiometry and Photometry (Artech House, Boston-London, 1994).
3 M. Janecek, IEEE Trans. Nucl. Sci. 59, 490 (2012).
4 Technical Guide: Integrating Sphere Theory and Applications (LabSphere Inc.), available from http://www.labsphere.com.
5 P-S. Shaw and Z. Li, Appl. Optics 47, 3962 (2008).
6 P-S. Shaw, U. Arp, and K. R. Lykke, Metrologia 46, S191 (2009).
7 P-S. Shaw, Z. Li, U. Arp, and K. R. Lykke, Appl. Optics 46, 5119 (2007).
8 I. Pelant and J. Valenta, Luminescence Spectroscopy of Semiconductors (Oxford University Press, Oxford, 2012).
9 J. Valenta and M. Greben, AIP Adv. 5, 047131 (2015).
10 J. F. James, Spectrograph Design Fundamentals (Cambridge University Press, Cambridge, 2007).
11 U. Resch-Genger and P. C. DeRose, Pure Appl. Chem. 84, 1815 (2012).
12 D. G. Goebel, Appl. Optics 6, 125 (1967).
13 J. Valenta, Nanosci. Methods 3, 11 (2014).
14 D. O. Faulkner, J. J. McDowell, A. J. Price, D. D. Perovic, N. P. Kherani, and G. A. Ozin, Laser Photonics Rev. 6, 802 (2012).
15 J. Laube, S. Gutsch, D. Wang, C. Käbel, M. Zacharias, and D. Hiller, Appl. Phys. Lett. 108, 043106 (2016).
16 M. Čížek, J. Valenta, P. Hruška, O. Melikhova, I. Procházka, M. Novotný, and J. Buliř, Appl. Phys. Lett. 106, 251902 (2015).
17 S. N. Baker and G. A. Baker, Angew. Chem. Int. Ed. 49, 6726 (2010).