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Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report)*

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Abstract: The use of standards for the measurement of photoluminescence quantum yields (QYs) in dilute solutions is reviewed. Only three standards can be considered well established. Another group of six standards has been investigated by several independent researchers. A large group of standards is frequently used in recent literature, but the validity of these is less certain. The needs for future development comprise: (i) confirmation of the validity of the QY values of many commonly used standard materials, preferably in the form of SI traceable standards; (ii) extension of the set of standard materials to the UV and near-IR spectral ranges; and (iii) good standards or robust protocols for the measurements of low QYs.

Keywords: IUPAC Analytical Chemistry Division; IUPAC Organic and Biomolecular Chemistry Division; IUPAC Physical and Biophysical Chemistry Division; measurements in solution; photoluminescence; photons; quantum yield; standards.

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1. INTRODUCTION

For any photoluminescent species, the quantum yield (QY) of its luminescence is a basic property, and its measurement is an important step in the characterization of the species. According to the definition of the QY [1], only two quantities need to be known, viz. the number of photons absorbed and the num-

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ber of photons emitted per unit of time. Unfortunately, reliable measurements of these quantities can be hard to obtain. In this paper, we consider the easiest situation, namely, for species in dilute solution. In this case, it is customary to measure the fluorescence spectrum and compare its integrated intensity with the same quantity for a reference system with a known QY. This measurement can be done using standard absorption and emission spectrometers [2].

The QY can be calculated from eq. 1:

$$\Phi_f^i = \frac{F^i f_s n_i^2}{F^s f_i n_s^2} \Phi_f^s \tag{1}$$

where Φ_f^i and Φ_f^s are the photoluminescence QY of the sample and that of the standard, respectively; the subscript f is used because in most cases one is dealing with fluorescence. F^i and F^s are the integrated intensities (areas) of sample and standard spectra, respectively (in units of photons); f_x is the absorption factor (also known under the obsolete term "absorptance") [1], the fraction of the light impinging on the sample that is absorbed ($f_x = 1 - 10^{-A_x}$, where A = absorbance); the refractive indices of the sample and reference solution are n_i and n_s, respectively. In principle, excitation wavelengths for sample and reference can be different, but this is generally not advisable because it introduces an additional uncertainty in the relative photon flux at the two wavelengths.

Although the procedure appears simple and straightforward, there are important and often underestimated sources of error, which have been discussed elsewhere and will only briefly be summarized below. The main topic of this paper is the choice of the QY standard, a compound "for which the quantum yield is known". An IUPAC recommendation on this topic was published by Eaton in 1988 [3], and numerous papers have addressed the topic since then. Remarkably, the problems that were signaled in the 1988 paper have by no means been solved in the two decades that have passed. In this contribution, the current practice of the use of standards for measuring photoluminescence QY in solutions will be reviewed. As discussed below, for some standards improved values have been obtained, which do not seem to be sufficiently well known in the community of photoluminescence users, and new standards have been proposed. The latter are almost all based on relative measurements with respect to a few "established" values. There remains a need for more standards with reliable quantitative data, in particular for wavelength regions <400 nm and >650 nm. Furthermore, reference materials are needed for low QYs, or clear-cut procedures should be defined for dealing with large differences in luminescence intensity between sample and reference.

2. SOURCES OF ERROR IN ROUTINE DETERMINATION OF QUANTUM YIELD

The measurement of photoluminescence QY by comparison with a standard is deceptively simple [4]. It is just a matter of measuring two absorbance values and two emission spectra, and applying eq. 1. In practice there are pitfalls, which are discussed in more detail elsewhere [5]. The absorption factor must be accurately determined for solutions with a low absorbance, typically $A < 0.1$, in order to avoid internal filter effects and errors arising from uneven distribution of the excited species in the detected volume. This implies that scattering losses at interfaces and spurious absorption by impurities in the solvent (especially in the UV) should be properly taken into account. To minimize such effects, it is commonly recommended to use the same sample cell and the same absorbance at the excitation wavelength for sample and reference.

For the measurement of the integrated emission intensity, the wavelength dependence of the spectral response of the detection system should be properly corrected, and the linearity of the detector should be checked [2]. Using as much as possible the same emission spectral range and similar emission intensities for sample and reference can reduce errors resulting from imperfect correction.

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3. REQUIREMENTS FOR QUANTUM YIELD STANDARDS

In general, for a reference compound to be practically useful, it should have a reliably determined QY, and foolproof purification and handling procedures. The solvent, pH, concentration, temperature, and excitation wavelength range that can be used must be specified. Whether oxygen is removed or not is also important in some cases. As stated above, in order to minimize errors owing to imperfect calibration of the spectrometer, the standard should also match the spectrum of the sample of interest as closely as possible.

This implies a need for a large range of standards, which cover different spectral ranges and different QYs. Compilations can be found in recent editions of popular textbooks, e.g., by Lakowicz [6], and the *Handbook of Photochemistry* [7]. Unfortunately, the literature references in these tables are not fully up-to-date, and some are to work done about 40 years ago, part of which should be checked again with more modern instrumentation.

Many of the compounds that have been proposed as QY standards are strongly absorbing and fluorescing dyes, with narrow bands and small Stokes shifts. This limits the useful wavelength range for excitation, even if the QY is not wavelength-dependent, because a large part of the absorption band overlaps with the emission band. Since one needs to integrate the entire emission band, the excitation should be at a wavelength shorter than the onset of the emission band. As discussed more extensively in ref. [5], this means that one can only use the blue side of the long-wavelength absorption band. In this range, the absorption changes quite strongly with wavelength, which makes it difficult to accurately measure the absorption factor. Furthermore, one cannot always increase the concentration to obtain the desired absorption factor at the excitation wavelength, because the photophysical parameters are concentration-dependent owing to a tendency toward aggregation. Again, this is a phenomenon observed with many dyes. In Tables 1–3, wavelength ranges are indicated in which excitation should be possible.

4. A SMALL SET OF WELL-ESTABLISHED STANDARDS

Among the standards that can be found in frequently cited tabulations, three appear to be the best established, namely, quinine bisulfate, fluorescein, and rhodamine 6G. On the basis of numerous papers, there is little doubt that their QY values under well-defined conditions are known to within ±4 % or better. An overview is given in Table 1. Many other frequently used references may be reliable too, but we could not find systematic studies to confirm this.

- For quinine sulfate (QS) in 0.5 M sulfuric acid, Melhuish's old value of the fluorescence QY $\Phi_f = 0.55$ (at low concentration and at 25 °C) still seems the best value. A recent study of Suzuki et al. [12] suggests that Melhuish's extrapolation to infinite dilution was based on an inaccurate self-quenching rate constant. These authors claim that the correct value is significantly higher: $\Phi_f = 0.60$ at 10^{-5} M.

  At 10 times lower acid concentration, the QY as well as the decay time of QS are somewhat smaller [10,13]. Clearly, care should be taken to avoid chloride ions [11], and the long lifetime might make QS sensitive to other quenchers. Oxygen, however, seems to be unimportant in this respect. The dependence of the emission QY on the excitation wavelength has been investigated. Eastman's result does not indicate a large effect of exciting at 250 nm instead of 350–366 nm [21], and Velapoldi and Mielenz did not find a significant effect in the range 224–390 nm [14]. Pardo et al. [22], on the other hand, claim that the QY is somewhat higher at the long-wavelength edge of the absorption band (>360 nm). The photophysical behavior of QS is not without complications [10], possibly owing to the presence of different conformers. An effect of the counterion is apparent from the observation that the QY of a solution in 0.1 M $HClO_4$, which is available as a certified standard from the National Institute of Standards and

Technology (NIST) as Standard Reference Material (SRM) 936 [14], is higher than the values obtained in H_2SO_4.

A number of compounds with similar spectral properties but uncomplicated photophysics have been proposed as alternatives to QS [22,23], but these have not yet gained much popularity (see below).

- Fluorescein in 0.1 M NaOH has been studied by several authors [15,18]. The thermal blooming values of Magde et al. give $\Phi_f = 0.925$ [16], and other recent data obtained in different ways are in good agreement with this result [13,17]. The wavelength range for excitation has not been fully explored. A precaution: fluorescein solutions are not very stable, and should be prepared freshly before use. It has been reported that there is no effect of concentration below 10^{-5} M [18].
- Rhodamine 6G was studied by Magde et al. in water and a series of alcohols [16]. Interaction with OH groups was found to increase radiationless decay, causing the QY to increase in higher alcohols, and upon deuteration of the solvent. Rhodamine 6G in ethanol, $\Phi_f = 0.95$, is a well-established standard, frequently used in recent years.

As argued above, the small Stokes shifts limit the useful range of excitation of fluorescein and rhodamine 6G. The excitation wavelengths used in the thermal blooming experiments of Magde et al., for example, cannot be used in fluorescence experiments because the excitation light would interfere with detection of the emission.

Table 1 Reported data for well-established photoluminescence QY standards.

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			Quinine sulfate				
380–580 (451)	280–380 (347)	H_2SO_4, 0.5 M	366	0.546	[8–10]	1961	25 °C; value is corrected for self-quenching
		H_2SO_4, 0.05 M	366	0.53 ± 0.02	[11]	1977	Optoacoustic; chloride quenching demonstrated
		H_2SO_4, 0.05 M	350	0.52 ± 0.02	[12]	2009	Integrating sphere; 5×10^{-3} M
		H_2SO_4, 0.05 M	350	0.60 ± 0.02	[12]	2009	Integrating sphere; 10^{-5} M
		H_2SO_4, 0.05 M		0.52 ± 0.02	[10]	1983	Relative to QS in H_2SO_4, 0.5 M
		H_2SO_4, 0.05 M		0.51 ± 0.02	[13]	2004	25 °C; Comparative measurement to NIST SRM 936 (next entry)
		HClO4, 0.1 M	347.5	0.60 ± 0.02	[14]	1980	NIST SRM 936

(*continues on next page*)

Table 1 (*Continued*).

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			Fluorescein				
490–620 (515)	470–490 (491)	NaOH, 0.1 M	496	0.95 ± 0.03	[15]	1978	22 °C; thermal blooming
			488 or 514	0.925 ± 0.015	[16]	2002	Thermal blooming
			470	0.91 ± 0.05	[17]	2006	Integrating sphere
			488	0.92 ± 0.04	[18]	1989	Thermal lensing; no effect of concentration in range 10^{-5}–10^{-7} M
		Borate buffer pH 9.1		0.93 ± 0.02	[13]	2004	25 °C; comparative measurement to NIST SRM 936, ref. [14]
			Rhodamine 6G				
510–700 (552)	470–510 (530)	EtOH	488	0.94	[19]	1996	Not quenched by oxygen; independent of concentration up to 2×10^{-4} M
		EtOH	530	0.95 ± 0.015	[16]	2002	Thermal blooming
		H_2O	530	0.92 ± 0.02	[16]	2002	Thermal blooming

[a]Wavelength range of the emission band; emission maximum in parentheses.

[b]Wavelength range that can be used for excitation (see text); absorption maximum in parentheses.

[c]Excitation wavelength for reported QY (see text). Spectral data mostly from the PhotochemCAD database [20]. Wavelengths given in nm.

5. AN IMPRESSION OF THE CURRENT PRACTICE IN THE DETERMINATION OF FLUORESCENCE QUANTUM YIELDS

For this study, we have scanned some 250 arbitrarily chosen papers reporting photoluminescence QYs in the years 2003–2009. Surely, this is not an exhaustive sample, but some observations were made which are worth mentioning here.

- By far the most popular standard still is QS in H_2SO_4.
- 9,10-Diphenylanthracene (DPA), rhodamine 6G, and tris(2,2'-bipyridyl)ruthenium dichloride are also very popular references.
- Many authors do not seem to worry about significant differences between the emission wavelength ranges or the QYs of sample and reference.
- Authors use standards with excitation wavelengths that have not been verified to give the same QY as the published ones.
- Within certain scientific communities, authors use QYs for "key compounds" in such a community as a reference. Examples are: porphyrins, perylene imides, transition-metal complexes ($Ru(bpy)_3$), flavines, europium and terbium complexes. An advantage of the use of such references is that they usually have similar absorption and emission wavelength ranges as the compound of interest. Such reference materials are often secondary standards (at best), and are not always widely used outside the community. Thus, they cannot be considered generally suitable standards.

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- For well-established standards, different authors use slightly different values based on different literature citations. For example, for QS, cited values range from 0.52 to 0.57, for Rhodamine 6G from 0.94 to 1.0. For Rhodamine 6G in water, some authors referred to a paper by Olmsted from 1979, which gives the incorrect $\Phi_f = 0.74$ [24]; it should be 0.90 according to more recent work [16].
- Some authors do not mention the standard used, or just cite a value for the QY of the standard without a literature reference.
- It appears that many authors are satisfied with "reasonably accurate" values of QYs, because they use them (and possibly derived quantities such as radiative rate constants) only in a comparative manner.

A good account of the requirements for a proper documentation of QY measurements is given in ref. [5].

6. A LARGER SET OF POTENTIALLY USEFUL STANDARDS

In addition to the three reference materials discussed above, several others have been studied with apparent care by one or more groups. These are listed in Table 2. Another group of less frequently used standards will be discussed in the next section.

- DPA is one of the most popular reference materials. Reasonable agreement about its QY exists in the case of cyclohexane as the solvent. The two papers from 1983 are highly cited, in particular the one by Meech [10]. The QY values in other solvents are less certain, although Meech and Phillips claim that the QY is the same within error in four nonpolar solvents, including benzene. This is confirmed by the recent study of Suzuki et al. [12], who found a QY of 0.97 ± 0.03, slightly higher than the QY values reported earlier. Hamai and Hirayama established that there is no excitation wavelength dependence in the range 275–405 nm [25]. In view of the observation of non-exponential fluorescence decay of commercial samples of DPA [34], purification is necessary [25,26].
- β-Carboline [23] and a series of analogs [22] have been proposed as alternatives to QS. They cover a very similar spectral range but their photophysical behavior is more straightforward than that of QS. Of the series of compounds studied by Pardo et al. [22], harmaline is worth mentioning separately, because it extends the wavelength range to the red. Independent verification of the results obtained with these promising compounds is desirable.
- The claim of $\Phi_f = 1.0$ for rhodamine 101 in ethanol or methanol goes back to the early work of Drexhage [28], and is supported by recent integrating sphere measurements [17]. A later report from Drexhage's group gives $\Phi_f = 0.96$ [30]. Pereira et al. reported that the QY of rhodamine 101 is equal to that of rhodamine 6G (Table 1) [35]. Very recent work from Würth et al. finds $\Phi_f = 0.90$ [36]. In order to make sure that the carboxylic acid group is protonated, most (but not all) authors add some acid to the solvent. The large overlap of absorption and emission spectra of rhodamine 101 can lead to complications owing to reabsorption of emitted light [35].
- SulfoRhodamine 101 was included in a careful comparative study by Velapoldi and Tønnesen [13], but also in this case, independent verification is desirable.
- Cresyl violet has been studied by Magde using two different calorimetric methods [32]. Two other studies [24,31] found slightly higher QYs. A careful study by Isak and Eyring [33] showed that the fluorescence QY of cresyl violet decreases substantially with increasing concentrations above 1 μM. Unfortunately, this work appears to be much less known than the paper by Magde and coworkers.

Table 2 Photoluminescence QY standards investigated by several independent authors, or claimed as reliable standards.

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			9,10-Diphenylanthracene				
390–500 (404)	275–380 (372)	Cyclo-hexane	325	0.90 ± 0.04	[25]	1983	Actinometric
		Cyclo-hexane	300–370	0.93 ± 0.03	[10]	1983	Comparative; integrating sphere
		Cyclo-hexane	366	0.955	[26]	1977	Calorimetry
		Cyclo-hexane	355	0.97 ± 0.03	[12]	2009	Integrating sphere and photoacoustic calorimetry
		EtOH		0.885	[26]	1977	Calorimetry
		EtOH	330–380	0.95	[27]	1976	Relative to QS
			β-Carboline = norharmane				
400–600 (454)	330–370	H_2SO_4, 0.5 M	360	0.60	[23]	1985	25 °C; relative to QS; temp. dependence reported; $c \leq 2 \times 10^{-5}$ M
		H_2SO_4, 0.5 M	330–360	0.58 ± 0.02	[22]	1992	
			Harmaline				
430–600 (498)	330–390	H_2SO_4, 0.005 M	330–360	0.32 ± 0.02	[22]	1992	
			Rhodamine 101				
(600)	500–550 (576)	MeOH		1.0	[28]	1976	Often incorrectly attributed to Karstens [29], who merely showed that the QY is independent of temperature
		Acidified MeOH		0.96	[30]	1991	Thermal blooming
			535	1.00 ± 0.05	[17]	2006	Integrating sphere
			Sulforhodamine 101				
575–680 (591)	510–560 (576)	EtOH		0.95 ± 0.02	[13]	2004	Comparative measurement to NIST SRM 936 [14]

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Table 2 (*Continued*).

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			Cresyl violet				
580–750 (623)	540–590 (602)	EtOH, 24 °C		0.56	[31]	1981	Thermal blooming; not temperature-dependent
		MeOH, 22 °C		0.54 ± 0.03	[32]	1979	Calorimetric; very similar QY in nitrobenzene and in glycerol
		MeOH, 24 °C		0.57	[31]	1981	Thermal blooming; not temperature-dependent
		MeOH	610	0.51–0.67	[33]	1992	Photothermal method; QY decreases with increasing concentration in the range 6×10^{-7}–3×10^{-4} M

[a,b,c]See footnotes in Table 1. Wavelengths in nm.

7. OTHER QUANTUM YIELD STANDARDS FOUND IN THE LITERATURE

In Table 3 compound/solvent combinations are listed that are more or less frequently cited as QY references. This list is by no means exhaustive. Mostly, these are secondary standards, measured relative to QS or other reference compounds. Many of these are potentially useful and deserve more attention. Some of the references are rather old and have not been confirmed by other methods or by a systematic comparison with a set of standards. When using standards from this list it is advisable to cross-check with two different standards.

- For the UV absorbing simple aromatic compounds, including the amino acids, literature values are more than 30 years old, and a systematic verification of the reported QY is needed. Recently, Suzuki et al. reported determinations of the absolute QY using integrating sphere measurements of naphthalene, anthracene, and tryptophan in very good agreement with the early literature values [12].
- POPOP is an attractive dye as a decay time standard [34], but its QY does not seem to have been very thoroughly checked.
- Many coumarines have broad absorption and emission bands, and relatively large Stokes shifts, which are favorable properties. The photophysical properties depend rather strongly on solvent polarity. QYs have been reported for a number of coumarines [28,43].
- The excited state decay of rhodamine B was found to be strongly temperature dependent, in contrast to that of rhodamine 101 [61]. According to Karstens and Kobs [29], at room temperature $\Phi_f \approx 0.5$, but Velapoldi and Tønnesen find $\Phi_f = 0.70$ [13]. The situation is unclear.
- Perylene imide derivatives have gained popularity over the past two decades owing to their strong fluorescence and high photostability. The photophysical properties do not depend on the substituent on the nitrogen atom(s), unless the substituents are active in energy or electron transfer. For the diimides, QYs were first published in 1987 (*N*,*N*′-di(2,5-di-*tert*-butyl) derivative: $\Phi_f = 0.99$ in $CHCl_3$ [44], *N*,*N*′-di(hexylheptyl) derivative 0.99 ± 0.05 in CH_2Cl_2 [62]). The bay-substituted "Perylene Red" is a particularly good dye, of which the basic properties were investigated by Seybold and Wagenblast [45]. The QYs are close to one in solvents of low and medium polarity, and somewhat lower in ethanol and methanol. Kalinin et al. also proposed a more com-

plicated perylene imide derivative as a QY standard, but the synthetic accessibility will limit its application [63].

- Two lanthanide complexes were recently developed as secondary standards for the measurements of QYs of other europium and terbium compounds. They are excited in the UV, and emission occurs in the characteristic green and red spectral ranges for these ions [50].
- Complexes of Ru^{2+} and Os^{2+} emit rather weakly, and are sensitive to oxygen and to effects of hydrogen bonding [47–49,53]. Despite these complications, they are frequently used. The recent results from Suzuki et al. reveal considerably higher QY for $Ru^{2+}(bpy)_3$ salts than the accepted values. It has been suggested, however, that the integration sphere technique is not ideal for the measurement of low QY [36]. Further independent measurements should resolve the disagreement.
- Iridium complexes have recently been investigated extensively in view of their favorable properties for application in "organic" light-emitting diodes. A key compound in the field is the green-emitting iridium tris(phenylpyridine) $Ir(ppy)_3$. For its luminescence yield, for several years an incorrect value of 0.4 has been in the literature. More recently, it was shown to be as high as 0.75 in toluene [64] and 0.89 in dichloroethane [65]. Because of the long excited-state lifetimes (microseconds) quenching by oxygen is significant, and other quenchers may also cause problems. When using such standards, it is recommendable to check the luminescence decay time to ensure that quenching does not occur.
- Near-IR emitters are a subject of active current research [66]. In this field, reliable standards are needed. Most of the published QYs are based on relative measurements, often using very old literature data. Some examples are listed in Table 3.

Table 3 Some photoluminescence QY standards cited in recent literature handbooks.

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			Benzene				
270–320	235–260 (255)	Hexane	254	0.053 ± 0.008 0.058	[9] [37]	1968 1970	Deoxygenated
			Phenylalanine				
270–320 (280)	230–260 (258)	Water, 23 °C	260	0.022 ± 0.003	[38]	1976	Reference QS
			Tyrosine				
290–340 (303)	250–280 (274)	Water, 23 °C	275	0.13 ± 0.01	[38]	1976	Reference QS
			Phenol				
270–330 (292)	250–270 (271)	*n*-hexane		0.075	[39]	1990	Reference anisole in *n*-hexane
		Cyclo-hexane		0.08	[40]	1971	
		Water, 23 °C	275	0.13 ± 0.01	[38]	1976	Reference QS

(*continues on next page*)

Table 3 (*Continued*).

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			Naphthalene				
300–380 (322)	240–290 (276)	Cyclo-hexane		0.23	[40]	1971	Reference QS
			270	0.23 ± 0.01	[12]	2009	Absolute measurement using integrating sphere
			Terphenyl				
310–380 (338)	240–305 (276)	Cyclo-hexane		0.92	[40]	1971	
			Tryptophan				
310–430 (356)	240–300 (278)	Water, 23 °C	280	0.12 ± 0.01	[38]	1976	
		pH 6.1	270	0.15 ± 0.01	[12]	2009	Absolute measurement using integrating sphere
			Phenanthrene				
345–410 (365)	260–335 (294)	EtOH	254, 313	0.125 ± 0.007	[9]	1968	
			2-Amino-pyridine				
315–480	285	H_2SO_4, 0.05 M	285	0.60 ± 0.05	[41]	1968	
		H_2SO_4, 0.05–0.5 M	280–315	0.66 ± 0.05	[10]	1983	Sensitive to temperature
			Anthracene				
370–450 (397)	310–365 (356)	Cyclo-hexane		0.36	[40]	1971	
		EtOH	366	0.27	[9]	1968	Sensitive to oxygen and temperature
			340	0.28 ± 0.02	[12]	2009	Absolute measurement using integrating sphere
			POPOP				
380–470 (407)	310–370 (371)	Cyclo-hexane	366	0.975 ± 0.03	[26]	1977	Calorimetric
		EtOH	366	0.885	[26]	1977	Calorimetric
			Perylene				
430–530 (436)	360–420 (436)	Cyclo-hexane		0.94	[40]	1971	
		Benzene		0.89	[8]	1961	
			366	0.99 ± 0.03	[9]	1968	
		EtOH		0.92	[42]	1971	

(*continues on next page*)

Table 3 (*Continued*).

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			Rhodamine B				
560–590 (570)	500–540 (545)	MeOH	348	0.70 ± 0.02	[13]	2004	Comparative measurement to SRM 936 (ref. [14])
		EtOH	450–565	0.5	[29]	1980	QY at room temperature; increases to ~1.0 upon cooling to ca. 200 K
			Coumarine 153				
480–650 (531)	370–470 (421)	EtOH		0.38	[43]	1985	Deaerated; related coumarins and different solvents also reported
(455)	(393)	Cyclo-hexane		0.90	[43]	1985	
			"Perylene orange"				
530–640 (537)	430–505 (528)	$CHCl_3$	485–515	0.99 ± 0.05	[44]	1987	Values in other solvents reported as well
				1.00	[45]	1989	
			"Perylene red"				
570–700 (608)	400–550 (573)	$CHCl_3$		0.96	[45]	1989	Other solvents, see [46]
			$Ru(bpy)_3^{2+}$				
550–700 (625)	380–530 (452)	H_2O	436	0.042	[47]	1976	N_2-saturated; temperature and solvent isotope effects reported
		H_2O	436	0.028	[48]	1982	Air-saturated
			450	0.063 ± 0.002	[12]	2009	Integrating sphere; N_2-saturated
			450	0.040 ± 0.002	[12]	2009	Integrating sphere; air-saturated
		MeCN	436	0.06	[49]	1982	Nitrogen-saturated; also other solvents
			450	0.094 ± 0.004	[12]	2009	Integrating sphere; N_2-saturated
			450	0.018 ± 0.002	[12]	2009	Integrating sphere; air-saturated
			$Cs_3[Tb(dpa)_3]$				
570–650	260–285 (279)	0.1 M tris buffer	279	0.22 ± 0.025	[50]	2004	References cresyl violet and rhodamine 101

(*continues on next page*)

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Table 3 (*Continued*).

Emission[a]	Excitation[b]	Solvent/ medium	λ_{exc}[c]	Value	Ref.	Year	Comment
			$Cs_3[Eu(dpa)_3]$				
590–700	260–285 (279)	0.1 M tris buffer	279	0.24 ± 0.025	[50]	2004	References cresyl violet and rhodamine 101
			Tetraphenyl porphyrin				
640–740 (649)	490–610 (515)	MeCN		0.15	[51]	1970	Reference 3,6-diaminophthalimide [52]
			$Os(bpy)_3^{2+}$				
600–850		MeCN		0.005	[53]	1986	$Ru(bpy)_3^{2+}$ as reference
			$Os(phen)_3^{2+}$				
600–900		MeCN		0.021	[53]	1986	
			Nile blue				
610–800 (670)	200–610 (633)	EtOH		0.27	[31]	1981	Thermal blooming
			Oxazine 1				
625–800 (670)	530–615 (646)	EtOH		0.11	[31]	1981	Thermal blooming
			Zn-phthalocyanine				
660–780 (678)	600–660 (674)	Benzene	633	0.30	[54]	1969	Reference chlorophyll b [55]
		PrOH		0.45	[51]	1970	Reference 3,6-diaminophthalimide [52]
			t_4-PcMg[d]				
670–750 (691)	600–670 (681)	$CHCl_3$	630	0.84	[56]	1994	Reference chloroaluminium-phthalocyanine in chloro-toluene [57]
			Aza-BDP[e]				
700–780 (715)	600–670 (688)	$CHCl_3$		0.36	[58]	2004	Reference t_4-PcMg[c] [56]
			Indocyanine green				
760–1000 (813)	550–750 (795)	DMSO	678	0.106 ± 0.005	[59]	1997	Reference HITCI [60]

[a,b,c]See footnotes in Table 1.
[d]Tetra-(*tert*-butyl)-phthalocyanato magnesium.
[e]BF_2 chelate of [5-(4-methoxyphenyl)-3-phenyl-1*H*-pyrrol-2-yl]-[5-(4-methoxyphenyl)-3-phenylpyrrol-2-ylidene]amine [58].
Wavelengths given in nm.

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8. WHAT IS MISSING?

Taking together the three well-established standards (Table 1), and the larger sets of (somewhat) less-established ones (Tables 2 and 3), it is fair to say that there is a need for confirmation and consolidation of reported values, for new standards for the near-IR range, and for a reliable procedure to measure low QYs. For standard spectrometers, the correction curves of the instrument response vs. wavelength is relatively flat in the visible, but goes up steeply toward the UV and at long wavelengths, which makes the need for good standards for those ranges only more pressing.

The QYs for most reference compounds are high, typically >0.5, but researchers are often interested in low QYs, e.g., of the order of 0.001 to 0.01 [67]. Either robust protocols for correction for nonlinearity or alternative standards with low QY are required.

Some promising standards have been proposed in the literature, which are worth a more thorough investigation and testing. For some of the old standards, in particular the amino acids, the literature values that are cited are 40 years old, and a reinvestigation is recommendable.

Recently, several authors have reported absolute measurements of QYs of dyes in dilute solution using integrating spheres, which are mostly consistent with literature data obtained using relative methods and other measurements [12,17,65]. With these experiments, older standards can be consolidated, and less-established ones can be checked. Proper use of the integrating sphere, however, requires considerable care [36,68]. It can be expected that in the next decade the list of well-established reference materials for the measurement of photoluminescence QY will grow steadily. Ideally, SI traceable materials should become available [69].

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