Fluorescence of ceramic color standards

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Fluorescence has been found in color standards available for use in calibration and verification of color measuring instruments. The fluorescence is excited at wavelengths below about 600 nm and emitted above 700 nm, within the response range of silicon photodiodes, but at the edge of the response of most photomultipliers and outside the range commonly scanned in commercial colorimeters. The degree of fluorescence on two of a set of 12 glossy ceramic tiles is enough to introduce significant error when those tiles have been calibrated in one mode of measurement and are used in another. We report the nature of the fluorescence and the implications for color measurement.

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1. Introduction

Many color measurement instruments require the use of calibrated reflectance or color standards for their establishment and maintenance. In particular, color standards are used to check an instrument and track down the source of errors to make comparisons between instruments and ensure agreement or to calibrate tristimulus colorimeters [1–3].

One of the properties of an ideal standard is that it be nonfluorescent [3]. This requirement guarantees that the reflectance of the standard at a particular wavelength (and by implication its color specification) is independent of the source used or mode of measurement (broadband source with narrowband detector or narrowband source with broadband detector) used by the instrument. When fluorescence is present, the reflectance spectrum will be distorted by either:

- an increase in apparent reflectance at the excitation wavelengths in a narrowband-source/broadband-detector mode or
- an increase in apparent reflectance at the emission wavelengths in a broadband-source/narrowband-detector mode.

It has been shown, for example, that even a narrow band of fluorescence in a white standard used to calibrate spectrometers introduces significant disparities in the color coordinates measured in the two different modes [4] and that fluorescence of white reference materials on exposure to UV can introduce errors in a measurement [5].

Two recent observations have demonstrated the importance of checking for fluorescence in reference artifacts. The first arose when, in the course of extending a set of green reference tiles for use in horticultural measurements, we re-realized the color coordinates of four tiles that had been purchased with calibration by our client. For three tiles, as described below, our measurements matched the calibrated values, but for the fourth, we obtained a significantly different reflectance spectrum using the Measurements Standards Laboratory (MSL) reference spectrophotometer. However, agreement with the calibrated values was obtained when the measurements on this tile were repeated with a handheld color meter. The discrepancy was traced to

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fluorescence in the tile that was emitted at the longer wavelengths detected by a silicon photodiode but was neither detected by a photomultiplier nor within the range commonly scanned by spectrometer-based instruments. The presence of the fluorescence, while notable, was not a problem for the client, as the tile had been calibrated on a system that operated in the same mode as the instrument with which the tile was being used by the client.

The second observation concerned a set of CCSII tiles (formerly BCRA Series II), one of the most commonly used sets of color-standard tiles [3,6]. As a test of our ability to realize a color scale, we measured the 12 tiles in this set, which had just been purchased from and calibrated by another national measurement institute. For 10 tiles, as described below, agreement was obtained to within our combined uncertainties after accounting for thermochromism; however, for the other two tiles, we found that the reflectance spectra differed significantly. Again this was traced to fluorescence emitted at the long wavelength end of the range of a silicon photodiode. This fluorescence was sufficient to introduce significant errors when a tile calibrated in one mode is used in a different mode. This paper describes the nature of the fluorescence and the implications for color measurement.

2. Experimental Setup

A. Reflectance Measurements

Reflectance spectra were obtained on three instruments. The first, a narrowband-source/broadband-detector system was the MSL reference spectrophotometer. Reflectance measurements were made, in a 6° incidence, diffuse efflux geometry, with the specular component included (6°:di) every 5 nm between 380 and 780 nm. A schematic diagram of the optical system is shown in Fig. 1. The source used for these measurements is a quartz tungsten halogen lamp, and the monochromator is a McPherson 2051 with a prism predisperser. Stray-light filters reduce the stray light in the system to less than one part in 10^6 over the spectral range of interest. The incident beam has a size of approximately 5 mm × 5 mm, a 2 nm bandwidth, and an angle of incidence on the tile of 6°. The detector is placed normal to the plane of the incident and specularly reflected beam. The inner surface of the integrating sphere is coated with pressed halon, and the sample port comprises approximately 0.5% of the internal surface area. The reflectance of the tile, ρ_t, is determined by comparison with a matte white reference, the reflectance, ρ_r, of which has been obtained by transfer from a standard calibrated by the National Institute of Standards and Technology [7]. The scattered stray light is accounted for by the use of a black cone in place of the sample. To take into account the change in reflectance of the sphere when the reference standard is replaced by the tile or the black cone on the sample port, ratios are obtained of the signal obtained when the light is incident on the port to that when it is incident on the sphere wall adjacent to the port. The reflectance of the tile at a particular wavelength is determined as

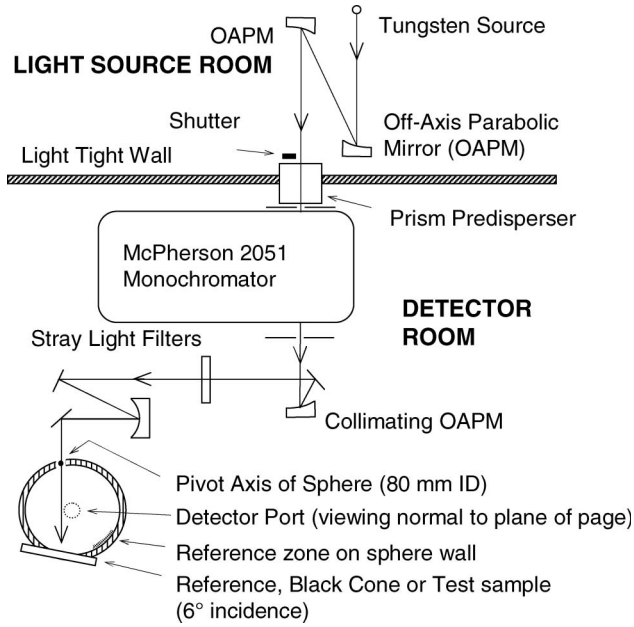

Fig. 1. Schematic diagram of the color measurement system used at MSL.

$$\rho_t = \rho_r \frac{(T - C)}{(S - C)}, \tag{1}$$

where T, S, and C are the aforementioned ratios when the tile, reference standard, and black cone cover the sample port. Either a photomultiplier tube (EMI 9798AQ) or a three-element silicon-diode trap detector can be used on the detector port, recessed into the wall so that the detector surface is effectively baffled from the entrance and sample ports. The photomultiplier tube was operated at 300 V, the temperature of the room was 20 °C ± 0.5 °C, and the humidity remained in the range from 40% to 60%.

Reflectance spectra were also obtained at MSL using a Konica Minolta CM-2500d spectrophotometer, which measures in an 8°:di geometry using a pulsed xenon lamp as a source and a prism with silicon photodiode array as detector, i.e., in a broadband-source/narrowband-detector mode.

To test the impact of the fluorescence on measurements made with a particular commercial narrowband-source/broadband-detector spectrophotometer employing a photomultiplier, a PerkinElmer Lambda 900 instrument with 0°:45° attachment was used at the National Physical Laboratory (NPL) with the addition of a KV550 filter in front of the detector, as shown in Fig. 2.

B. Fluorescence Measurements

To measure the fluorescence spectrum, the tile of interest was placed at the focal point of the entrance optics of MSL's McPherson 2035 double monochro-

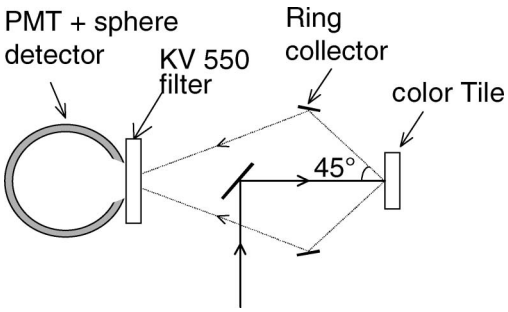

Fig. 2. Modified 0°:45° attachment for PerkinElmer Lambda 900 spectrophotometer measurements using a photomultiplier tube.

mator, and a spot of approximately 2 mm diameter was illuminated with 488 nm emission from an argon-ion laser. The 488 nm emission line was chosen because it was well within the range of excitation wavelengths for the tiles, sufficiently powerful to generate measurable signals, and conveniently available. The homochromic reflectance was eliminated with a Schott OG550 cut-on glass filter placed between the tile and the monochromator. A silicon diode fitted to the exit slit of the monochromator was used to measure the resulting signal over the range from 600 to 1200 nm at 20 nm intervals, using a measurement bandwidth of 8 nm. The spectral shape was then normalized by the known spectral response function of the filter, monochromator, and silicon detector combination. A schematic of the system is shown in Fig. 3.

To compare the spectrally integrated fluorescence of nominally identical tiles from different sets, measurements were made at NPL with the narrowband-source/broadband-detector setup, shown in Fig. 4. Tiles from four sets were irradiated at near-normal incidence by laser light at 488 nm, 532 nm, or both. Scattered light leaving the sample at approximately 20° from normal was measured with a Hamamatsu 1337 silicon photodiode. A Schott KV550 filter was used to cut out the incident wavelength while transmitting fluorescence.

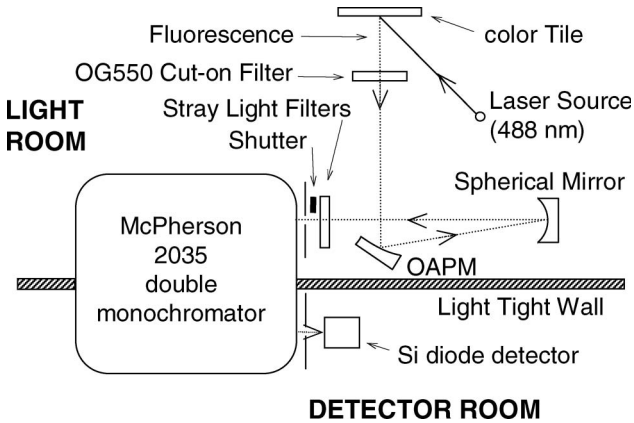

Fig. 3. Schematic diagram of the fluorescence detection system used at MSL.

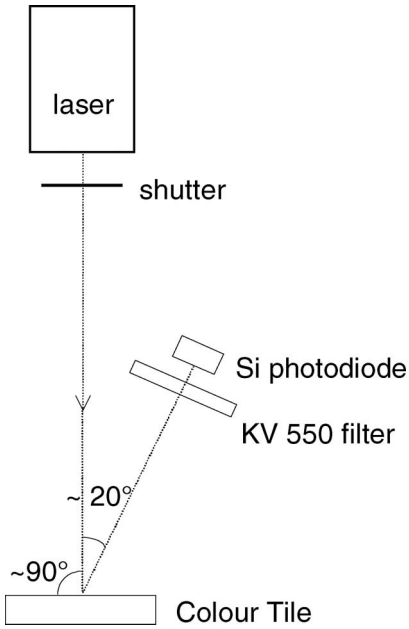

Fig. 4. Apparatus for comparison of tiles from different sets.

3. Results

Reflectance spectra of four different green tiles (identified here as *G*1, *G*2, *G*3, and *G*4) of an MSL client, and of the set of 12 color standards, were obtained on the MSL reference spectrophotometer in a 6°:di geometry using a silicon-diode trap detector. With regard to the green tiles, it was found that the results were in agreement with the original calibrations for three of the tiles, with differences of less than 0.01 in reflectance values with a combined uncertainty of 0.015. However, over a 150 nm range of the

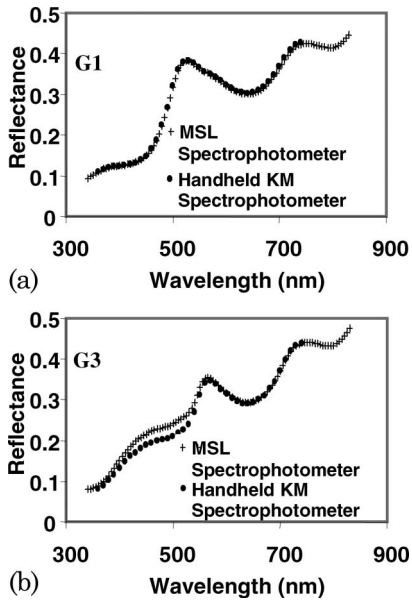

Fig. 5. Reflectance spectra in 6°:di geometry taken with both the MSL reference spectrophotometer using a silicon-diode trap detector and a handheld KM spectrophotometer for two color tiles: (a) *G*1 and (b) *G*3.

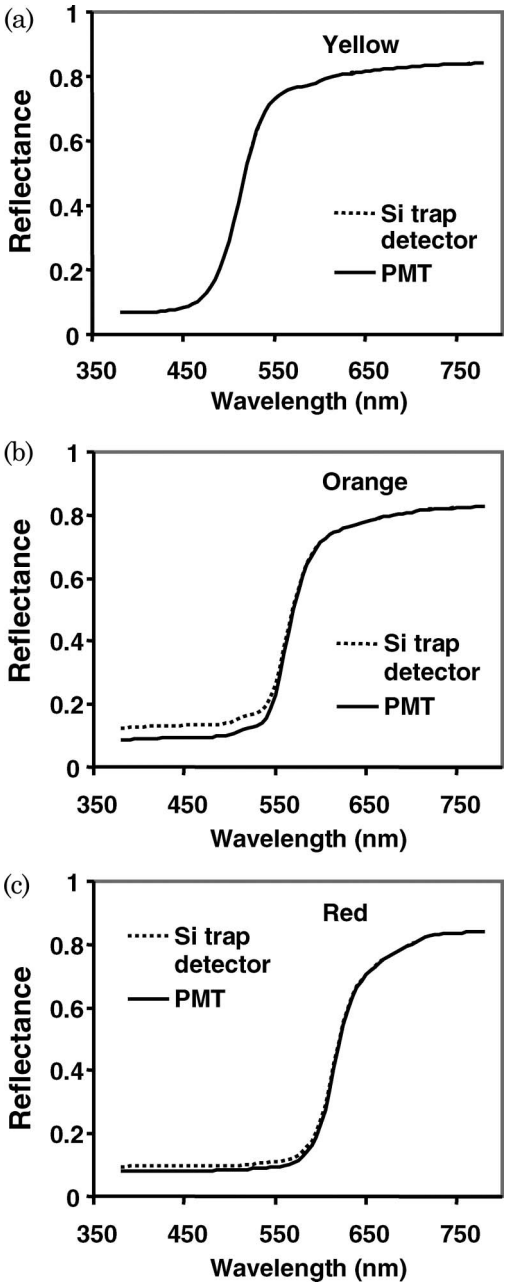

Fig. 6. Reflectance spectra in 6°:di geometry taken with both a photomultiplier tube and a silicon-diode trap detector for (a) yellow, (b) orange, and (c) red color tiles.

spectrum for *G*3, differences of between 0.020 and 0.035 in reflectance values with a combined uncertainty of 0.015 were found. Additional spectra obtained using the handheld CM-2500d spectrophotometer, on the other hand, gave values of reflectance that agreed to within the combined uncertainty for each of the four tiles. Figure 5 shows the spectra obtained on each of the two systems for *G*1 [Fig. 5(a)] and *G*3 [Fig. 5(b)].

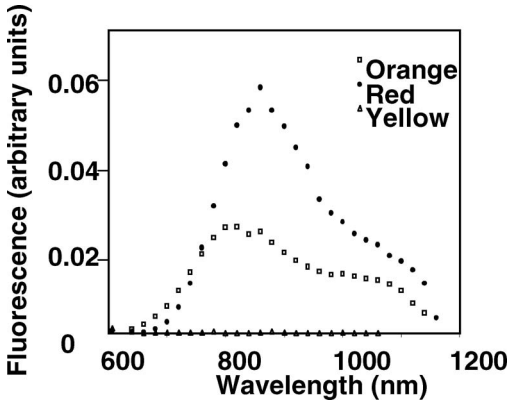

Fig. 7. Fluorescence emitted by three CCSII tiles under excitation by a 488 nm laser. The collection efficiency of the fluorescent emission is not identical for the tiles, so the traces are not necessarily indicative of relative magnitudes.

In the case of the set of 12 color standards, we also noted that the reflectance spectra for two of the tiles, the orange and red tiles, did not agree with the calibrated values. Differences in reflectance of greater than 0.04 were found over a 170 nm range, in which the combined uncertainties were less than 0.01, on the orange tile; differences of greater than 0.017 were found over a 230 nm range, in which combined uncertainties were less than 0.01, on the red tile; at all other wavelengths and for all of the other tiles, the differences were within the combined uncertainties. This time, for comparison, the tiles were remeasured on the MSL reference spectrophotometer using the photomultiplier tube as the detector, and agreement with calibrated values within the combined uncertainties was found for all tiles. The spectra measured by both systems are shown in Fig. 6 for the yellow [Fig. 6(a)], orange [Fig. 6(b)], and red [Fig. 6(c)] tiles. The differences described above are evident in the spectra for the red and orange tiles over the wavelength range in which the tiles are absorbing. The difference in reflectance propagates through to a difference in color coordinates, and ΔE^*_{ab} between the measurement methods is shown for the complete set of tiles in Table 1. It will be noted that for two tiles, the red and orange tiles, ΔE^*_{ab} is larger than for all other tiles by factors of 10 and 30, respectively.

Table 1. Difference in Color Coordinates (ΔE^*_{ab}) for CIE Illuminant A and CIE 1964 Standard 10° Observer for 12 Tiles When Reflectance Is Measured Using a Silicon-Diode Trap Detector or Photomultiplier Tube

Tile	ΔE^*_{ab}	Tile	ΔE^*_{ab}	Tile	ΔE^*_{ab}
Pale grey	0.37	Deep pink	0.09	Green	0.32
Mid grey	0.30	Red	3.50	Difference green	0.28
Difference grey	0.23	Orange	9.61	Cyan	0.33
Deep grey	0.28	Yellow	0.05	Deep blue	0.16

Table 2. Fraction of Scattered Signal, Using Apparatus Shown in Fig. 4, Attributable to Fluorescence for Isochromatic Tiles from Different Sets

Color	Set A (488 nm)	Set A (532 nm)	Set B (488 nm)	Set B (532 nm)	Set C (532 nm)	Set D (532 nm)
Pale grey	0%	0%		0%	0%	0%
Orange	30%	28%	24%	15%	16%	34%
Red	24%	27%	24%	26%	26%	46%
Yellow	1%	0%		0%	0%	0%

The essential difference between the two measurements is the bandwidth of the detector. The silicon-diode trap is sensitive to light of wavelengths between 200 and 1200 nm, while the handheld spectrophotometer has a very narrow bandwidth (approximately 10 nm) and the photomultiplier tube is sensitive to wavelengths between 200 and 800 nm. The excess light giving rise to the higher signal recorded by the silicon-diode detector in Fig. 6 must, therefore, be in the 800–1200 nm range. As it is only seen on some of the tiles, it is not systemic stray light or fluorescence generated by the sphere or white standard, but rather radiation generated by the tiles themselves. Fluorescence of wavelength in the range from 800 to 1200 nm, in addition to the reflected light of the source wavelength, would be detected by the silicon-diode trap detector when the source is tuned to wavelengths in the range from 300 to 550 nm and would account for the discrepancies.

A simple qualitative confirmation of the presence of fluorescence was carried out by placing a Kodak Wratten gelatin filter (#87) with a 740 nm cut-on between the detector port of the sphere and the silicon-diode trap detector on the MSL reference spectrophotometer. The tiles were illuminated by 550 nm light, and it was noted that no signal was obtained when the reference white standard or the yellow tiles were applied to the sample port, but a significant signal was obtained for the orange and red tiles.

To further investigate the nature of the fluorescence, two of the green tiles ($G1$ and $G3$) and three tiles of the set (yellow, orange, and red) were tested for fluorescence using the method described in the previous section. The resulting curves for the yellow, orange, and red tiles are shown in Fig. 7. Fluorescence was observed for the orange and red tiles, but none was detected from the yellow tile. Similarly, the $G1$ tile showed no fluorescence, while the $G3$ tile yielded fluorescence with a very similar spectral shape to that of the orange and red tiles.

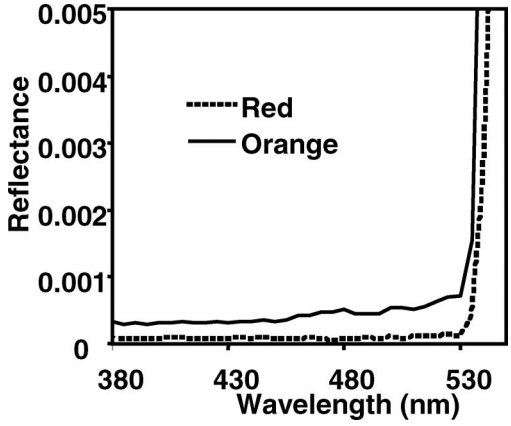

Fig. 8. Reflectance measured in 0°:45° geometry using a PerkinElmer Lambda 900 but with a KV550 cut-on filter in front of the detector to allow transmittance of fluorescence at wavelengths longer than 550 nm.

The result of the tile set comparisons is shown in Table 2. Each value is the ratio of the signal with the KV550 filter between the sample and the detector compared to the signal without the filter. The exact values are specific to the experimental arrangement and the detector bandwidth. The important feature, however, is the wide variation in values between nominally isochromatic tiles.

Figure 8 shows measurement scans using a PerkinElmer Lambda 900 with the modified detector attachment shown in Fig. 2. The data were normalized with respect to a calibrated white tile measured without the KV550 filter and shows that, for a system like this one, the error introduced by the fluorescence is small.

4. Discussion and Conclusion

The fluorescence described above will result in errors when a tile calibrated in one mode is used for calibration or verification in another mode. For example, if either the red or orange tile were calibrated on a spectrophotometer system such as the one at MSL (and some other first-tier laboratories) using a silicon-diode-based detector system, and then used to calibrate any system that either used a narrower band detector such as a photomultiplier tube, or a broadband-source/narrow-band detector mode, the color coordinates would be in error by the amount shown in Table 1. Tristimulus colorimeters and color spectrometers using xenon flashlamps and silicon-diode arrays are examples of instruments for which this degree of error would arise. In fact, because the

Table 3. Potential Errors in Color Parameters for CCSII Orange Tile (Narrowband-Detector—Broadband-Detector)

	Illuminant A		Illuminant D65	
	2° Observer	10° Observer	2° Observer	10° Observer
L^*	−1.14	−1.20	−1.71	−1.85
$a*$	3.01	3.03	3.48	3.74
b^*	8.99	9.05	8.17	7.98
x	0.0119	0.0121	0.0251	0.0261
y	−0.0014	−0.0016	0.0077	0.0070
Y	−1.78	−1.85	−2.34	−2.45

Table 4. Potential Errors in Color Parameters for CCSII Red Tile (Narrowband Detector—Broadband Detector)

	Illuminant A		Illuminant D65	
	2° Observer	10° Observer	2° Observer	10° Observer
L^*	−1.52	−1.54	−1.88	−1.91
a^*	2.45	2.22	2.64	2.44
b^*	2.23	2.22	1.63	1.59
x	0.0103	0.0098	0.0160	0.0153
y	−0.0045	−0.0040	−0.0009	−0.0005
Y	−1.40	−1.40	−1.47	−1.47

fluorescence extends into the visible range, as shown in Fig. 7, the apparent reflectance will be elevated to some degree for a narrowband-source/broadband-detector measurement even when a photomultiplier tube is used. Equally, the apparent reflectance at wavelengths between about 680 and 780 nm will be elevated somewhat in broadband-source/narrowband-detector systems by the presence of the fluorescence.

The degree of error will depend on the amount of fluorescence each tile exhibits. The results in Table 2 show that the fluorescence in nominally identical tiles can vary by up to a factor of 2, due to differing concentrations of fluorophore or pigment degradation over time. Another factor to consider is the particular difference in spectral responsivity between two systems—even two different photomultiplier tubes, for example, may give different results if their sensitivities over the range of wavelengths in Fig. 7 are different. Figure 8 shows that the fluorescence does not cause a large reflectance measurement error for this particular photomultiplier-equipped system, while Figs. 5 and 6 show that large reflectance errors may arise in other systems. Hence, correction factors to reflectance values and color specifications must be calculated for each individual tile and combination of measurement modes.

In the extreme case, if CCSII orange and red tiles with the same degree of fluorescence as those described here are calibrated on a system like the one at MSL and used in a broadband-source/narrowband-detector system, the errors arising would be of the order found in Tables 3 and 4 for measurements of L^*, a^*, and b^*, or x, y, and Y for two commonly used illuminants and both the 1931 2° and 1964 10° observers.

Generation of visible fluorescence by UV excitation is well known and can be eliminated by filtering of the source. However, fluorescence generated by visible wavelengths may often not be tested for. In the case of the tiles examined here, this latter form of fluorescence is shown to introduce potentially large errors and should always be tested for prior to standards being calibrated or disseminated.

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