Use of optical fibre in spectrometry and colorimetry with remote probes

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Measurement of colour is mainly performed using colorimeters but the size of these instruments does not allow to perform measurements in all cases. For this reason we have employed Fibre Optic Reflectance Spectrometry (FORS) to measure colour. With this work we want to give a preliminary study about colour measurements obtained by a spectrometer with remote optical fibre probes in order to obtain colorimetric values. A comparison between a standard colorimeter and a FORS system was done using 28 + 28 colour samples evaluating the influence of optical fibre and of two different geometric set up: the integrating sphere with specular included (SPINC) and the coaxial fibre probe 45°x:45° with specular component excluded (SPEX). The results showed a difference in colorimetric data between the different set up when the chroma value was greater than 40. The FORS system proved to have good reliability in terms of repeatability and relative colour measurements.

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Introduction

The international method for colour measurements requires the use of colorimeter but in some cases the sizes of these instruments don't allow them to perform measurements. Applications in the field of Cultural Heritage [1,2] such as pigment characterisations on statues or ceramic do not allow the use of an integrating sphere. We studied the applicability of optical fibre for the realisation of remote probes that allow more flexibility with the capability of colour analysis for irregular or hardly accessible surfaces like in the case of measuring colour in oral cavity [3-5]. The use of optical fibre was consolidated for spectroscopy measurements [6] (in particular for UV-VIS-NIR spectroscopy), but depending on the geometric measurement, it may interfere with the detection of the spectrum and, in consequence, create a further error in the definition of the colour of the sample analysed. The use of optical fibre spectrophotometers then allows the colorimetric analysis of objects that cannot be analysed with the colorimeter. Therefore, there is a need to compare the results obtained with FORS and those obtained with a standard measure performed with the colorimeter. This aim is important because the differences due to the light detector geometries, to the spectrum resolution and to the surface properties can lead to different colour data. For instance standard colorimeters use an integrating sphere where all the scattered radiation is collected whereas a fibre optic probe collects only a small portion of the backscattered light.

Materials and Methods

Measurement of reflected visible spectrum was used to determine objectively the colour of samples printed on matt paper or obtained using sheets of translucent paper overlapped on the printed specimens.

Colorimeter: Chroma Meter CR400/410 by Konica Minolta calibrated with a white ceramic tile and black surface provided by the manufacturer.

Spectrophotometric set up: Portable spectrophotometer (HR4000, Ocean Optics®, Dunedin, FL, USA) was calibrated to a reflectance standard (white Spectralon® 99%) and connected to a laptop for data analysis. It detected light in the range 380-1100, colorimetric data was calculated in 380-780 nm range every 5 nm [7].

Source light: Measurements were carried out under standard illumination (D65), using halogen light source (HL2000, Ocean Optics®, Dunedin, FL, USA) - with a cyan filter with a cut-off absorption until 600 nm in order to enhance the blue component of the source and to improve the signal to noise ratio. in 380-420 nm range.

Fibre optics probe: light was transmitted by a 2 m long quartz fibre optics bundle with a diameter of 400 μm (Ocean Optics® Dunedin, FL, USA), connected to the probe. We used two probes type: a thin tubular coaxial probe (length = 10 cm, diameter 1 cm) in 45°×:45° geometry and an integrating sphere in 8°/diffuse geometry (Figure 1). In both these geometries the detection area is about 2 mm² (Figure 2).

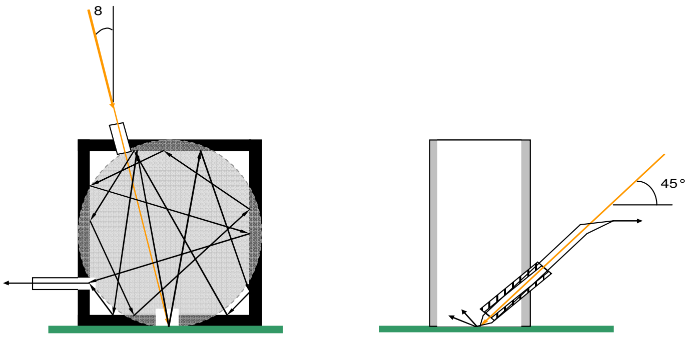

Figure 1: Probes – Integrating sphere (left) and coaxial fibre geometries (right).

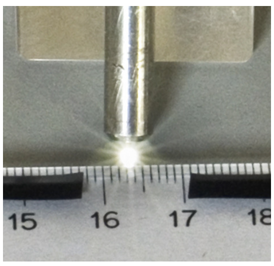

Figure 2: Lighting area with 45°×:45° coaxial probe.

Using the convolution multiplication between illuminant spectrum (D65), sample reflectance factor and tristimulus function we can obtain the *XYZ* coordinates, and again by applying a normalisation to the total value of each coordinate we have the CIExyz coordinate. The non-linearity of this space didn't allow us to compare colour differences. In order to achieve this we used the *CIELAB* 1976 space that can be considered linear at least near the origin [7].

The spectral data used for colorimetric calculation was extracted from the recorded spectrum in the range of 380-780 nm with a 5 nm resolution according the international CIE recommendations.

To evaluate the colour differences, Visual Difference Index (VDI, called ΔE) was used. Other possible non-statistical factors that may affect the results of the measurement were all those terms inherent with the convolution product. Such as the instability of the light source (which is however compensated by frequent calibration), the surface evenness which we tried to overcome using homogeneous printed samples, such as coloured cardboard. The analysed area of about 1 cm^2 and all the variations of reflectance factor are related to the changes of the beam path in the fibre optics and their connections. In particular, the latter factor is critical as we tried to experimentally obtain the greatest possible flexibility of the measurement apparatus. A preliminary study was therefore specifically addressed in regards to measure the stability of the results with the change in the arrangement of optical fibres.

Results

Fibre optic position

A first step was to evaluate the influence of fibre optic bundle position in colorimetric data. This, in theory, can dramatically influence the possibility to obtain reliable data for example in monitoring colour change in cleaning of paintings. We set up an experiment with two separate bundles, length 2 m, core diameter 400 μm bended in four different radius position (Figure 3) for both in and out bundle. Reflectance value of a white standard (Spectralon© 99%) is the mean over five measurements for each bending configuration.

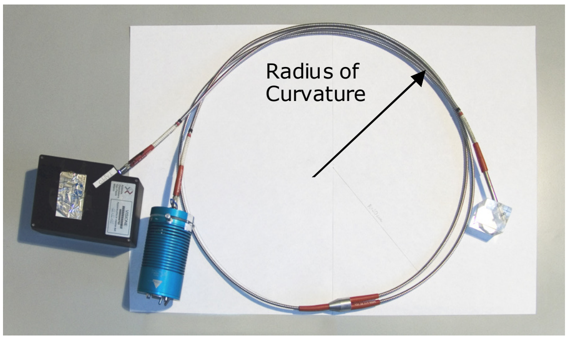

Figure 3: Position of the fibre optics for the evaluation of data variation in relation with the curvature.

In Table 1, the results of the four configurations are given in *xyz*, $L^*a^*b^*$ coordinates and E values.

$$E = (L^{*2} + a^{*2} + b^{*2})^{1/2} \quad (1)$$

Measurements show a standard deviation from the mean value less than the unit and we stress that the error in each measurements configuration had the same value in the variation of the configuration. This was due to the different configurations. Finally, we found that even little movement of the connector between the bundle and the spectrophotometer produce huge variation in reflectance factor measurements and therefore in the colorimetric values.

Fibre optics considered	*Radius of curvature (cm)*	*x*	*y*	*z*	*L**	*a**	*b**	*E*
in fibre	10	0.313	0.329	0.358	100.12	0.17	-0.89	100.12
	20	0.313	0.331	0.356	100.21	-0.08	-0.19	100.21
	30	0.313	0.330	0.357	101.08	-0.07	-0.54	101.08
	40	0.314	0.331	0.355	100.22	0.12	-0.12	100.22
out fibre	10	0.311	0.328	0.361	100.56	0.41	-1.77	100.57
	20	0.312	0.328	0.360	100.26	0.49	-1.64	100.27
	30	0.312	0.328	0.360	100.70	0.28	-1.36	100.71
	40	0.312	0.329	0.359	100.11	0.34	-1.26	100.12
both fibres	10	0.310	0.326	0.363	100.99	0.51	-2.42	101.02
	20	0.311	0.326	0.363	101.20	0.70	-2.51	101.23
	30	0.311	0.327	0.362	101.44	0.60	-2.27	101.47
	40	0.310	0.327	0.363	101.98	0.44	-2.38	102.01
	straight	0.311	0.327	0.361	101.36	0.45	-1.88	101.38
	std dev	0.001	0.002	0.003	0.60	0.24	0.81	0.61

Table 1: Measure of a 99% white reference for different displacement of the fibre. Each data is the average of 5 measurements.

Comparison between coaxial fibre, integrating sphere and colorimeter

Data obtained using 45°×:45° geometry and integrating sphere were compared [2], using a 28 samples set (Figure 4 – left) of different coloured matt printed paper, and with a statistics of 10 measurements each. In Figure 5 results are shown in CIE1931 and CIELAB 1976 spaces. In a^*b^* plane we plotted also the data obtained using the colorimeter. Results obtained with the different probes showed the same values only when tested with chroma<40, or, also including lighting value L^*, where E<80. In particular those samples with red hue, showed the biggest differences. Finally, lightness coordinate obtained with the coaxial probe, was about 4 units greater than those measured with the integrating sphere.

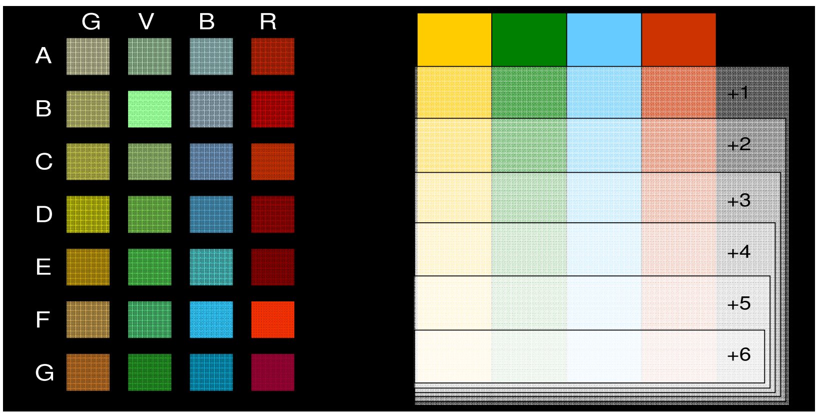

Figure 4: Two sets of colour samples: on the right the 28 printed colours; on the left the scheme of the six step attenuations of saturated colours with translucent layers.

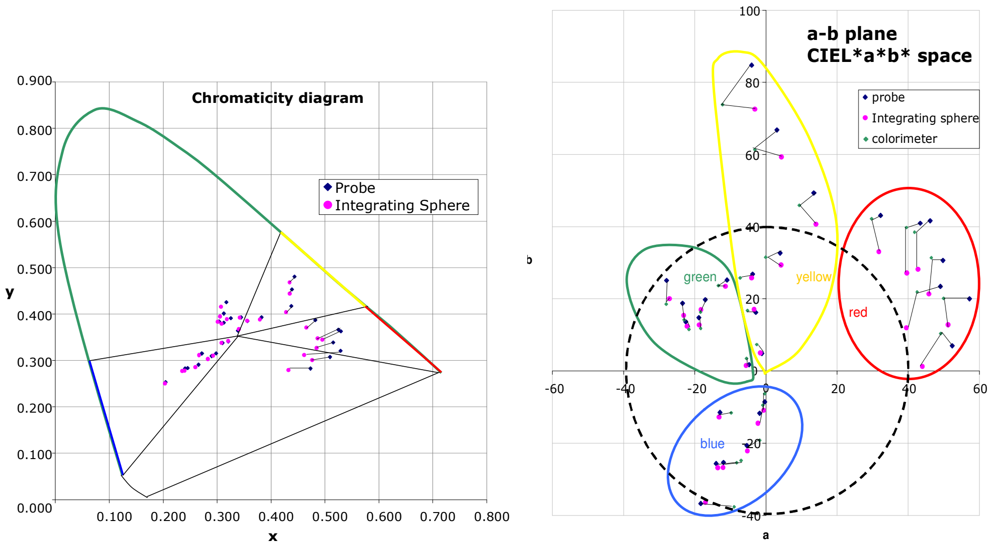

Figure 5: Representation of colour samples showed in the CIE 1931 xy chromaticity diagram (left) and in the a-b plane of the CIELAB 1976 space. This graph also represents data obtained with the colorimeter. Data within E>80 is not in agreement, due to the non linearity of the space in this region (right).

Study of samples with different saturation

Starting from the previous results of the difference in reflectance factor data due to the different probe, we tried to find a relationship between the two measurement sets. For this purpose we realised four sets of 7 colours each by printing 4 primary hues and desaturating them by overlapping sheets of diffusing translucent paper (from A, fully saturated to G, fully desaturated as shown in the right-hand image in Figure 4). This allowed us to avoid variations of hue due to the printing system. In this way we obtained samples with *x-y* coordinates near the achromatic region in which the two probes gave results with the best agreement. Results are shown in Figure 6.

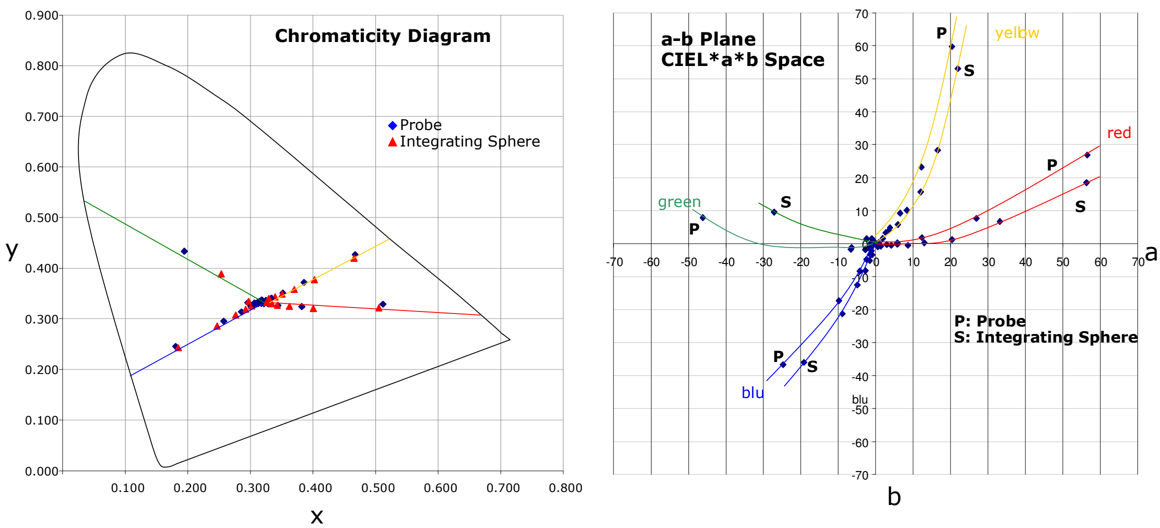

Figure 6: Plot of colorimetric data for the 4 primary hues and their different saturation in CIE 1931 (left) and CIELAB 1976 (right) colorimetric spaces.

In both the colorimetric spaces for any primary hue, all data stay on the line connecting the saturated hue value with the achromatic centre. The two sets of measurements were well aligned in the *x-y* space, but not as well in the *a*b** plane, in fact we observed a systematic split of the data obtained with the two probes systems. Green and yellow hues showed the biggest differences. The biggest gap we found was in the green sample without translucent paper: the reason being that this was the only glossy sample of the set, and the specular component of diffuse light was completely lost in coaxial geometry, but was included using the integrating sphere. As general result we stress that the data with coaxial probe showed higher values that the integrating sphere toward green (a<0) and yellow components (b>0).

Comparison between reflectance spectra

In this part of the study we tried to understand the cause of the differences in colorimetric data obtained using integrating sphere and coaxial probe.

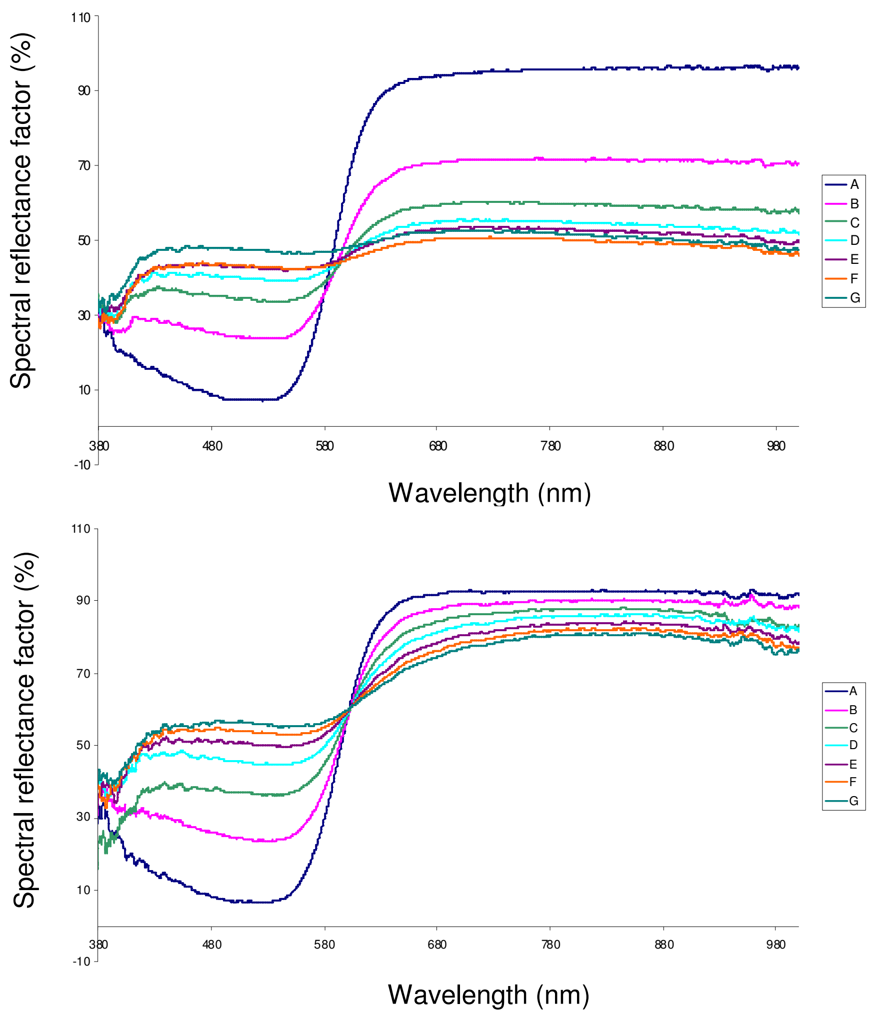

Figure 7: Reflectance spectra of different saturation of a red paper obtained with integrating sphere (top) and coaxial probe (bottom). Legend: A – red paper only, B – 1 translucent sheet, C – 2 sheets, D – 3 sheets, E – 4 sheets, F – 5 sheets, G – 6 sheets.

In Figure 7, for example, reflectance spectra of the 7 difference saturation of a red sample are shown: on top the results with the integrating sphere, at bottom those with the coaxial probe. The red sample without translucent paper has the spectrum with the largest step. After laying several sheets of translucent paper one upon the other we reached an opaque layer condition with a flat 57% reflectance spectrum. The desaturated samples describes intermediate condition between pure red and pure translucent samples, in-fact corresponding to 605 nm wavelength all samples have a reflectance factor of 57%. This behaviour was described from Kubelka-Munk model for two pigments mixture [8,9] and it is in good agreement with this experimental situation. In Figure 7 (bottom) we see that spectra obtained with coaxial geometry are less accurate than those obtained with the other probe, but with approximately the same behaviour.

Conclusions

The use of spectroscopic system with fibre optic bundle probes in order to obtain colorimetric data permitted us to distinguish effectively different hue samples. Fibre position affects results with lower errors than the statistical error due to measurements on different areas of the same colour specimen. On the other hand the repeatability of measurements is strongly connected with the stability of the light source and of the optical connection between fibre bundle and spectrometer device.

Colour measurements obtained with a 45°×:45° system differ from those obtained with a commercial colorimeter as well as the integrating sphere system, these differences become larger as we move far from the central achromatic area of the chromaticity diagram. Best agreement was found in the area with chroma lower than 40 around the achromatic centre using D65 standard illuminant. This difference could be due to little difference in reflectance spectrum in the central part.

The repeatability of measurements with the coaxial probe allows at least its use in relative evaluation of colour change for example in cleaning of ancient painting or in restoration dentistry.

Moreover the high manageability and the reduced size of this probe allows to perform relative colour measure when the surface to be sampled is not reachable by a colorimeter.

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