Evolution of grey standards–glistering standards for monitoring spectrometer performance

Anthony M.C. Davies
Norwich Near Infrared Consultancy, 75 Intwood Road, Cringleford, Norwich, NR4 6AA, UK.

Introduction

The need for a spectrometer standard has been a concern for many years and this has lead previously to the ideas of 'Sphere',[1] an electronic device to aid instrument standardisation and calibration transfer, 'Grain blocks',[2] permanent samples for standardising near infrared instruments and "Grey Standards". Grey standards (GS) were described in the Tips and Ideas Column of *NIR news*[3] and were the subject of a poster at NIR-97.[4] GS were made from five aluminium disks painted white, black or three shades of grey, which fitted into the standard sample cups of NIRSystems 6500 spectrometers. The purpose of GS was to provide a robust set of standards, which can be used in several modes:

- To determine instrument noise at different absorbancies
- To analyses the noise components
- To test the stability of the ordinate scale at different absorbancies
- To compare the relative linearities of the ordinate scales of different spectrometers

The evolution of "Grey Standards"

Although GS showed initial promise, it became apparent that the samples were not as consistent as had been hoped and that this was likely to be due to variation in the orientation of samples because of the readily observable variation in the painted surface.

Efforts to remove these effects lead by a series of stepping-stones that ended with a new design of standard. The new standard is based on the use of a gold-coloured reflector. Thomas Gray said "Nor all that glisters gold"[5] hence the new design has been named "Glistering standards" (because they are not a gold standard!).

Glistering standards (GS2) consist of a single aluminium disk, which has been anodised in chromic acid according to the "Alocrom 1200" procedure, as the reflector with a series of polymer (PET) masks having varying amounts of grey tint printed on them. This combination was selected because:

- The Alocrom surface has a flat spectrum in the 1100–2500 nm range
- The tinting on the polymer is produced by a laser printer and the carbon black also has a flat spectrum in the 1100–2500 nm range
- The poly(ethylene terephthalate) (PET) polymer provides a series of peaks, which can be used to measure wavelength stability

The masks are shown in Figure 1 and the spectra obtained by an NIRSystems 6500 spectrometer are shown in Figure 2.

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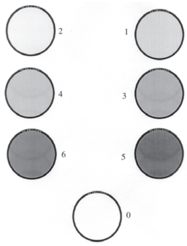

Figure 1. The masks used for glistering standards. These are printed directly on to 3M™ laser print film and this drawing is that seen when viewed through the film.

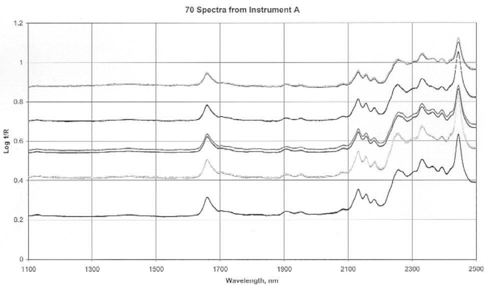

Figure 2. Spectra of the glistering standards.

Methods

Spectroscopy

Each GS2 mask is placed in a standard sample cup, with the words "this way up " readable (this ensures the direction of scanning is always the same) with the gold-coloured aluminium disk on top. Each standard was scanned ten times without moving it from the holder in a NIRSystems 6500 spectrometer (Foss NIRSystems, Silver Spring, MA, USA) against a fresh reading of the ceramic between each re-reading of the GS2 mask (i.e. treating them just like a sample). The seven standards thus produced 70 spectra. The results from three instruments: A, B, and C are presented in this poster.

Data analysis

Files in NSAS format were imported into Unscrambler™ software (Camo AS, Trondheim, Norway) version 7.0. and exported to Excel™ (97) spreadsheet (Microsoft, USA). Average spectral response was calculated on a flat portion of the spectrum, 1150–1450 nm, for each mask. The replicate spectra from each GS2 mask were averaged and this average spectrum was used to calculate difference spectra (noise spectra) from which the spectral noise was estimated as the average standard deviation

Table 1 Analysis of spectral noise.

	Instrument A		Instrument B		Instrument C	
Mask #	Av. STD Noise × 10^{-6}	10 Spectra noise × 10^{-6}	Av. STD Noise × 10^{-6}	10 Spectra noise × 10^{-6}	Av. STD noise × 10^{-6}	10 Spectra noise × 10^{-6}
0	277	822	53	96	47	148
1	255	1183	137	178	29	130
2	226	976	176	206	26	135
3	199	617	74	144	33	160
4	100	819	89	274	31	238
5	106	386	54	94	50	427
6	136	298	61	105	51	284

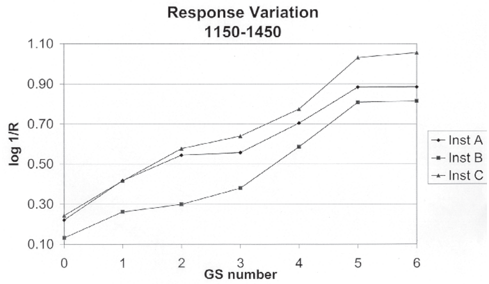

Figure 3. Averaged results for glistering standards for three instruments.

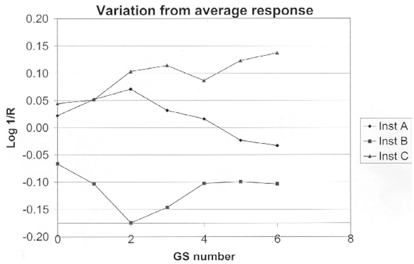

Figure 4. Difference in response for the three instruments compared to the mean of instruments A–C.

of the noise spectra. The standard deviations over 10 spectra were also calculated for each mask. The Unscrambler was used to analyse spectral variation by principal component analysis (PCA).

Results

Spectral Response

The averaged spectral responses of the three instruments are shown in Figure 3 and differences from the overall average are shown in Figure 4.

Spectral Noise

The results of the noise analysis are shown in Table 1 and some typical noise spectra are shown in Figures 5–7.

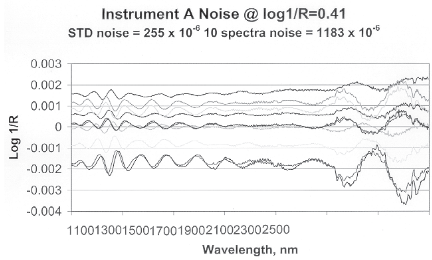

Figure 5. Plot of noise spectra from GS2-0.41 for instrument A.

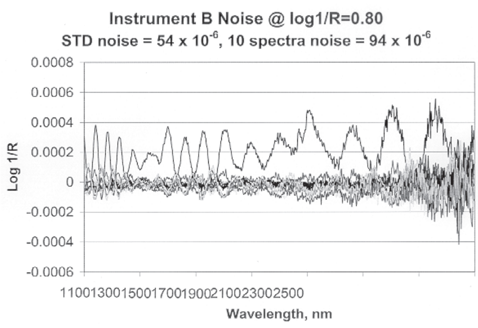

Figure 6. Plot of noise spectra from GS2-1.80 for Instrument B.

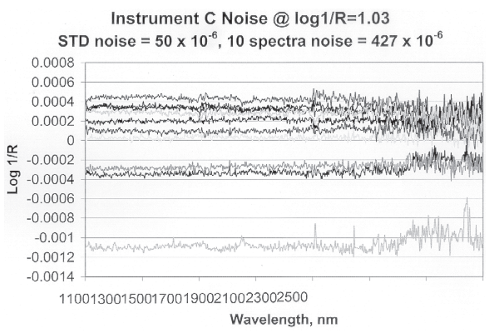

Figure 7. Plot of noise spectra from GS2-1.03 for Instrument C.

Noise components

The results from the PCA are show in the loadings plots shown in Figures 8–10.

Discussion

Spectral response

The response of instrument B is generally lower than the other two. Instruments A and C are more similar and a repeatability test on instrument C indicted that the variations shown in Figure 4 may not be significant. More work is required to uncover the source of a random bias in repeat samplings. This does not effect the rest of the analysis, which requires readings from unchanged samples.

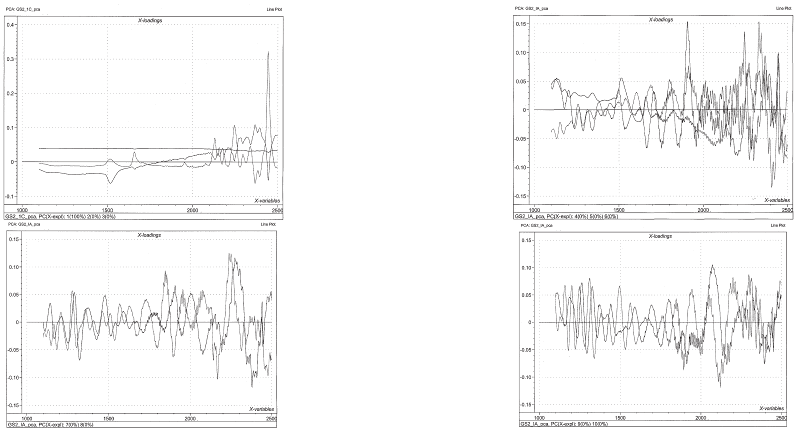

Figure 8. Loadings plot for PCs 1–3, purchase 4–6, PCs 7,8 and PC 9,10 for Instrument A.

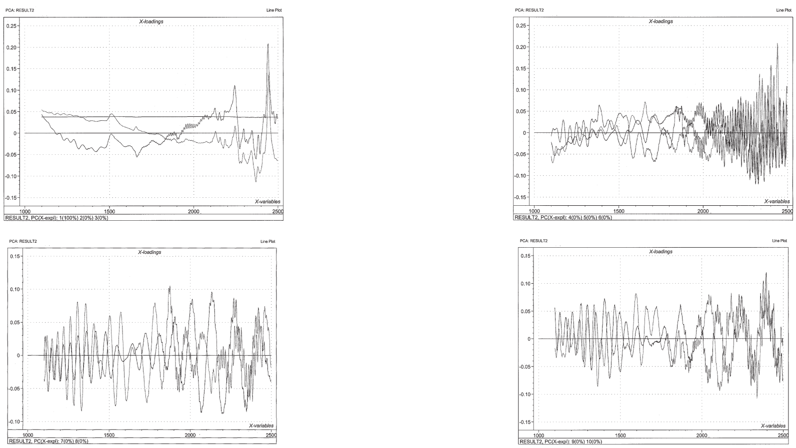

Figure 9. Loadings plot for PCs 1–3, Pcs 4–6, PCs 7,8 and PCs 9,10 for Instrument B.

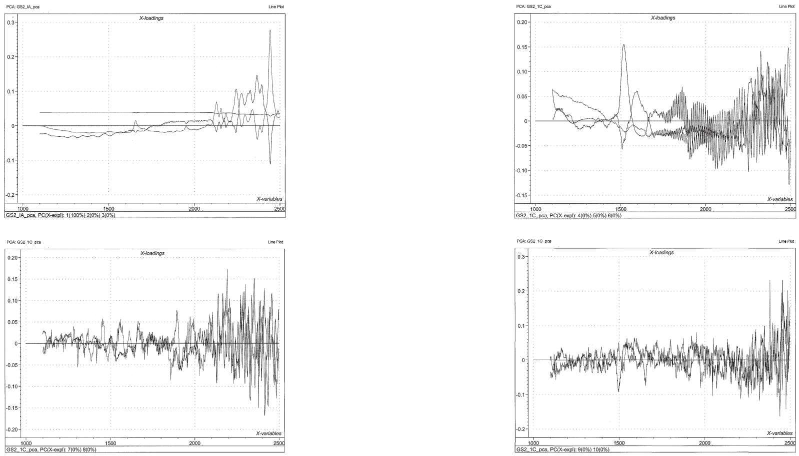

Figure 10. Loadings plot for PCs 1–3, Pcs 4–6, PCs 7, 8 and PCs 9, 10 for Instrument C.

Acknowledgements

The idea of using "Alocrom " came from Mr C. Oakes of Foss Electric Development (UK) Ltd. who also arranged for this form of anodising on the previous Grey Standards. Mr Karl H. Norris suggested that standards should have a wavelength marker, which lead to the idea of using laser print film, Professor Heinz Siesler identified the main component of the laser film polymer and Mr Ian Michael assisted in the production of the masks. The author expresses his gratitude to these and also to Mr Ian Cowe for many helpful discussions, to Mr Colin Eddison of Foss Electric Development (UK) Ltd for allowing the use of their 6500 spectrometer for the development of the idea and to the two experimenters who tested the standards on their spectrometers.

References

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5. T. Gray, Ode on a distant prospect of Eton College (1747).