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Contamination and UV ageing of diffuser targets used in satellite inflight and ground reference test site calibrations

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Abstract. Diffuser reflectance targets are key components in in-orbit calibrations and for verifying ground reference test sites. In this work, Spectralon, Diffusil, and Heraeus diffusers were exposed to exhaust gases and ultraviolet (UV) radiation in the ambient air conditions and their degradations were monitored by measuring changes in spectral reflectances. Spectralon is a state-of-the-art diffuser made of polytetrafluoroethylene, and Diffusil and Heraeus diffusers are made of fused silica with gas bubbles inside. Based on the contamination tests, Spectralon degrades faster than fused silica diffusers. For the samples exposed to contamination for 20 minutes, the 250 nm – 400 nm total diffuse spectral reflectance of Spectralon degraded 3–5 times more when exposed to petrol-like emission and 16–23 times more when exposed to diesel-like emission, compared with Diffusil. When the reflectance changes of Spectralon were compared with those of Heraeus, Spectralon degraded 3–4 times more when exposed to petrol-like emission for 20 minutes and 5–7 times more when exposed to diesel-like emission for 7.5 minutes. When the samples contaminated were exposed to UV radiation in the ambient air, their reflectance gradually restored back to the original level. In conclusion, fused silica diffusers are more resistant to hydrocarbon contaminants present in ground reference test sites, and thus more stable under UV radiation in the air.

1. Introduction
Diffuser reflectance targets are key components in calibrating satellite sensors to support climate research, agriculture and forest monitoring \cite{1, 2}. Inflight calibration systems use onboard diffusers as references, either as references for satellite Earth-reflectance products, or, combined with the known solar spectral irradiance, as references for satellite radiance products. Vicarious methods are also commonly used for satellite inflight calibration and validation. These use top-of-the-atmosphere reflectance models for reference test sites, e.g. RadCalNet \cite{3}, based on ground reflectance and atmospheric transmittance measurements and an atmospheric retrieval algorithm. Diffuser reflectance targets are also used in the characterisation and monitoring of such ground-based reference test sites. As reflectance targets are so critical for both onboard and vicarious satellite calibration it is essential to understand how these degrade in space and field environments. Degradation in both spectral reflectance and any changes in the bidirectional reflectance distribution function (BRDF) of the samples must be monitored. Unfortunately,
space and field measurements involve contaminants, which can deteriorate the stability of the Spectralon diffusers currently used [1, 4].

In this work Spectralon diffusers made of polytetrafluoroethylene (PTFE) are compared with alternative diffusers Diffusil and Heraeus, made of ultra-pure synthetic fused silica glass with gas bubbles. Especially Diffusil diffusers have been measured to have good BRDF properties [5]. Earlier studies have shown that pure Spectralon is photochemically stable and will not react with ultraviolet (UV) radiation [4]. However, if Spectralon contains residues e.g. of hydrocarbons, it becomes unstable under UV radiation [6]. In satellites, the diffusers are exposed to hydrocarbons due to the widely-used Pennzane lubricant [1] and possibly due to rocket fuel. In ground reference test sites, car emissions are a possible source of hydrocarbons [7].

The main objective of this paper is to find the best pre-ageing method for Spectralon targets, and to study alternative diffuser materials with more stable characteristics that could possibly replace Spectralon in the future. The second section introduces the setups for contaminating and UV ageing of the diffuser targets. The ageing results are discussed in Section 3. Finally, conclusions are drawn in Section 4.

2. Contaminating the samples
The setup used for contaminating the diffuser samples is shown in Fig. 1. The setup uses a propane flame produced using a mini-CAST soot source (JING mini-CAST Soot Generator Model 6203 Type C) as a particle emission source, which produces particles with composition and size similar to incomplete combustion of the fuel in car engines. The particle sizes (diameters) of the exhaust gases produced can be varied between 10 nm – 200 nm by mixing propane, nitrogen gas, oxidation air, and dilution air. The furnace at 400 °C can be used to remove volatile particles from the exhaust gas. Volatile particles have low boiling points and as the gas cools down, they condense on the surface of larger particles. The dilution air increases the velocity of the gas flow to encourage the particles to stick to the surface of the diffuser samples. Another purpose of the dilution air is to prevent volatile particles from recoalescing when the furnace is in use. A dilution loop in the setup is used for safety reasons as it allows particles to be filtered from gas flow when changing the samples.

Car emissions have wide particle size distributions; for diesel exhaust gases the peak of the distribution is ∼100 nm, whereas for petrol exhaust gases it is ∼20 nm [8]. Figure 2 shows the replicated distributions with the settings listed in Table 1. The particle sizes are determined by selection with a differential mobility analyser, which is calibrated with polystyrene latex spheres. The uncertainty of these sizes (k = 2) is about 5 %. Such particle emission distributions were used for contaminating the samples as detailed in Table 2. The particle size distributions in Fig. 2 are plotted at a logarithmic horizontal scale as the airborne particle emissions have been observed to follow near log-normal distributions [8]. From theoretical perspective, the log-normal particle size distribution can be derived from a random residence time approach [9].
Figure 1. Contamination setup (a) and Diffusil sample on the holder of the chamber (b).

Figure 2. Particle size distributions with the concentrations of undiluted exhaust produced by the contamination setup to replicate petrol (crosses) and diesel (circles) exhaust measured in Ref. [8]. The petrol and diesel distributions [8] are normalised to the peaks of our particle size distributions.

Table 1. Settings for the gas inputs of the soot aerosol generator to produce petrol-like and diesel-like particle size distributions.

<table>
<thead>
<tr>
<th>Type of emission</th>
<th>Particle size at the peak of the distribution (nm)</th>
<th>Propane (ml/min)</th>
<th>Nitrogen gas (ml/min)</th>
<th>Oxidation air (l/min)</th>
<th>Dilution air (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrol-like emission</td>
<td>20</td>
<td>20</td>
<td>10</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>Diesel-like emission</td>
<td>100</td>
<td>16</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

As listed in Table 2, we studied 10 Spectralon, 10 Diffusil, and 6 Heraeus samples. From each data set, samples were exposed either to petrol-like or diesel-like particle emission. Diffusil
samples have polished and rough sides and in this paper, we report the results for the rough sides. One Spectralon and one Diffusil sample were kept as uncontaminated references. Two Spectralon and two Diffusil samples were also exposed to the particle emissions with volatile particles evaporated from the exhaust gas by heating the gas with the furnace at 400 °C.

Table 2. Contamination times for Spectralon, Diffusil, and Heraeus sample sets. Petrol-like contamination refers to the 20 nm particle size distribution and diesel-like contamination refers to the 100 nm particle size distribution.

<table>
<thead>
<tr>
<th>Diffuser type</th>
<th>Total number of samples</th>
<th>Sample ID</th>
<th>Type of particle emission</th>
<th>Exposure time / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectralon USRS-99-020 by Labsphere</td>
<td>10</td>
<td>S1</td>
<td>Uncontaminated</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S2</td>
<td>Diesel-like</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S3</td>
<td>Diesel-like</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S4</td>
<td>Diesel-like</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S5</td>
<td>Diesel-like</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S6</td>
<td>Diesel-like, volatile particles removed</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S7</td>
<td>Petrol-like</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S8</td>
<td>Petrol-like</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S9</td>
<td>Petrol-like</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S10</td>
<td>Petrol-like, volatile particles removed</td>
<td>20.0</td>
</tr>
<tr>
<td>Diffusil R by Opsira</td>
<td>10</td>
<td>D1</td>
<td>Uncontaminated</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>Diesel-like</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D3</td>
<td>Diesel-like</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D4</td>
<td>Diesel-like</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D5</td>
<td>Diesel-like</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D6</td>
<td>Diesel-like, volatile particles removed</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D7</td>
<td>Petrol-like</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D8</td>
<td>Petrol-like</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D9</td>
<td>Petrol-like</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D10</td>
<td>Petrol-like, volatile particles removed</td>
<td>20.0</td>
</tr>
<tr>
<td>OM100 by Heraeus</td>
<td>6</td>
<td>H1</td>
<td>Diesel-like</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H2</td>
<td>Diesel-like</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H3</td>
<td>Diesel-like</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H4</td>
<td>Petrol-like</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H5</td>
<td>Petrol-like</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H6</td>
<td>Petrol-like</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Degradation of the contaminated samples was monitored by measuring their 0°:45° spectral radiance factor and total diffuse spectral reflectance at 250 nm – 850 nm with a Perkin Elmer Lambda 900 spectrophotometer. To study how contaminated diffuser surfaces react to UV radiation, we radiated the samples gradually under the broadband spectrum of a xenon (Xe) lamp with the setup illustrated in Fig. 3 and monitored their degradation.
3. Results

3.1. Degradation due to contaminants

Spectralon is porous to hydrocarbon particles [1, 2, 4], which can be seen in Figs. 4(a) and 4(b) as a drastic drop in the total diffuse spectral reflectance at UV and visible (VIS) regions. The total diffuse spectral reflectance of an uncontaminated Spectralon reference, plotted as a black solid line, did not change. Contaminated Spectralon samples changed both in the UV and VIS. Diesel-like particle emission in Fig. 4(b) was more damaging to Spectralon than petrol-like particle emission in Fig. 4(a). In both cases, exhaust gas including volatile particles caused more degradation than that without volatile particles.

The total diffuse spectral reflectance of an uncontaminated Diffusil reference degraded 1% at the UV region after 9 months, seen as a black solid line in Fig. 4(c). Fused silica diffusers change in the UV region due to hydrogen enrichment by defects, e.g. by non-bridging oxygen-hole and E'-centres [12]. The reflectances of Diffusil and Heraeus samples exposed to petrol-like particle emission also changed as seen in Figs. 4(c) and 4(e). Petrol-like particle emission was more damaging to these fused silica diffusers than diesel-like particle emission shown in Figs. 4(d) and 4(f). The reflectances of the Diffusil samples exposed to diesel-like particle emission did not change as systematically as those of the other samples. One possibility is that the ∼100 nm particles did not stick to the surface and fell off when the samples were moved during the experiments. For fused silica diffusers, petrol-like emission was more damaging and in all these tests they were more resistant to contamination compared with Spectralon. The degradation of 0°:45° spectral reflectance was similar to the degradation of diffuse spectral reflectance for the diffuser samples studied.
Figure 4. Ratios of the diffuse reflectances measured after and before the contamination for Spectralon (a)–(b), Diffusil (c)–(d), and Heraeus (e)–(f) samples. The degradation of the samples exposed to petrol-like particle emission are shown in figures on left and the degradation of the samples exposed to diesel-like particle emission are shown in figures on right. At this stage, the samples were not exposed to UV radiation.
3.2. Effect of combined contamination and UV radiation

We exposed the samples contaminated to the Xe lamp radiation with the setup illustrated in Fig. 3 and we noticed that UV radiation gradually cleaned the contaminated surfaces. Examples of such bleaching effect are presented in Fig. 5 for two Spectralon diffusers. The results for other diffuser types were systematically similar and the bleaching was relatively more effective for heavily contaminated diffuser surfaces.

![Graphs showing spectral reflectance and reflectance as a function of UV exposure time](image)

Figure 5. Examples of UV bleaching seen as the changing spectral reflectance of Spectralon samples; the sample #S9 exposed to petrol-like emission for 20 min and UV (a)–(b) and the sample #S2 exposed to diesel-like emission for 2.5 min and UV (c)–(d).

Based on our tests, mainly concerning ground reference test sites, the primary car emissions reduce reflectance. However, UV radiation in the presence of air bleaches the contaminated surfaces of Spectralon, Diffusil, and Heraeus diffusers. In the case of Spectralon, such bleaching in the air has also been noted in Ref. [13]. Bleaching takes place as UV radiation can break the relatively weak bonds of hydrocarbon molecules on the diffuser surface and the unstable hydrocarbons reach with the ambient air.

Based on literature in the case of in-orbit conditions [14], Spectralon is absorptive to vacuum UV radiation [15]. Such photon energies can break bonds between fluorine and carbon leading
to the surface erosion of Spectralon [2,16] and thus the surface loses fluorine [14,17]. Broken carbon chains react with hydrocarbons outgassed, e.g. from lubricants [1], thus forming larger hydrocarbons. However, in the low-level orbit, atomic oxygen would bleach the surface [2,14]. The atomic oxygen is formed when solar UVB and UVC radiation breaks the atmospheric oxygen molecules [18] according to Eq. (1). The atomic oxygen can further react with oxygen molecules and form ozone as shown in Eq. (2) that is also reactive. Top-of-the-atmospheric air is thin and sometimes the oxygen atom cannot find an oxygen molecule.

\[
O_2 + h\omega \rightarrow 2O \quad (1)
\]

\[
O + O_2 \rightarrow O_3 \quad (2)
\]

In new Earth observation satellites, the problems related to the excess UV exposure of a diffuser target are reduced by having a diffuser wheel with a working diffuser and a reference diffuser [19]. The reference diffuser is only used for monitoring the degradation of the working diffuser and it is rarely exposed to UV radiation. However, the reference diffuser may still change e.g. due to contamination induced degradation.

4. Conclusions
Three diffuser technologies: Spectralon, Diffusil, and Heraeus, were exposed to hydrocarbon contaminants and UV radiation in the air. Hydrocarbon contamination degraded the reflectance of Spectralon more than they degraded fused silica diffusers. The 250 nm – 400 nm total diffuse spectral reflectance of Spectralon degraded 3–5 times more when exposed to petrol-like particle emission for 20 minutes and 16–23 times more when exposed to diesel-like particle emission for 20 minutes, compared with Diffusil. Comparing the degradation of Spectralon against that of Heraeus showed almost similar results; Spectralon degraded 3–4 times more when exposed to petrol-like particle emission for 20 minutes and 5–7 times more when exposed to diesel-like particle emission for 7.5 minutes. 

When the samples contaminated were exposed to UV radiation in the air, their reflectance gradually restored back to the original level. This means that in the air, hydrocarbon degradation competes with UV bleaching and we could not develop an optimal pre-ageing method for Spectralon panels used in the ground reference test sites. The results presented in this paper are only indicative as we did not study the effect of some other contaminants, such as sand grains and secondary car emissions.

Based on the earlier studies of Spectralon in vacuum conditions, both UV radiation and contaminants caused reflectance degradation. Based on the findings presented in this paper, fused silica diffusers are more resistant to hydrocarbon contaminants present in ground reference test sites compared with Spectralon, and thus more stable under UV radiation in the air. However, further tests are needed to see how fused silica diffusers perform in vacuum conditions when exposed to hydrocarbon contaminants and UV radiation.

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