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Rugged optical mirrors for Fourier-Transform Spectrometers operated in harsh environments

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The Total Carbon Column Observing Network (TCCON) and the Network for the Detection of Atmospheric Composition Change (NDACC) operate a number of Fourier-Transform Spectrometers (FTSs) that measure trace gases in the atmosphere by observing solar spectra. To guide the sunlight into the FTS, a solar tracker has to be placed outside. This device needs high-quality optical mirrors with good reflectivity in the near and mid infrared.

More and more FTS stations are operated in remote locations with harsh environments. Optical mirrors are usually made for laboratory conditions and might not last very long there. At the MPI-BGC's TCCON site on Ascension Island, several mirrors from different optical manufacturers were destroyed within weeks.

To continue operation, the MPI-BGC had to develop rugged mirrors that could sustain the harsh conditions for months or even years. While commercially available mirrors are typically made from a substrate coverered with a thin reflective coating, these rugged mirrors were made from stainless steel with no additional coating. Except for their lower reflectivity (which can easily be compensated for), their optical properties are comparable to existing mirrors. However, their rugged design makes them mostly immune to corrosion and scratching. Unlike most coated mirrors, they can also be cleaned easily.

1 Introduction

1.1 Atmospheric trace gas measurements with Fourier-Transform Spectroscopy

Many atmospheric molecules have characteristic spectral lines in the infrared region of the spectrum. When infrared radiation from the sun travels through the atmosphere, it is absorbed by the trace gases molecules in a characteristic way. By spectrally analyzing the incoming sunlight on the ground, the total number of molecules in the light

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path – the so-called total column – can be measured. Fourier-Transform Spectrometers (FTSs) are ideal for such measurements in the near infrared (NIR) as well as the mid infrared (MIR). Unlike many other spectrometers, they combine large spectral bandwidth – which allows them to measure many species – with high spectral resolution that provides high accuracy.

Both the Network for the Detection of Atmospheric Composition Change (NDACC) (Kurylo and Zander, 2000) as well as the Total Carbon Column Observing Network (TCCON) (Wunch et al., 2011) have set up FTS sites all over the world (see Fig. 1). Historically, NDACC has been focused on trace gases related to stratospheric and tropospheric chemistry. TCCON's goal is to measure greenhouse gases (GHGs) like CO₂, CH₄, CO, N₂O and others with a precision in the sub-percent range – a very ambitious target for a remote-sensing measurement. Many of the early stations were set up in the rural and urban environments of their home institutions. In the recent years, the networks have also expanded to more remote locations that are diffcult to reach or have extreme environmental conditions. One example is the TCCON station that was set up by the Max Planck Institute for Biogeochemistry (MPI-BGC) on Ascension Island in the South Atlantic Ocean – the first equatorial station in TCCON (Geibel et al., 2010). Like the other TCCON stations, the FTS is an IFS125HR built by Bruker Optik GmbH in Ettlingen, Germany.

1.2 Solar tracker and optical mirrors

The solar tracker is the device that is responsible for guiding the sunlight into the FTS. It uses two optical mirrors that can be rotated around an azimuth and an elevation axis. During the day, the mirrors follow the sun so that the sunlight is guided straight down into the FTS that is usually located directly underneath. While the FTS itself is usually protected from the elements inside a building or container, the solar tracker has to be outside to follow the sun. It is typically mounted on a roof and is only protected from direct precipitation by a cover or dome.

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- Unprotected gold coating: usually consisting of a single gold layer that is either vapor-deposited or sputtered. An additional adhesive layer between the substrate and the gold layer is usually needed. Advantages: very good reflectivity over a large bandwidth. Disadvantages: soft surface that is easily scratched.
- Protected gold coating: like the unprotected gold coating but with an additional layer of SiO₂ or other oxide on top of the gold layer. Advantages: as long as the protective layer is not damaged, the surface is much more resistant to scratches than the unprotected gold coating with similar reflective properties. Disadvantages: more difficult to make and more expensive.
- Protected or unprotected aluminium coating: similar to the gold-coated mirrors except that Al is used as the reflective surface. Advantages: Al sticks better to the substrate and can be applied without an additional adhesive layer. Provides a more durable surface especially with an additional protective SiO₂ coating. Disadvantages: slightly lower reflectivity than gold.
- Dielectric coating: multiple layers with different refractive indexes. Advantages: layers are typically made from hard materials and provide a durable surface. Disadvantages: limited bandwidth and difficult to make.

So far, not much has been published about how such mirrors behave outside normal laboratory conditions. Chu et al. (2010) studied the effects of reactive gases on gold coatings and Krijger et al. (2014) have started a study on degrading effects of mirrors in space.

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While the FTS itself is usually well protected inside a building or container, the solar tracker has to be outside. Even if the solar tracker is covered from direct precipitation, it will be exposed to the environmental conditions when the sky is clear and the sun is shining.

Optical components like the solar tracker mirrors are usually made for clean laboratory conditions and a limited temperature range. In a harsh environment, the equipment – and especially the solar tracker mirrors – can be degraded or damaged by this exposure. This effect might be slow or fast, depending on the environmental conditions.

In a harsh environment, the following effects may be encountered. They all result in a loss of mirror reflectivity that would eventually disrupt the measurements.

- Dust and dirt deposition: In principle, this does not result in permanent damage if
 the deposited material is not corrosive. However, if the mirror surface cannot be
 cleaned, this deposition will build up and eventually render the mirror unusable.
- Corrosion: This is a permanent effect that degrades the mirror surface. It may be caused by the deposition of reactive substances like sea salt, often in combination with humidity or liquid water. Another reason for corrosion may be reactive gases in polluted air.
- Scratches: They also cause permanent damage to the mirror surface. Scratches
 may be caused by objects touching the surface or by mechanical abrasion from
 blowing sand or dust. They may also be the result of cleaning if the surface is not
 hard enough.

2.1 Unprotected gold coating mirror performance

The original solar tracker mirrors by Bruker have a vapor-deposited gold coating on a glass substrate. There is no additional protective layer. In rural or urban areas, these

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mirrors typically last for several years. However, in the harsh environment of Ascension Island, the surface lost large parts of its coating already three weeks after installation (see Fig. 2). One attempt to clean the mirrors by rinsing them with distilled water and ethanol without touching the surface only did more damage. After six months of exposure, the gold coating was completely lost.

The problem with the coating was first noticed as a decrease of the signal of the solar tracker's quadrant diode. Figure 3 shows this normalized signal over a period of 3.5 months. The maximum signal on the quadrant diode for each day was normalized to one and plotted over time. The loss in signal corresponds roughly to the loss in total reflectivity for the two mirrors of the solar tracker. The original Bruker mirrors lost about 80 % of their combined reflectivity within two weeks of operation on Ascension Island.

2.2 Mirror corrosion test

In September 2012, an empirical test of several sample mirrors was conducted. The mirrors were of different design and made by different manufacturers. They were all sent to Ascension Island and put outside for one month. During this time, they were exposed to sea salt spray, dust, wind, sunlight, and rain. The combined effect of constant wind and fine quartz sand might also have had an additional abrasive effect on the mirror surfaces. One half of each mirror was covered with an adhesive foil to preserve the original surface for later comparison. The results of the mirror tests are summarized in Table 1.

Mirror #6 was the original mirror type with unprotected gold coating. It was sent along as a reference. During the test, its coating was lost completely. Other mirrors, namely ones with protected gold coatings, performed much better. However, it should be noted that none of the mirrors were designed for such conditions. Also, the effect of regular cleaning could not be tested this way.

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Following the mirror test, a second set of mirrors with a protected gold coating was produced by Layertec. These mirrors were made in the same way as the sample mirror #5 in Table 1 which had shown no signs of degradation during the mirror test. The new mirrors were installed in March 2013. Figure 4 shows that these mirrors also lost about 80% of their reflectivity within four weeks of operation. However, this initial loss was most likely caused by dust deposition. By rinsing the mirrors with distilled water and ethanol, the reflectivity could be restored several times (Fig. 4).

However, apparently the mirrors did not take the cleaning procedure well. After the fifth cleaning, first visible damage to the surface appeared. During the sixth cleaning procdure, large parts of the coating were destroyed. Figure 5 shows the damage to the elevation mirror. After six months of operation, the coating on this mirror was completely lost. On the less exposed azimuth mirror, about 50 % of the coating were lost.

Rugged mirrors

A rugged mirror would have to be able to endure the conditions described in Sect. 2 without significant loss of reflectivity at least over a period of several months. This period should be long enough so that mirrors only have to be exchanged during regular maintenance visits. Table 2 lists several properties that are important to achieve this goal.

Rugged mirror material

None of the tested coated mirrors were able to withstand the harsh environmental conditions on Ascension Island for more than a few weeks. An alternative design are mirrors made from solid material with a polished surface. Some of the considered materials were

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- Chromium: very hard, very resistant to corrosion. However, it is a brittle material and therefore difficult to machine and polish.
- Silicon: not expected to suffer from corrosion, very hard surface, easy to polish.
 However, it only has a low reflectivity of only 50% in the NIR and MIR. Since the solar tracker has two mirrors, that would result in a 75% signal loss.
- Germanium: very similar properties as Silicon.
- Gold: resistant to corrosion, highly reflective in the NIR and MIR. However, too
 expensive for a solid mirror and too soft for polishing.
- Platinum: very resistant to corrosion and hard enough for polishing. However, even more expensive than gold.
- Stainless steel: dozens of alloys with a wide range of properties are available.
 Medium reflectivity of 65 % in the NIR and MIR had been measured for a polished steel plate of type 1.4301 even though this material did suffer from corrosion during the test (see Sect. 2.2).

Stainless steel appeared to be a good choice for a solid mirror material. The main issue was to select an alloy with high corrosion resistance and good surface properties for polishing.

The Pitting Resistance Equivalent Number (PREN) is a measure for the corrosion resistance of stainless steel. The higher the PREN, the more resistant the steel is against corrosion. The PREN is calculated from the mass percentages of Chromium (Cr), Molybdenum (Mo), and Nitrogen (N) in the alloy as

PREN =
$$1 \times \%$$
Cr + $3.3 \times \%$ Mo + $16 \times \%$ N. (1)

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In general, alloys with PREN > 32 are considered to be seawater resistant. Figure 6 lists PRENs for several common stainless steel types.

For the properties of a stainless steel mirror, the crystalline structure of the alloy is as crucial as its corrosion resistance. Stainless steel comes in different crystalline structures: ferritic, martensitic, austenitic, as well as duplex. Duplex stainless steels, like type 1.4462 in Fig. 6, are a mixture of austenitic and ferritic microstructure constituents. They offer very high corrosion resistance. However, because of the two intermixed crystalline structures, they also have a granular surface structure which is not suitable for a mirror surface. For the stainless steel mirrors, an alloy that combines high corrosion resistance with excellent surface quality (labeled as 1.xxxx in Fig. 6) was chosen. It is commonly used for medical as well as industrial applications that involve high chlorine concentrations. Please note that the exact steel type cannot be provided here due to pending commercialization of the rugged mirror design.

3.2 Rugged mirror design

The rugged mirrors were designed to be drop-in replacements for the existing mirrors of the Bruker A547 solar tracker (a widely used model in the TCCON and wider FTS community). The principal shape of the mirror is a disc cut out of a cylinder with a diameter of 80 mm at an angle of 45°. The mirror surface is therefore a plane ellipse with a length of 113 mm and a width of 80 mm (see Fig. 7). This is almost the same design as the original Bruker mirror, only about 1 mm thicker. The mirror design for azimuth and elevation mirror is identical.

The main design goal of the rugged mirrors was the same as for the original Bruker mirrors: a flatness of better than 1λ at $633\,\mathrm{nm}$. This was verified by interferometric measurements at $460\,\mathrm{nm}$ by the company that lapped and polished the steel mirrors. In Fig. 8, the pattern of parallel bright and dark lines is characteristic for a flat surface. Surface irregularities would show up as distortions of the band-shaped structures, for example as closed lines that surround a local minimum or maximum.

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The second goal was a flat reflectivity response with no mirror-induced artifacts from the MIR to the NIR. This was verified using a Bruker IFS125HR FTS at the Karlsruhe Institute of Technology. A globar was used as the light source to cover the MIR to the NIR. This way, a spectral range of 1800 to 12000 cm⁻¹ could be covered. The reflectivity was measured by comparing the spectrum aquired from the direct light path to a spectrum aquired after a reflection on both mirrors.

To simulate the setup of the solar tracker, each mirror was oriented at an incindent angle of 45° to the incoming light. The double reflection also produced a stronger effect. Figure 9 shows the resulting reflectivity which was normalized for a single reflection. The different colors correspond to different IR bandpass filters that were used during the measurement.

The main result was that the steel surface did not produce visible artifacts in the spectrum. The reflectivity ranged from about 60 % in the NIR to almost 90 % in the MIR.

3.3 Endurance in harsh environments

The MPI-BGC stainless steel mirrors were installed during a maintenance visit in August/September 2013. Compared to the coated mirrors, their reflectivity was considerably lower from the beginning. This had to be compensated by adjusting the gain of the quadrant diode and opening the input iris aperture of the FTS by about 40 %.

These mirrors also showed a quick reflectivity loss due to dust deposition (Fig. 10). However, their reflectivity could be restored by cleaning without noticeable surface damage. For the cleaning, the mirrors were simply wiped with a damp microfibre cloth. Even after six months of operation, the most exposed elevation mirror showed only a few dull spots on the surface. A weak pattern of scratches perpendicular to the direction of cleaning was probably caused by blowing sand. The other mirror showed no obvious surface defects. After six months of operation, the total reflectivity of the two-mirror system (after cleaning) had not changed significantly.

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All coated mirrors that were tested on Ascension Island were heavily damaged after weeks or at most a few months of exposure. No coated mirror was able to be used for a period of six months, which would be the typical maintenance interval for the station.

The steel mirrors developed by MPI-BGC endured the harsh conditions for six months with only a minor loss of reflectivity and no major surface damage. The mirrors were easy to clean and were not adversely affected by the procedure in any way.

The first set of stainless steel mirrors was replaced during the third maintenance visit to Ascension Island in March 2014. By that time, the mirrors had been exposed to the harsh environment for about six months. More than 7500 spectra had been measured during this time period. The mirrors were replaced despite the fact that they showed only minor surface defects. By now the second set of steel mirrors has already been outside for more than one year without obvious degradation.

The rugged mirrors designed by MPI-BGC have proved to be a useful drop-in replacement for the existing mirror options of the Bruker A547 solar tracker. Because of their ruggedness, they are most likely the only viable option for harsh environments – especially in places with salt corrosion. Currently, they are also the only mirrors that allow regular cleaning. Their main disadvantage, the lower reflectivity, would most likely only be a problem at high-latitude sites with very low solar intensity. It might also be possible to improve the reflectivity by applying an additional hard chrome layer directly to the polished steel surface.

It should be straightforward to adapt these rugged mirrors for other solar trackers that are currently used in the FTS community.

Acknowledgements. The development of the rugged solar tracker mirrors was funded by the Max-Planck-Gesellschaft. On-site photos were taken by Nicholas John, ESA Ariane Station, North East Bay, Ascension Island. Sample mirrors for the outdoor mirror test were provided by (1) Axel Keens, Bruker Optik GmbH, Ettlingen, Germany (2) Armin Rupp, Optics Balzers GmbH, Eschborn, Germany (3) Georg Böttcher and Silvia Bark-Zollmann, Layertec GmbH, Mellingen, Germany. We would especially like to thank Ingrid Jung, Böhler-Uddeholm

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Deutschland GmbH, Düsseldorf, Germany, for providing good advice as well as a number of stainless steel samples that helped greatly in selecting the optimal steel type for the mirrors.

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Table 1. Results of mirror test after one month of outdoor exposure on Ascension Island. Details about the mirror suppliers are provided in the acknowledgements.

#	supplied by	substrate	surface/coating	performance
1	Bruker Optics	aluminium	galvanic gold coating	speckles and holes in coating
2	Bruker Optics	glass	gold with protective layer	no visible damage
3	Bruker Optics	glass	silver with protective layer	no visible damage
4	Optics Balzers	glass	gold with protective layer	several small holes in coating
5	Layertec	glass	gold with protective layer	no visible damage
6	Bruker Optics	glass	unprotected gold coating	coating completely lost
7	NA	steel (1.4301)	polished	speckles and dull areas

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Table 2. Design properties for rugged mirrors. The first column provides a measure of importance for the individual properties: required (+++), important (++), useful(+)

	mirror property
+++	high optical surface quality
+++	good reflectivity with flat characteristic in the NIR and MIR
+++	operational temperature range from at least -40 to +40 °C
+++	resistance to humidity and water
+++	resistance to salt and salt spray
+++	resistance to reactive species commonly found in polluted air (O_3, NO_x)
+++	hard surface that does not get scratched easily
+++	mirror surface can be cleaned regularly without negative effects
++	resistance to biological depositions
++	surface defects only result in slow degradation, not catastrophic loss of reflectivity
++	resistance to organic solvents (ethanol, acetone) for cleaning
+	cost-effectiveness would allow to change mirrors often in very harsh
	environments
+	be easy to replace without optical re-alignment
+	re-usability of refurbished used mirrors

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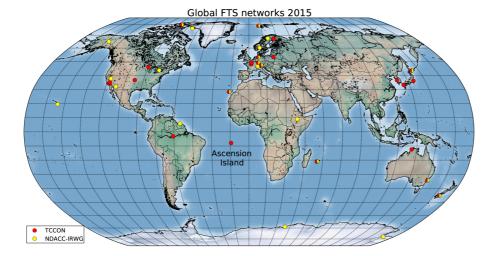


Figure 1. Map of active FTS sites in the TCCON and NDACC's Infrared Working Group (IRWG). The MPI-BGC's FTS is located on Ascension Island in the South Atlantic Ocean.

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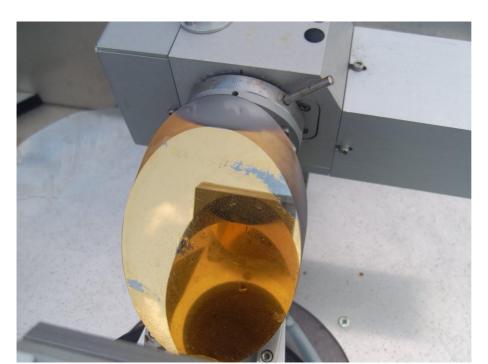


Figure 2. Surface damage on the original gold coated mirror (Bruker) after 20 days outside and one cleaning procedure. Photo: N. John.

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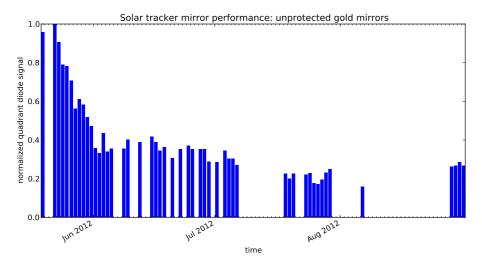


Figure 3. Reflectivity loss of the original unprotected gold coating mirrors (Bruker) on Ascension Island. The normalized maximum light intensity per day at the quadrant diode of the solar tracker is plotted as a measure of reflectivity loss over time. The plot shows the combined reflectivity loss for both solar tracker mirrors.

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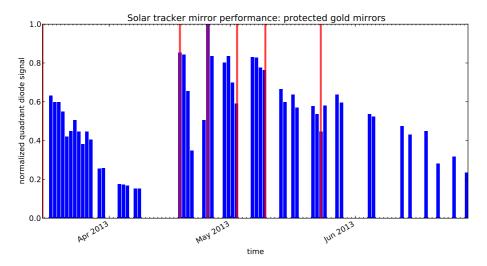


Figure 4. Reflectivity loss of the protected gold coating mirrors (Layertec), like Fig. 3. Red vertical lines indicate when the mirrors were cleaned.

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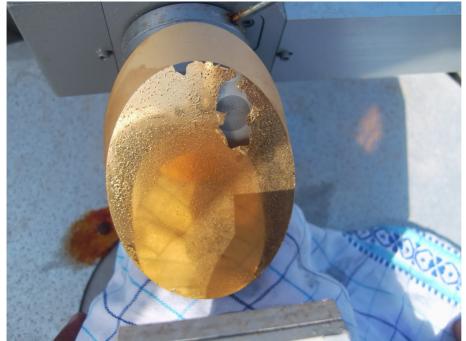


Figure 5. Surface damage on the protected-gold coating mirror (Layertec) after 70 days outside and six cleaning procedures. Photo: N. John.

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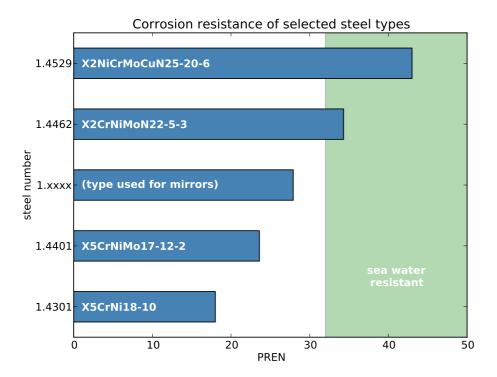


Figure 6. PREN for common stainless steel types. Steel numbers and grades are according to the European EN 10088-3 norm (European Committee for Standardization, CEN). The steel type labeled as 1.xxxx is the one that was chosen for the mirrors.

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Figure 7. Stainless steel mirror with lapped and polished optical grade surface.

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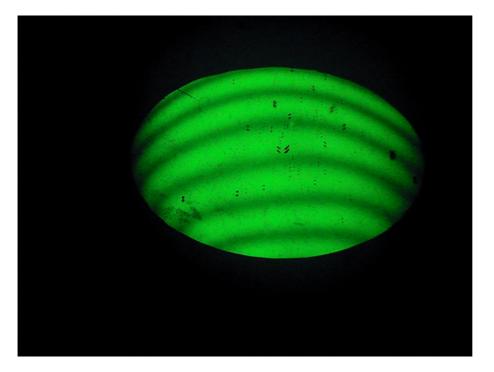


Figure 8. Interferometric test of the steel mirror's optical flatness at $\lambda = 460$ nm.

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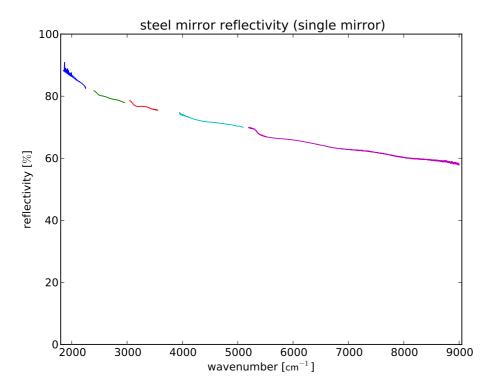


Figure 9. Measurements of the steel mirrors' reflectivity, normalized for a single reflection. The different colors correspond to different optical filters that were used.

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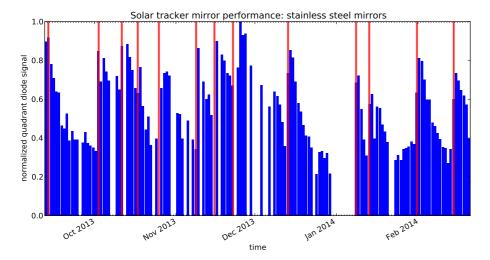


Figure 10. Reflectivity over time for the first set of stainless mirrors (MPI-BGC). Like in Fig. 4, the red vertical lines indicate when the mirrors were cleaned.

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