Identifying and classifying change in PTFE material within a manufacturer's lot of IMPROVE filters

Ann M. Dillner, Jason Giacomo and Bruno Debus, Air Quality Research Center, UC Davis

Executive Summary

IMPROVE blank filters collected in October 2019 produced anomalous results in HIPS suggesting a change in PTFE filter material in the middle of manufacturer's lot. These filters have a non-uniform appearance and also appeared shiny under careful visual inspection indicating a change in spectral reflectance. With the exception of blanks, separating uniform and non-uniform filters in the October data could not be achieved using HIPS. FTIR analysis, on the other hand, successfully identified both blanks and sampled filters as either uniform or non-uniform. The filter classification derived from the FTIR study enabled each filter to be assigned to the correct HIPS calibration such that no sample data was lost. FTIR calibrations were similarly built using the FTIR-derived filter classification to provide FTIR OC and EC data.

The Problem

HIPS measurements are calibrated using blank filters. A manufacturer's lot of filters are expected to be made from a consistent batch of PTFE material. Blank PTFE filters are non-absorbing and are used to calibrate the HIPS response based on the optical properties of the blank filters. After calibration, the blank filters' reflectance and transmittance response will fall on the no absorption line while sampled filters with absorption will fall below this line in the r vs t plot (Figure 1). Currently, HIPS is recalibrated for each new lot of filters as variations in optical properties of the PTFE are sometimes observed from lot to lot. In October 2019, the response of the blank filters changed in the middle of MTL lot 241 (two data points on figure 1). Although differences in blanks can easily be identified, the response of sampled filters vary significantly on the r and t plot and changes in PTFE are masked. For samples, HIPS analysis cannot determine if a specific filter belongs to the group of blanks that falls on the line or above the line.

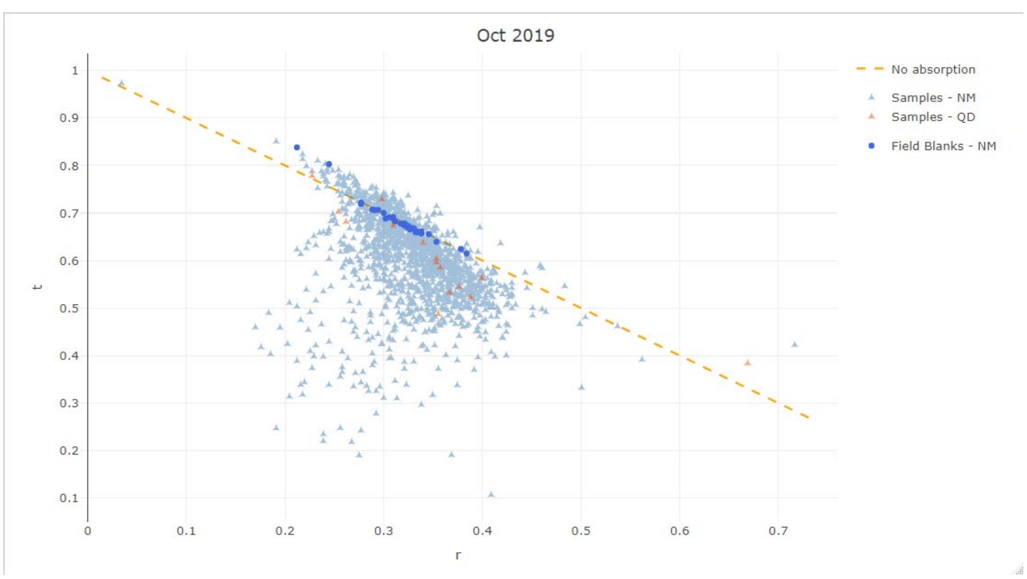


Figure 1. Blank and sampled filters in IMPROVE from October 2019 for Lot 241. Note the two blank filters that do not lie on the calibration line.

Blanks that did not lie on the calibration line were visually confirmed to be non-uniform and to have significant spectral reflectance compared to filters that lie on the calibration line. Throughout this document, filters will be referred to as non-uniform (off the lot 241 calibration line) or uniform (fall on the calibration line).

Identifying filter type on sampled filters

PTFE absorbs in the infrared over a wide range of wavelengths (traditionally expressed as wavenumbers, the inverse of wavelengths) with large doublet between 1300-1100 cm^{-1} and a peak between 550 and 510 cm^{-1} (C-F2 rocking peak is at 516 cm^{-1}, Figure 2).

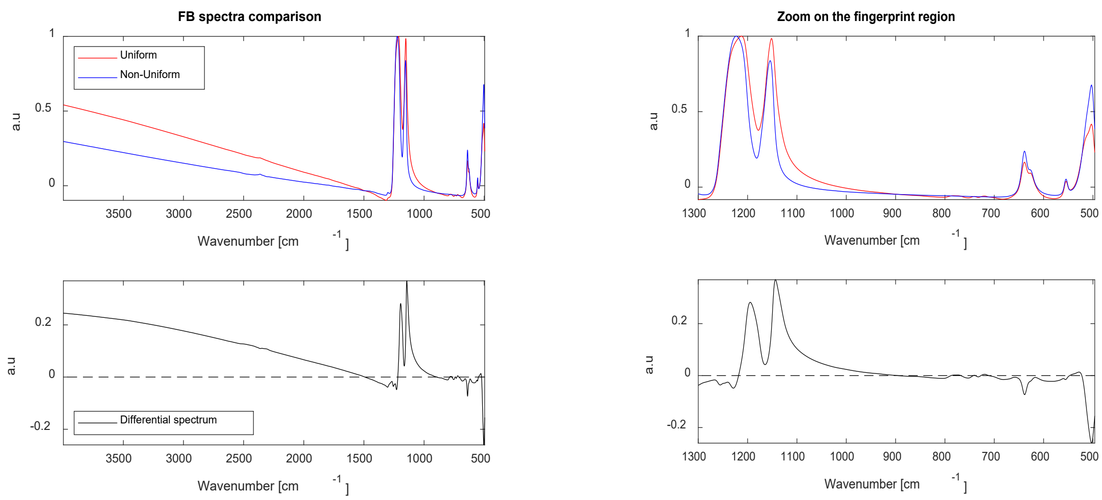


Figure 2. Spectra of a uniform and non-uniform filters (top). The full mid-infrared range (left) and the fingerprint region (right) are shown. The difference between the two spectra are shown in the bottom row, highlighting that the PTFE structure is different in uniform and non-uniform filters.

To determine if the difference in uniform and non-uniform samples could be identified using infrared spectra, second derivative spectra between 550 and 510 cm^{-1} of all blanks and samples from August 2019 through January 2020 were analyzed by principle component analysis (PCA) and clustered. The first two principle components were plotted and the data was colored by cluster (Figure 3). The blanks (Figure 3 - left) separate into two distinct groups associated with the two filter types. Non-uniform fall into one group (blue) and uniform blanks into the other (red). As shown in Figure 3 (right), the sampled spectra fall into the same two groups. Four Pall blank filters that were collected in December 2019 as a test, show distinct behavior on the PCA plot (Figure 3, circled) but are more similar to uniform MTL filters than non-uniform MTL filters.

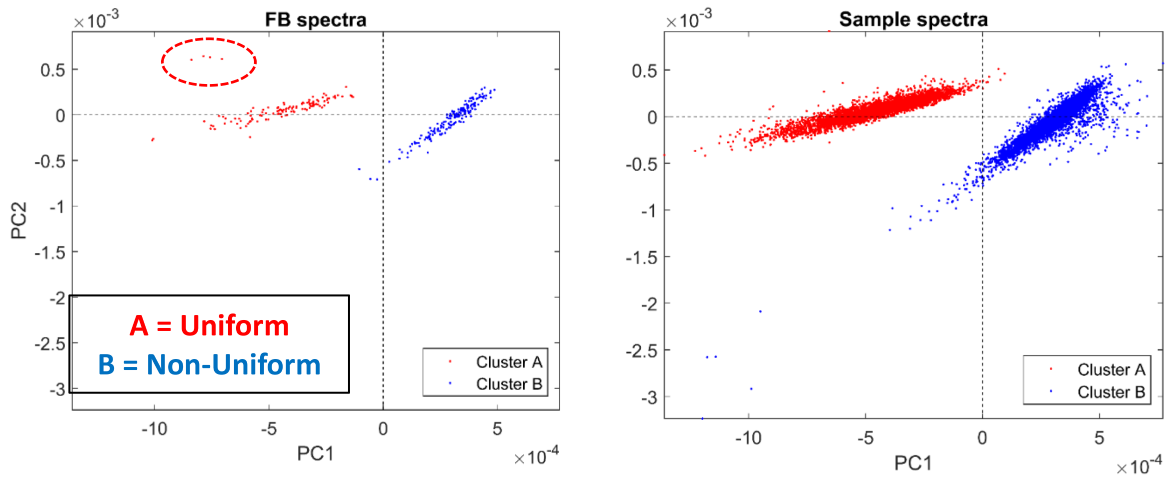


Figure 3. Principal component plots of blanks (left) and sampled (right) filters from August 2019 through January 2020 in the IMPROVE network. Cluster analysis identifies two unique groups.

These result shows that FTIR spectra can be used to differentiate between uniform and non-uniform MTL filters (as well as Pall filters). Figure 4 shows the difference in infrared response for the different PTFE materials in MTL Lot 241.

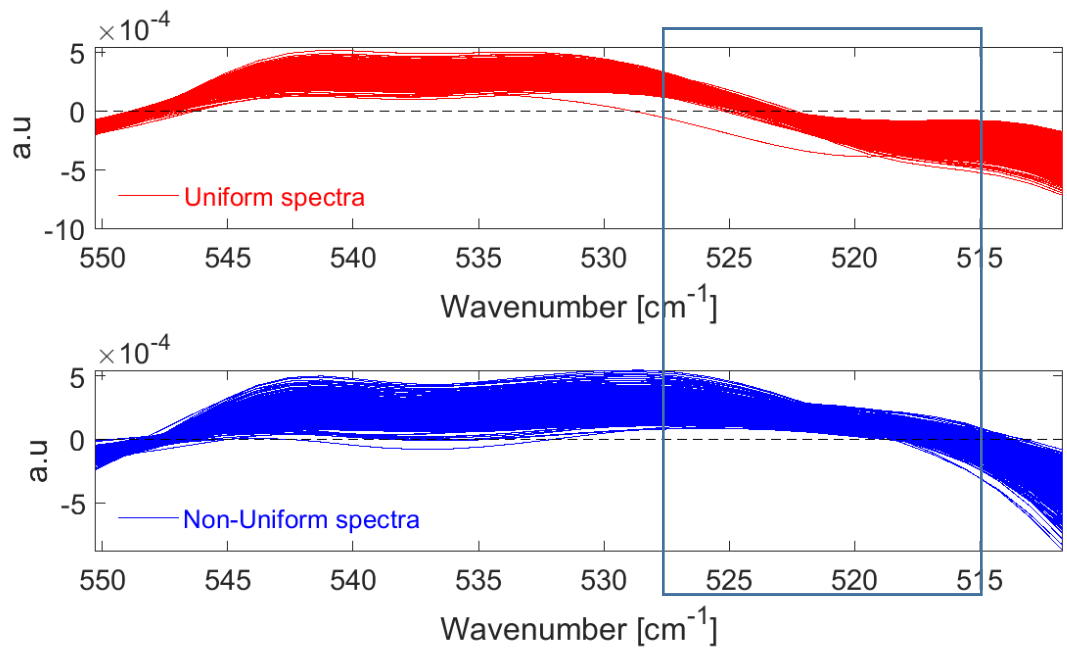


Figure 4. Clustered FTIR spectra in narrow IR band impacted by PTFE absorbance. Uniform (top) and non-uniform (bottom) clusters show a distinct spectral difference 527 and 515 cm^{-1} (boxed in region).

Using the filter lists for uniform and non-uniform filters obtained from the FTIR analysis and their corresponding barcodes, Figure 5, shows that the change in PTFE material occurred within the same lot (241). The non-uniform filters were given a new lot number 241a, for identification within the database.

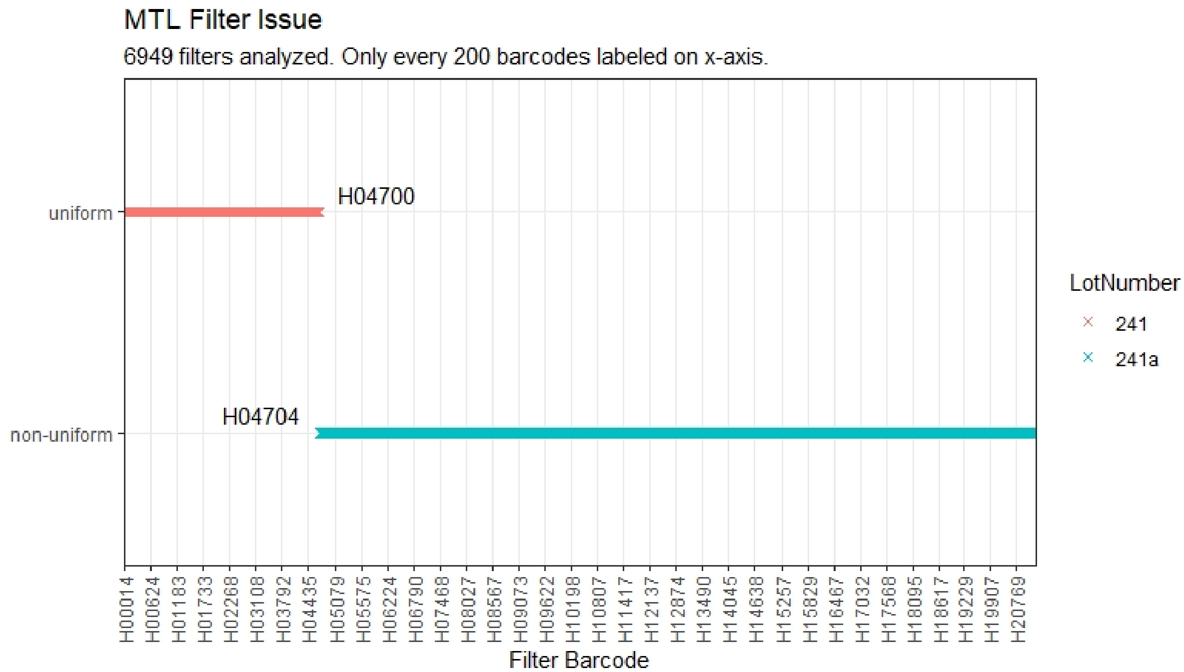


Figure 5. Filter barcodes plotted by uniform and non-uniform identification from FTIR

This change in PTFE material occurred during October 2019 and remained consistent thereafter as shown in Figure 6. After being presented with this evidence, MTL discovered that their supplier had been providing PTFE that was outside of specifications. In August 2020, MTL produced new filters to determine if the issue had been corrected. HIPS results (not shown) and FTIR PCA analysis (last panel, Figure 6) showed that the new filters are uniform and within the bounds of the original lot 241 filters.

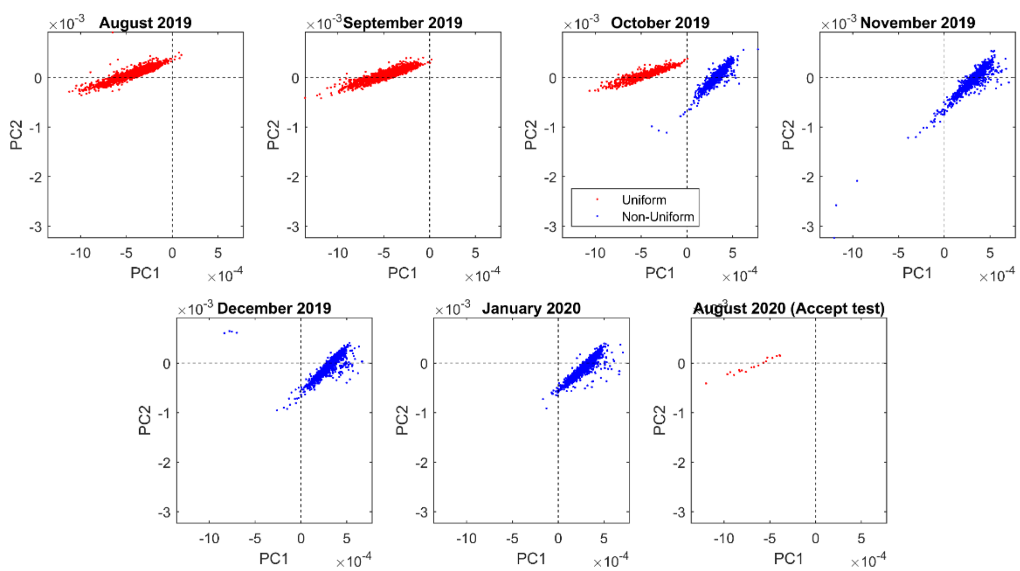
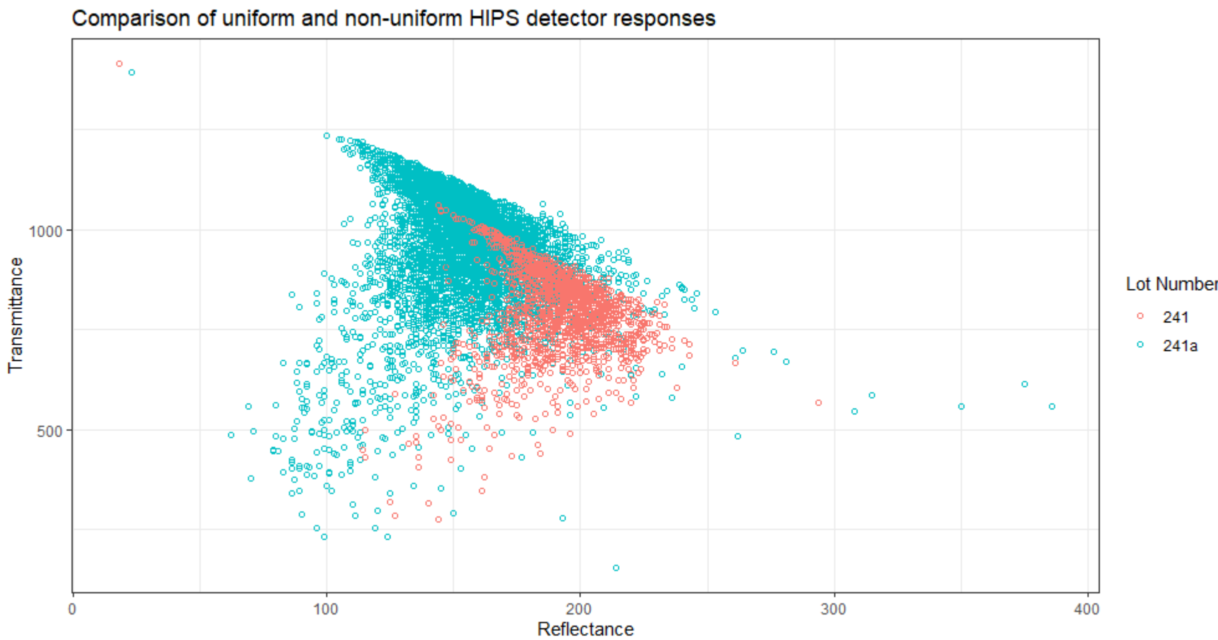


Figure 6. PCA results by month of Lot 241, showing that the change in PTFE occurred during October 2019. MTL corrected the problem in test filters sent to UC Davis in August 2020.

Updated HIPs and FTIR calibrations to account for PTFE changes

A HIPS calibration was developed for non-uniform filters (identified as lot 241a). Figure 7 shows the raw HIPS detector responses (top) and the calibrated results (bottom) for lot 241 filters. The calibrated data is all on or below the no absorption line, t + r = 1, indicating a successful calibration of non-uniform filters. This data was produced in the UCDavis data base, using the filter barcodes as shown in Figure 5.



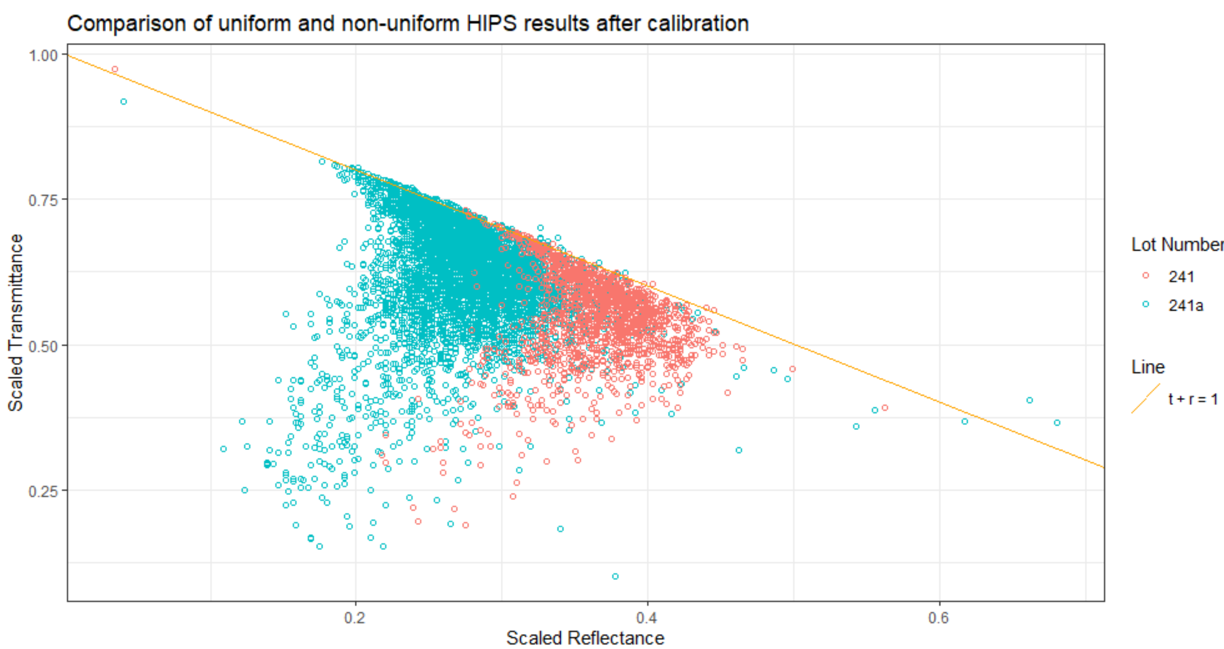


Figure 7. Raw (top) and calibrated (bottom) HIPS response to uniform and non-uniform filters. Proper calibration makes the two filter types fall on the t + r = 1 line and below indicating valid data.

FTIR spectra of non-uniform filters were used to develop calibrations for FTIR OC and EC. The TOR data used had not been validated at the time of the calibration development. A separate pair of calibrations were developed for uniform spectra.

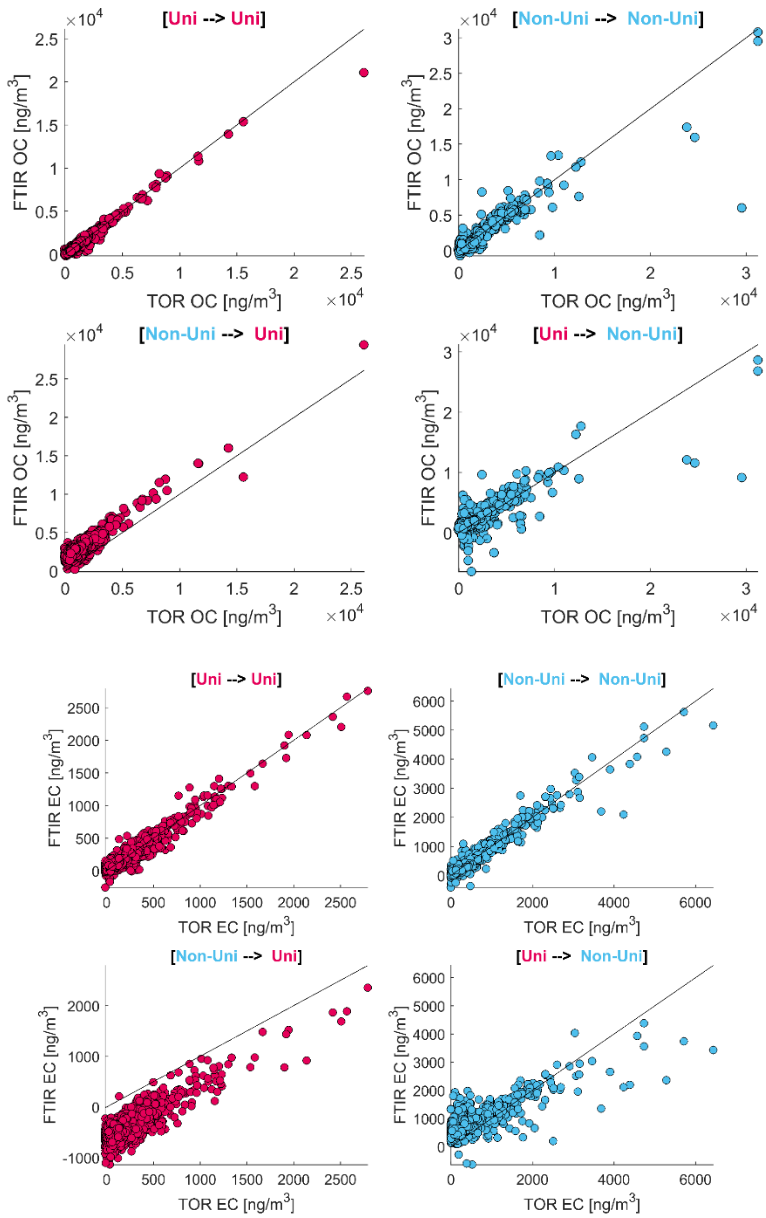


Figure 8. FTIR OC and EC predictions of uniform filters (left column) and non-uniform filters (right column) for OC (top two rows) and EC (bottom two rows). Both uniform and non-uniform calibrations were used to predict both uniform and non-uniform filters.

Figure 8 shows for both OC and EC that using the appropriate filter type for calibration development (uniform calibration for uniform filter prediction) results in high quality predictions (first and third rows) whereas using uniform calibration to predict non-uniform filters and vice versa results in large bias and error.

Using the filter identification obtained from FTIR and implemented by barcodes into the database, the appropriate HIPS and FTIR calibrations were applied to produce high quality data.

Classifier developed for routine identification of filter type

Based on identification of uniform and non-uniform filters by PCA of FTIR spectra, a classifier was developed which enables identification of the two filter types without relying on filer barcodes or repeating the PCA with new data. The classifier was developed with a limited number of samples and applied to the remaining samples during the August 2019 – January 2020 time period and 100% of the filters were classified appropriately.

For the RENO study, the barcode system in the database was used to determine the appropriate calibration for HIPS and FTIR data. However, based on the FTIR classifier, some of the filters that were identified as non-uniform by the classifier were identified as uniform by the barcode system. This breakdown in the barcode system occurred because some filters were manually weighed (when the MTL chamber was down) and these filters did not have barcodes. The classifier was implemented by the database group (on a temporary basis) to correctly identify all RENO filters, including those without barcodes, resulting in accurate data being reported for the RENO study.

The classifier was also applied to all IMPROVE network samples from February, 2020-July, 2020. (In July, 2020, Pall filters replaced MTL filters in the network). All but four were classified as expected by their barcode number. Three of the misclassified filters would likely have been identified and removed from the data during validation. This includes one filter with a scratch on it and two others that had unusual spectral behavior that were visually identifiable as a bad spectra. There was only one spectra identified as uniform when its barcode indicated it was non-uniform. Visual inspection of this one filter concurs with the classifier that this is a uniform filter but operationally, it is difficult to determine how a uniform filter could end up with a barcode in the non-uniform time period. So, for nearly one year of spectra (~20,000), only 1 filter was misclassified that would not have been caught in data validation.

Summary

FTIR spectra can be used to identify changes in PTFE material that adversely impact HIPS data.