

# Measurement and Speciation of Fluoride Emissions at a Phosphate Fertilizer Manufacturing Plant Using Open-Path FTIR and TDL

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## ABSTRACT

As part of a plant expansion permitting strategy, SF Phosphates Company (SFP) decided to perform a series of open-path Fourier Transform Infrared (FTIR) measurements. These measurements were undertaken to speciate the fluoride emissions from the phosphogypsum storage area at SFP's phosphate fertilizer complex located in Southwestern Wyoming. This effort was intended to determine the relative percentages of hydrogen fluoride (HF) and silicon tetrafluoride (SiF<sub>4</sub>) present in the total fluoride emissions from this area source because the applicable ambient air quality standards are specific to the HF species.

The initial phase of the project focused on monitoring directly over the phosphogypsum storage area, measuring HF and SiF<sub>4</sub> at different functional areas. Phase I indicated that a high percentage of the total gaseous fluoride being emitted was as SiF<sub>4</sub>. The second phase of the project focused on determination of an HF/SiF<sub>4</sub> ratio in ambient air downwind of the phosphogypsum storage area to better represent the overall emissions. In an effort to improve the detection levels for HF, a Tunable Diode Laser (TDL) unit was added during a portion of phase II, measuring HF concurrently along the same path as the FTIR measuring both species.

Examples of data collected over the phosphogypsum and process water storage areas are given with some discussion. Data from the concurrent FTIR/TDL measurements are presented. An overall HF/SiF<sub>4</sub> ratio was calculated using the HF data from the TDL and the SiF<sub>4</sub> data from the FTIR.

Data from the monitoring project were used in conjunction with dispersion modeling for the area source as part of a successful expansion permit application.

This paper will discuss the findings of the fluoride speciation project and compare results and strengths of the measurement techniques, summarizing a successful industrial application of

emerging technologies.

## **INTRODUCTION**

SF Phosphates Company (SFP) operates a phosphate fertilizer-manufacturing complex located 4.5 miles SE of Rock Springs, Wyoming. Phosphoric acid is produced at the plant by acidulation of phosphate rock ore with sulfuric acid. The phosphoric acid is further refined into liquid and dry phosphate fertilizer products. The sulfuric acid and phosphate rock reaction also produces calcium sulfate dihydrate, commonly referred to as phosphogypsum. Phosphogypsum is generally managed as a waste material in a large storage area, but the material does have many other beneficial uses. Phosphate ore typically includes fluoride minerals. This fluoride is emitted as gaseous HF and SiF<sub>4</sub> throughout the fertilizer manufacturing processes. The phosphogypsum storage area is the largest source of fluoride emissions.

The high desert of Southwestern Wyoming experiences hot and dry weather generally during the months of June, July and August. Total fluoride emissions from the phosphogypsum storage area are highest during these months. These higher summer total fluoride concentrations were raising compliance concerns and would hinder future facility expansion. Therefore, in support of an expansion permit application, SFP reviewed its existing fluoride measurement technology and relevant fluoride standards. SFP currently uses a fluoride dual tape sampler and associated laboratory analysis, which measures total fluoride. The State of Wyoming, however, has ambient air quality standards specific to HF. Because the current monitor is unable to distinguish between different gaseous fluoride species, all the fluoride measured has been reported as HF. In addition, this monitoring methodology is not real-time, which makes it difficult to use the data effectively.

From previous research efforts and published data<sup>1,2,3</sup>, SFP knew that some portion of the fluoride emitted was SiF<sub>4</sub>, but was unaware of the exact ratio. In addition, published data was not directly applicable to the SFP situation due to the unique climatic and operational characteristics present at the SFP facility. Therefore, SFP commissioned Terra Air Services division of Petris Technology to perform FTIR fluoride speciation studies during the summer of 1998, utilizing the relatively new optical remote sensing technology. The main objective was to determine an HF/SiF<sub>4</sub> ratio to use as a factor to apply to the existing total fluoride data. SFP hoped to then use this new data set in conjunction with dispersion modeling to demonstrate a non-significant ambient air impact as part of the expansion permit application.

## **INSTRUMENTATION**

During the project, an ETG Air-Sentry FTIR spectrometer was used for fluoride identification and quantitation. The ETG FTIR is mono-static, uses a Michelson interferometer, and MCT detector cooled with a Stirling engine. The system was operated at 1 cm<sup>-1</sup> resolution, and 66 scans were co-added for each spectrum (approx. 5 minutes each). The software package allows continuous data collection and analysis in near real-time, and uses classical least-squares regression analysis. Excepting time for moving and system upkeep, the FTIR was operated around the clock. At least one new background spectrum was taken at each new path site,

during upwind conditions when possible. The backgrounds were evaluated for presence of fluoride species and synthetic backgrounds produced when necessary. Backgrounds were subsequently re-evaluated for appropriate subtraction and spectra reprocessed as needed.

A Boreal Laser "GasFinder" HF TDL was added during the second phase of the project, in an effort to achieve lower detection limits for HF. The system uses a DFB laser diode tuned to a very narrow mid IR HF band free of water vapor interference. The self-contained system has an internal HF reference/QA cell, and broadcasts a data string approximately every 1-2 seconds including date and time, concentration, a data quality indicator, and operational status indicators.

## **FIELD MEASUREMENTS AND RESULTS**

### **Phase I**

The initial monitoring work was performed directly over phosphogypsum and process water areas, attempting to characterize the fluoride emissions. The phosphogypsum storage area consists of a series of solid material "stacks" and free water ponds designed to dry and store the solid material, and recover the water for plant operations. After the material is dried, it is used to continually build up these stack areas. The material is received into the area from the plant as hot slurry and is placed into a section of a stack area. As solids build up, the aqueous run-off is diverted, further cooling and reducing the solids content. Expectations for the project were to be able to measure emissions from a representative number of stack and pond areas and average the data to come up with an HF/SiF<sub>4</sub> ratio.

FTIR monitoring was performed at 10 different paths over approximately two weeks, usually directly over these pond and stack surfaces at heights of approximately 2-3 meters. Because of the large surface area of the ponds / stacks and the optical path proximity to the surface, wind direction was not a critical factor. The FTIR was usually moved to a new path each morning and data collected continuously until the following morning. Stack or solid areas in different stages of use were chosen, including fresh, hot slurry, various stages of drying phosphogypsum, aqueous run-off areas, and ponds with essentially liquid only.

A typical FTIR record of fluoride species over drying pond surfaces is shown in figure 1. Figure 2 shows a typical FTIR record of fluorides species over aqueous pond surfaces.

The data gathered did indeed show that a high percentage of the fluoride emitted from this area was SiF<sub>4</sub>. However, it was discovered that the HF/SiF<sub>4</sub> ratio varied widely with factors such as the dryness of the solid areas and the solar radiation incident (surface temperature) to the area being tested. Although additional useful operational information was obtained during phase I, it was realized that it would be difficult to compute an overall fluoride emission ratio representative of ambient air from the widely varying source areas.

### **Phase II**

Phase II was undertaken to measure a more representative ambient air HF/SiF<sub>4</sub> emission ratio

for use in SFP's air dispersion model, by selecting an appropriate site downwind of the phosphogypsum tailings area. Locating the path further downwind would also allow sampling an atmospheric environment more like that of the existing ambient air monitor, located roughly 2 km to the NE. To generate a representative HF/SiF<sub>4</sub> ratio, a site was selected far enough downwind to ensure averaging of the area source emissions, while capturing data for both fluoride species during as much of the monitoring as possible. Topography and a highway right-of-way limited the number of potential path sitings. By trial measurements, a site was selected approximately 500 meters to the NE of the storage area. A path of approximately 500 meters was established in a generally SE to NW direction, intersecting emissions based upon the predominant wind directions. Data was acquired at this site generally continuously by FTIR from 08/13/98 through the morning of 08/19/98.

During phase I, it had been found that the FTIR detection limits for SiF<sub>4</sub> remained much steadier than for HF due to the widely varying water vapor at the site. SiF<sub>4</sub> has a broad absorbance band relatively free of water vapor interference, while we found the HF to be highly affected. Between phase I and phase II, adjustments had been made to some of the wavelengths monitored for HF, which we hoped would steady the HF quantification levels. The adjustments improved the quantification levels, and low ppb levels could be achieved for HF with backgrounds matching the sample water vapor. Over any length of real time acquisition, however, we found the achievable HF quantitation levels to be more on the order of 20 - 100ppb HF. As phase II progressed, it became apparent that these levels were unsatisfactory, as the ambient HF levels were below or near the FTIR detection limit for much of the monitoring time period.

Because the HF was below the FTIR quantitation limits for much of the time, there were two basic choices for calculating an HF/SiF<sub>4</sub> ratio from the data. Our choice was to use the quantitation limit for HF and a value of zero for SiF<sub>4</sub> when no value was obtained at a data point. This conservative approach resulted in approximately 50/50 estimates for the ratio. The second option was to use only data points for which there were concentration values for both HF and SiF<sub>4</sub>. This method resulted in more favorable ratio (lower HF/SiF<sub>4</sub>), but the data set was much more limited. Since the wind was mainly from the desired prevailing SW direction during most of the project, we did not attempt to parse the data based on wind direction. In addition, SFP's reporting requirements are for 12-hour and longer-term averages, and are not based upon wind direction.

At this point, it was decided to add a TDL to the project to attempt lower-level HF measurements, since this would provide more comprehensive data proving lower the HF values and result in a more accurate ratio. Based on Terra Air Services' prior experience with their TDL on other projects, Boreal Laser was invited to join the project. The HF laser was put into operation on the same optical path as the FTIR on 08/20/98. Concurrent FTIR/TDL data was collected between 08/22/98 and 08/25/98. During periods when HF was at quantifiable levels by FTIR, the TDL data correlated well with the FTIR values. The Boreal system delivered stable detection limits of approximately 0.3ppb HF at 500 meters and recorded a data point

approximately every 1.8 seconds. The lower levels we were able to achieve with the laser enabled us to collect many more data points with values for both HF and SiF<sub>4</sub> species. This allowed calculation of more accurate values for the ambient air HF value and resulted in a lower HF/SiF<sub>4</sub> ratio.

The TDL was not available after 08/25/98, but FTIR data was collected along the same path through the morning of 08/29/98.

Figures 3 through 5 graphically present the TDL HF data overlaid with the FTIR HF and SiF<sub>4</sub> data collected between 08/22/98 and 08/25/98. The quantification limit was used as a data point when no value was recorded. The FTIR values are based on approximately 5-minute averaged spectra, and the approximately 1.8-second TDL HF data were averaged to correspond to the FTIR acquisition times.

Table 1 summarizes fluoride ratios calculated from the phase II data. All of the data presented in this table is from the same optical path. The data are broken into three monitoring periods, each of which consists of at least several days monitoring. A ratio for HF and SiF<sub>4</sub> data by FTIR only is calculated for all three periods. The second period, 08/22/98 to 08/25/98, is data from the concurrent TDL/FTIR monitoring. Fluoride ratios based on TDL HF data with FTIR SiF<sub>4</sub> data for this period are also presented. These calculations were made using the detection limit for HF when below the quantification limit and a value of zero for SiF<sub>4</sub> when below the quantification limit.

## **OBSERVATIONS**

1. SiF<sub>4</sub> clearly made up a significant portion of the phosphogypsum storage area fluoride emissions.
2. Relatively low levels of SiF<sub>4</sub> were observed on paths crossing aqueous pond surfaces. Over the dry and drying surfaces, the SiF<sub>4</sub> levels were very low at night and generally much higher during the day. While no solar radiation data was collected, real-time operator observation indicated very quick response and high correlation of solar radiation with SiF<sub>4</sub> emissions from these areas. SiF<sub>4</sub> emissions tended to follow the surface temperature of the dry and drying areas, which fluctuate quickly and widely with incident solar radiation.
3. The HF emissions showed in general much more gradual swings, and an overall-increasing trend during the day and an overall-decreasing trend during the night. It appears that mostly HF is emitted from the aqueous surfaces. The aqueous areas heat slowly throughout the day and slowly cool at night, and the HF emissions tended to follow this trend.
4. Because the SiF<sub>4</sub> emission appears to be much more sensitive to temperature, it is likely that the percentage fluoride contribution from SiF<sub>4</sub> is even higher during the hottest time periods of the summer months. Historically, the highest ambient air fluoride concentrations have been measured at SFP's existing ambient fluoride monitor in July (i.e., although phase II was conducted in August, it was not as hot and dry as the July time frame in 1998).

## CONCLUSIONS

The project resulted in successful differentiation of the gaseous fluoride species and calculations of very significant percentages of SiF<sub>4</sub> in the total fluoride emissions from the phosphogypsum storage area. The project data were instrumental in agreement on a new expansion permit.

It was realized that the data were limited and would probably not produce a fluoride ratio typical of the entire year. However, the project provided clear evidence that the true HF concentration from the phosphogypsum storage area is much less than 100 percent (as calculated from the total fluoride value). This data was used in conjunction with SFP's dispersion model in a conservative manner to demonstrate that SFP was not near the HF limits and that there was room for plant expansion. In order to replace the total fluoride measurement technology and to quantify the HF species that the standards are specific for, SFP with the state decided that it would be appropriate to install a permanent HF monitor. SFP is currently working on installation of a Boreal TDL monitor to meet this requirement, which will be operational full-time by the summer of 1999.

The project demonstrated synergy of two emerging technologies used to successfully solve a real industrial problem. Data collected showed that the techniques are comparable and compatible, and highlighted relative strengths of the two technologies. The FTIR is very versatile, allowing multiple analyte analysis and permanent records of the spectral data for later additional interpretation. TDL targets one analyte, and demonstrated excellent stability to water vapor, a low detection limit, and quick response. The Boreal TDL in particular includes useful features such as an internal HF reference cell and a continuous record of data quality and operation for each data point.

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**Table 1. Summary of Phase II Fluoride Ratios**

<u>Monitoring Period</u>	<u>FTIR only data</u>		<u>TDL data FTIR data</u>	
	<u>HF</u> <u>(ug F/m3)</u>	<u>SiF4</u> <u>(ug F/m3)</u>	<u>HF</u> <u>(ug F/m3)</u>	<u>SiF4</u> <u>(ug F/m3)</u>
<u>08/13/98 - 08/19/98</u>	54.9%	45.1%		
<u>08/22/98 - 08/25/98</u>	42.2%	57.8%	27.2%	72.8%
08/22/98 - 08/23/98	59.3%	40.7%	30.3%	69.7%
08/23/98 - 08/24/98	40.3%	59.7%	30.8%	69.2%
08/24/98 - 08/25/98	33.8%	66.2%	20.0%	80.0%
<u>08/25/98 - 08/29/98</u>	60.8%	39.2%		
<b>Overall averages</b>	<b>52.0%</b>	<b>48.0%</b>	<b>27.2%</b>	<b>72.8%</b>

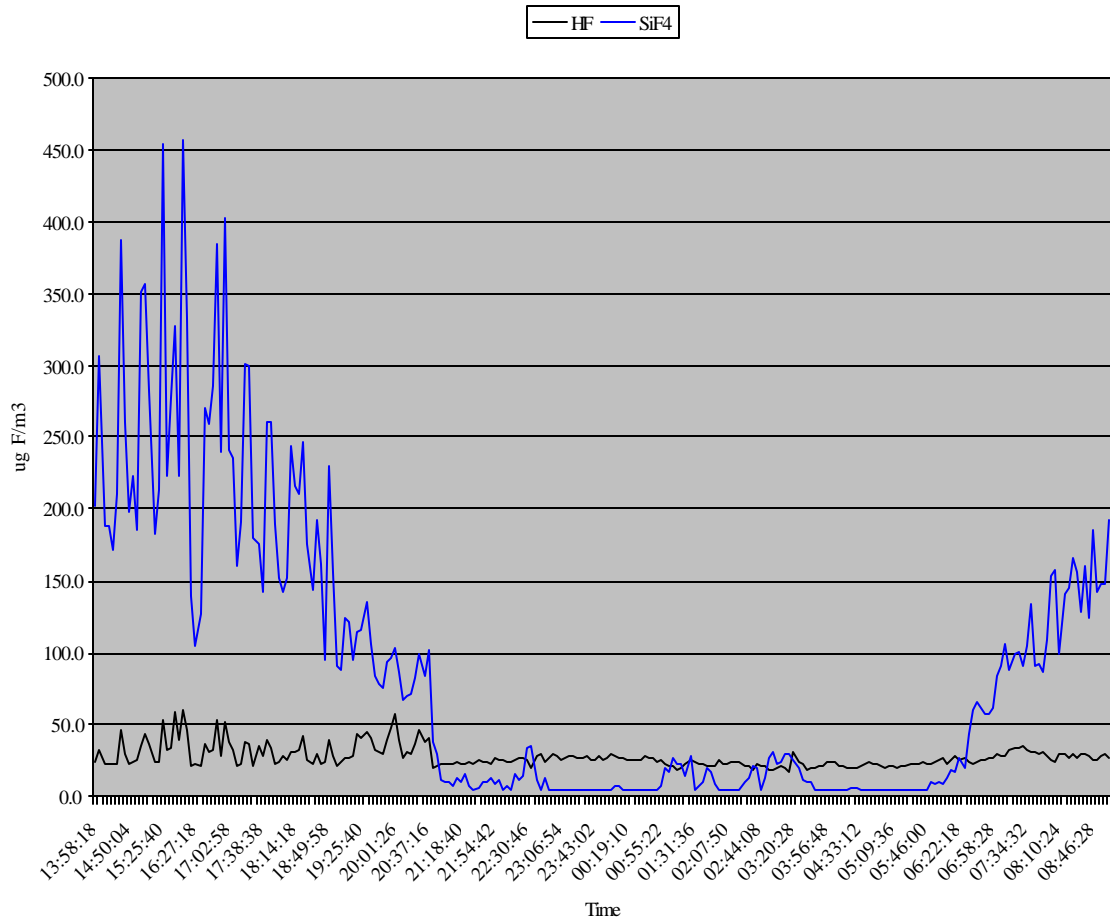


Figure 1. 07/16/98 FTIR data - Drying surface

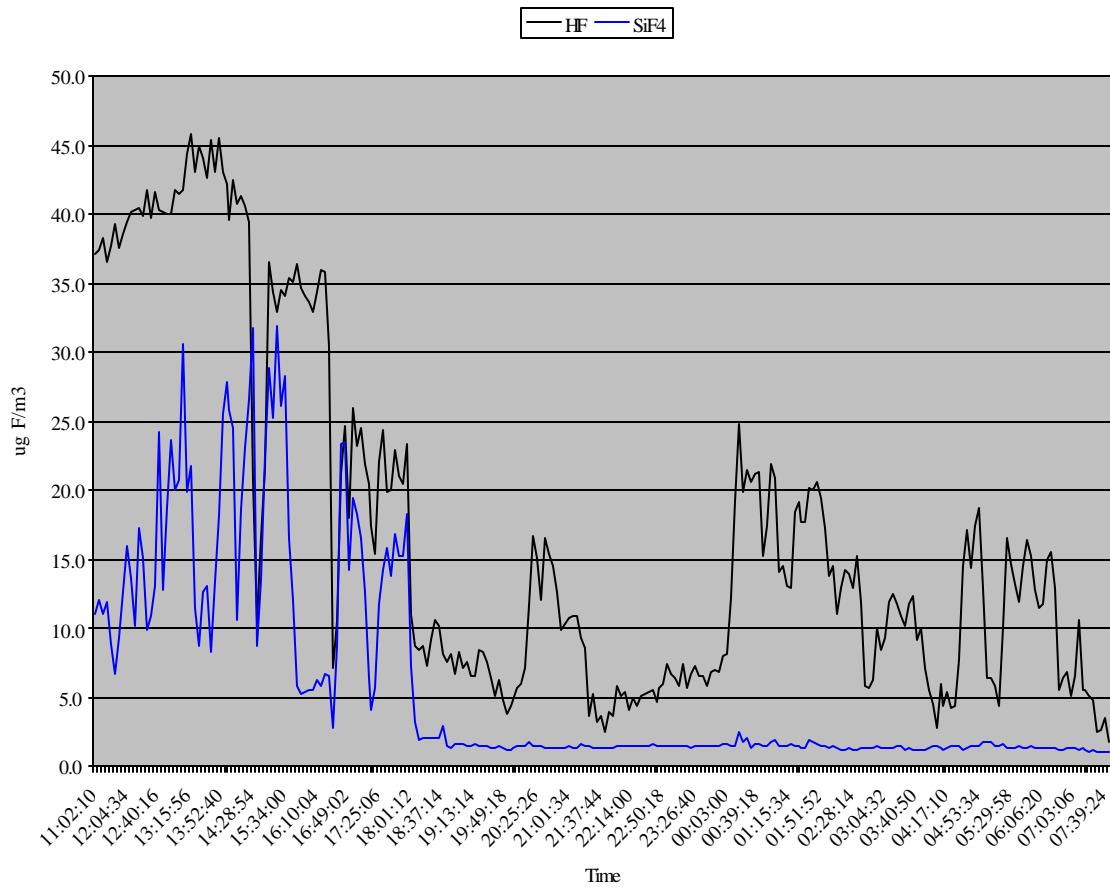


Figure 2. 07/22/98 FTIR data`- Aqueous surface

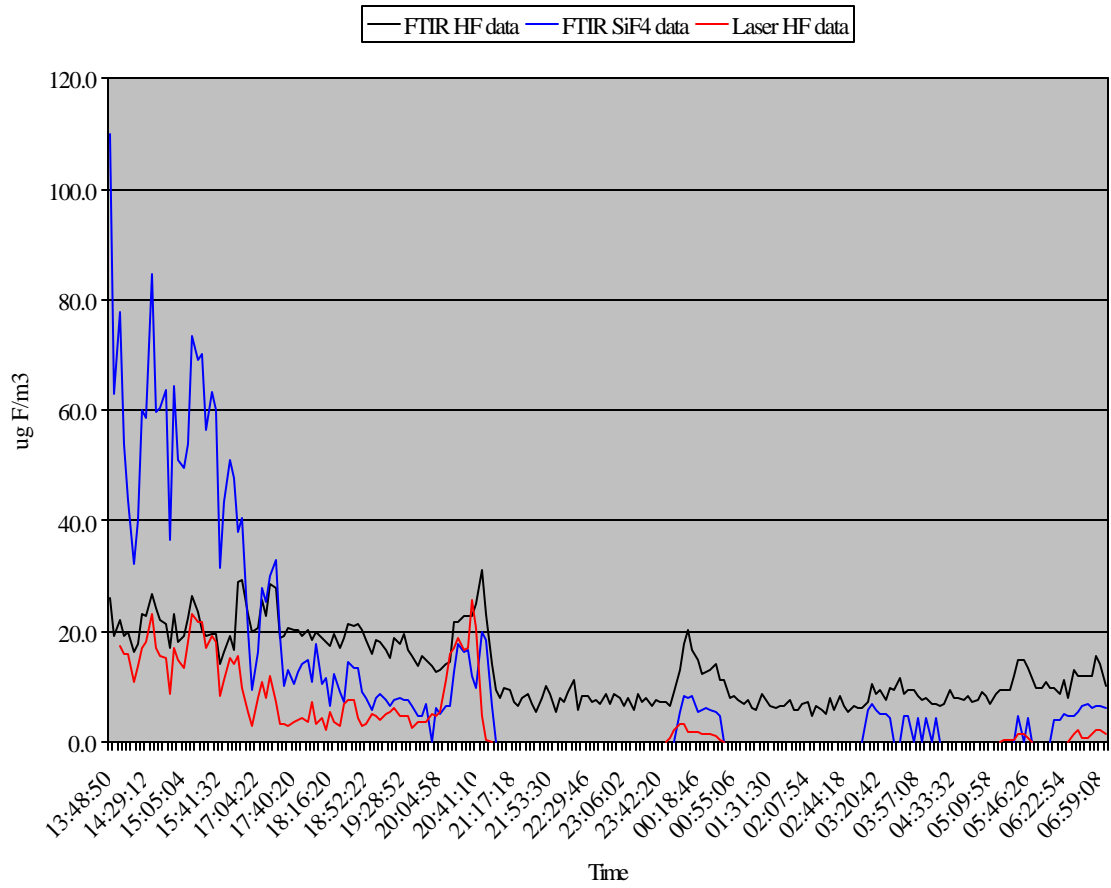
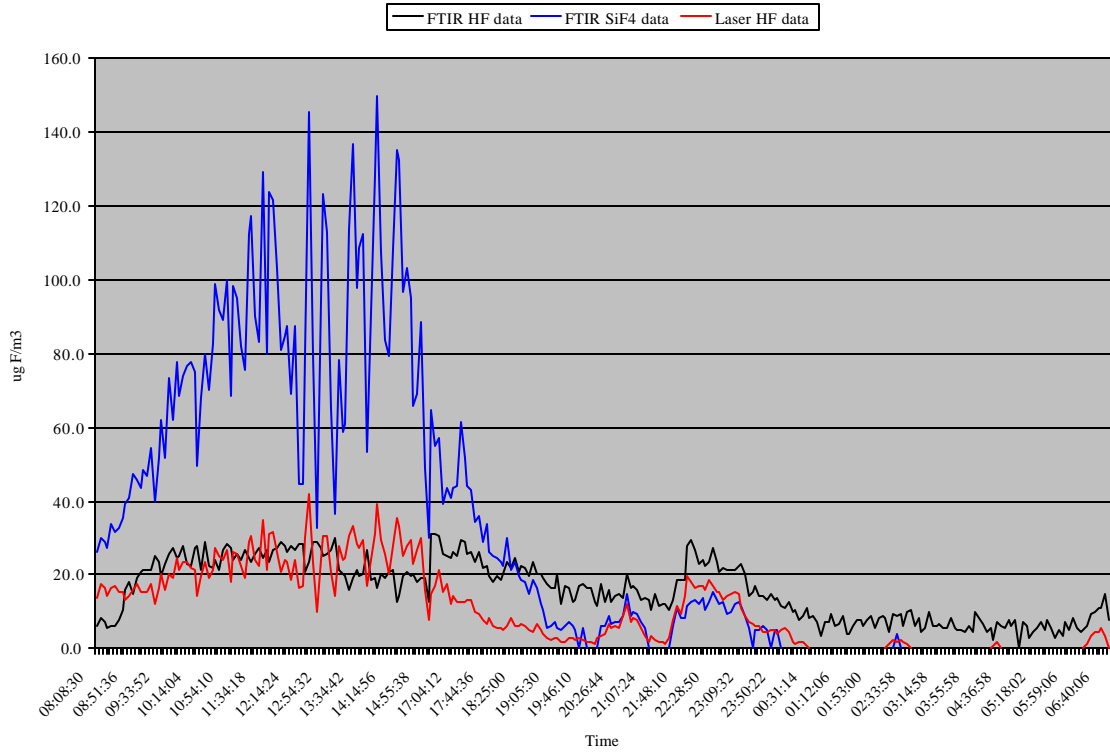


Figure 3. FTIR and TDL data 08/22/98 - 08/23/98



**Figure 4. FTIR and TDL data 08/23/98 - 08/24/98**

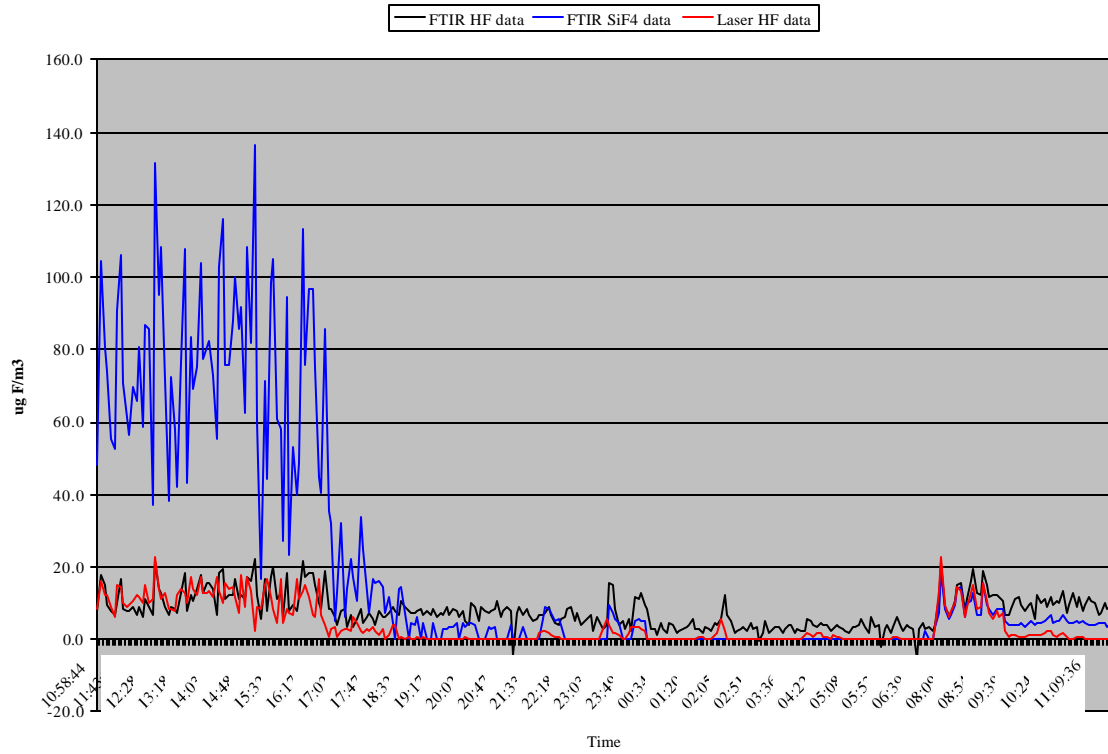


Figure 5. FTIR and TDL data 08/24/98 - 08/25/98

