TECH NOTE

Infrared Gas Identification in Any Conditions: XplorIR's Adaptive Atmospheric Correction

Introduction

Any toxic chemical may pose a danger to the public, especially if it's a toxic gas release. To understand the danger and the best way to deal with it you need to know both the identity and concentration. Without these two pieces of information, it's impossible to do an accurate risk assessment. FT-IR provides accurate chemical identification for a range of unknown samples. It produces unique spectra for each compound, is highly sensitive, can observe small chemical changes, and allows for a broad range of materials to be identified.

Infrared spectroscopy can identify any state of matter (powders, liquids, and gases) with the appropriate sample interface. It is a fundamental tool for the identification of powders and liquids for hazmat and military teams. It has not yet been widely deployed for gas identification though, due to interference from water vapor (humidity) and naturally occurring carbon dioxide. Both water and carbon dioxide are strong infrared absorbers. Additionally, they are both in the atmosphere at large concentrations. For example, at 70°F and 80% humidity, there's approximately 1.4% or 14,000 ppm water vapor in the air. Also, the average carbon dioxide concentration in air is approximately 500 ppm. Compared to IDLH values of hazardous materials which may range from 2 to 1,500 ppm, the concentrations of water and CO_2 are much higher. Clearly, these need to be addressed in order to accurately identify gas phase toxic chemicals by FT-IR.

The RedWave Technology XplorIR is a new piece of equipment which identifies gases and vapors with FTIR in a robust, handheld device. It can identify compounds at operationally relevant concentrations. This handheld unit only weighs ~5lbs; it has a built-in pump for sample analysis/cleaning. Identification can be performed at the scene without a need to collect or pre-treat the sample for analysis. With over 5,600 chemicals in its library, the XplorIR can identify a wide range of unknown gases. The XplorIR incorporates a series of advanced data analysis algorithms for atmospheric compensation and spectral matching which allow accurate sample identification even with humidity and carbon dioxide interference.

Data Analysis Algorithms

Conventional data processing in FTIR spectroscopy also attempts to deal with line shape and atmospheric interference, but it can't deal with the large concentration and non-linear nature of water vapor and carbon dioxide. Traditionally, a sample spectrum is ratioed to a background spectrum to account for line shape and atmospheric contributions. If any water vapor remains, it is typically subtracted out. Each of these processes in conventional processing basically relies on a 1:1 ratio between the sample and background. For powders and liquids, this works fine; however, water and carbon dioxide absorbances are so high in gas spectroscopy that simple processing is insufficient.

The XplorIR's data processing is fundamentally different. Instead of using a 1:1 relationship, the contribution from instrument line shape and atmospheric interferences are removed separately. In each of these steps the removal is tailored to the individual piece of data. This Adaptive Atmospheric Correction allows for precise water and carbon dioxide removal accounting for non-linearity and relative intensity differences, which make conventional processing unreliable. Additionally, the XplorIR also uses an Intelligent Subspace Scaling to emphasize the areas of the sample spectrum where information is present.

Finally, the search score incorporates both match and unique metrics to provide a true measure of confidence. Using these multiple techniques, the XplorIR is able to determine the identity of samples at low concentrations with a meaningful score.

Example: Ammonia

As a first example showing the power of the advanced data processing used in the XplorIR, we'll take the same piece of raw data, a 25 ppm sample spectrum of ammonia, through both conventional FTIR and XplorIR data processing. In Figure 1, a raw data file of 25 ppm ammonia is shown on the left; the water vapor and carbon dioxide are the largest absorbances observed. The ammonia signal is small, but it can be seen at 965 and 932 cm^{-1}. The data was processed with both conventional processing, shown in the upper right, and using the XplorIR result shown in the lower right. The absorbance of ammonia can be observed in both, but it's much more prominent in the XplorIR result. Also, the conventional processing shows residual water and carbon dioxide where none is present in the XplorIR result.

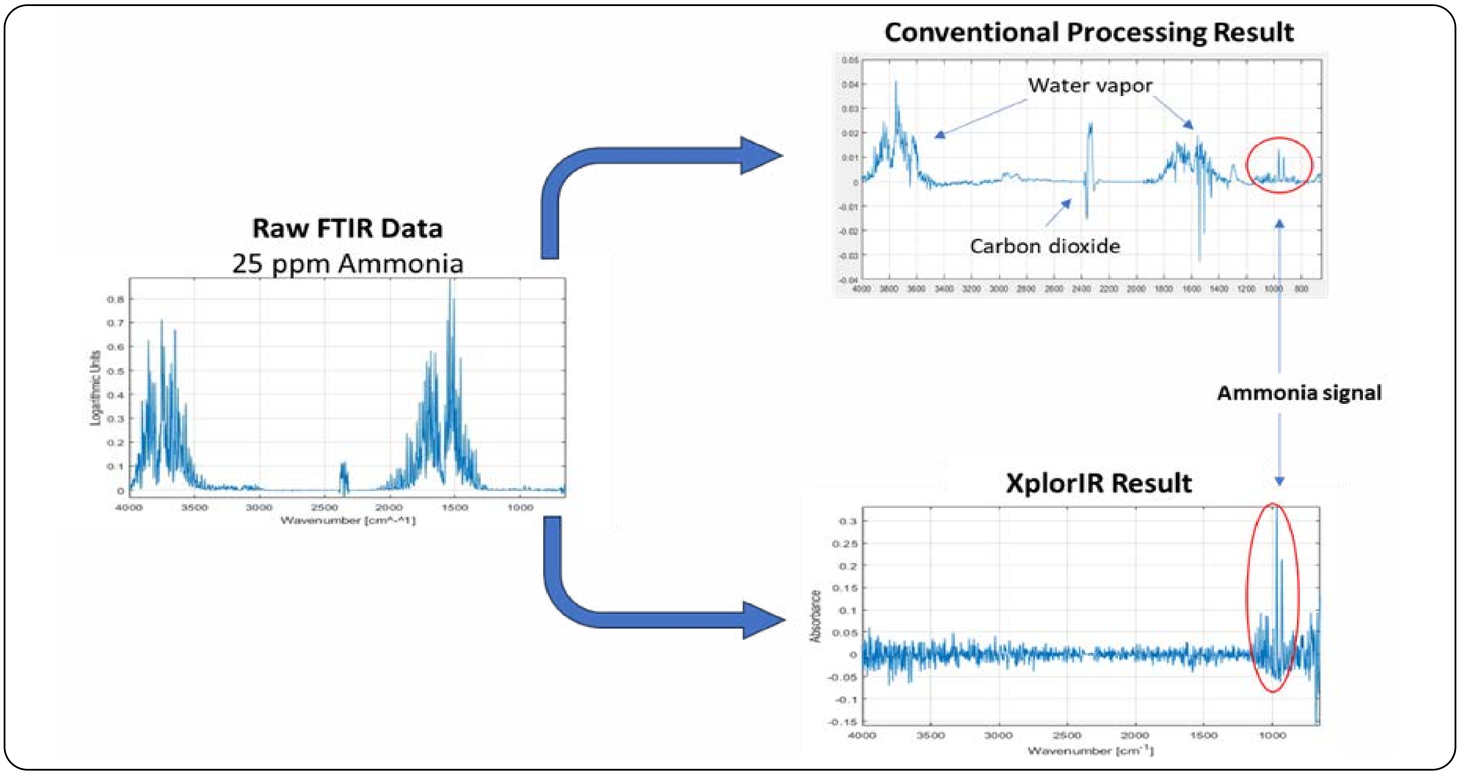

Figure 1 – Infrared absorbance spectrum of 25 ppm Ammonia processed with conventional processing and new XplorIR processing showing the advantage of Adaptive Atmospheric Correction.

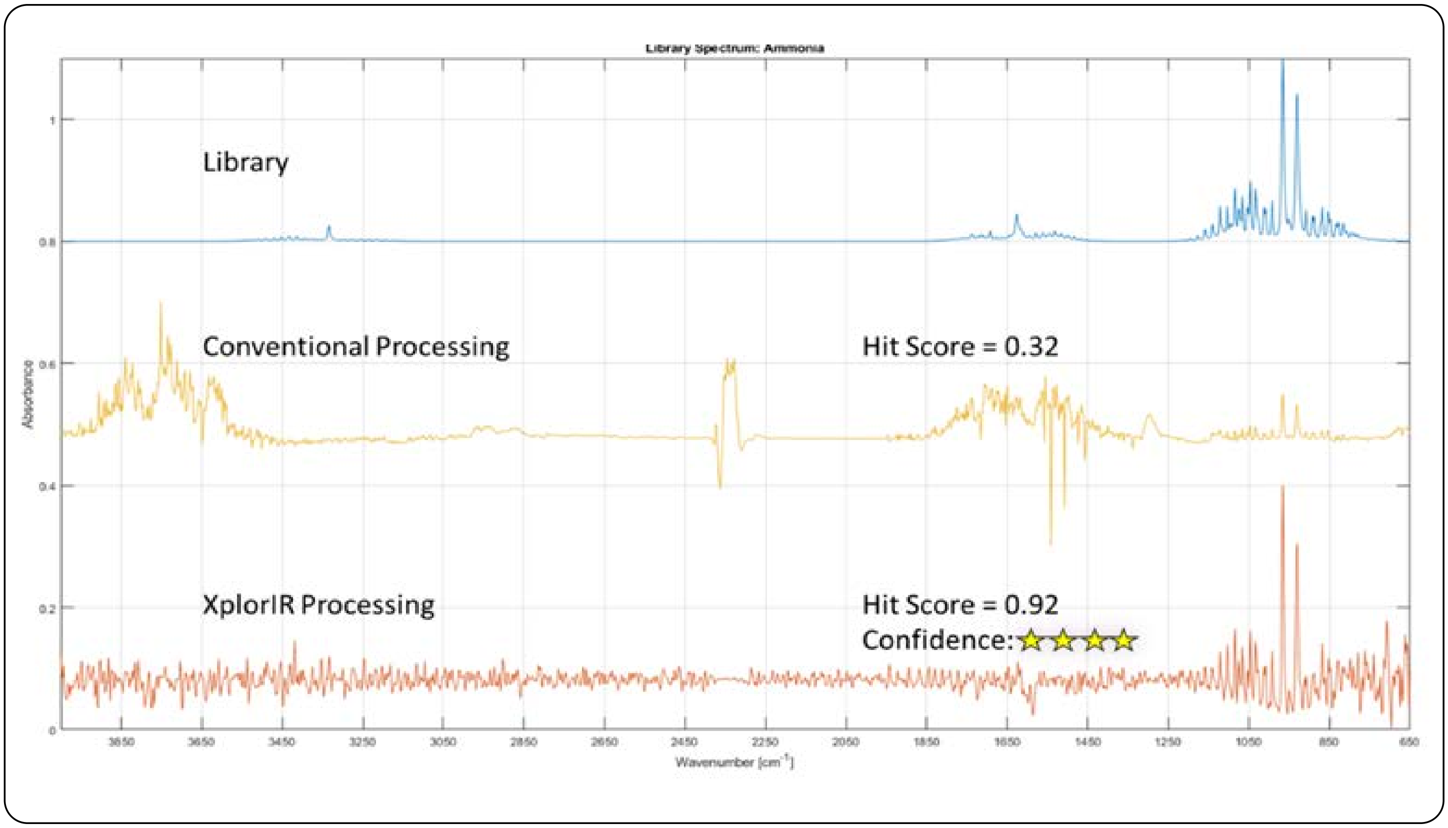

Figure 2 – Library spectrum of ammonia (top), spectrum of 25 ppm ammonia processed and searched conventionally (middle) and spectrum of 25 ppm ammonia processed and searched using XplorIR method (bottom).

XplorIR's Adaptive Atmospheric Correction eliminates interference from water and carbon dioxide making the signature of ammonia much more prominent. On the search side, Intelligent Subspace Scaling provides the correct identification with high confidence. Figure 2 shows a comparison between a library spectrum of ammonia, a sample of 25 ppm ammonia processed with conventional scaling and conventional searching, and the same ammonia spectrum processed and searched with the XplorIR method. Conventionally, the normalized dot product hit score would only be 0.32. Although the search produces the correct match, it is difficult to evaluate the quality of the match due to the low score. The XplorIR search, on the other hand, produces a high hit score of 0.92. Adding in a metric of uniqueness allows us to report the XplorIR result as a confidence of four out of five stars. The star reading gives the user an easy to understand means of qualifying the result.

Example: Sulfur Dioxide

Another example showing the power of the XplorIR data processing can be seen in the identification of sulfur dioxide. Sulfur dioxide is a toxic industrial chemical, that's listed on many chemical watch lists. As a small molecule, it has a very simple infrared spectrum, all of which is directly under the water vapor absorbance. Figure 3 shows the raw data from an XplorIR measurement of 30 ppm of sulfur dioxide in blue compared to the library spectrum in red on the left. SO_2 is completely obscured by the water vapor. The result after processing with Adaptive Atmospheric Correction is shown on the right again compared to a library spectrum of SO_2 in red. Even though this is a small signal due to a low concentration, it can be accurately matched to the library with high confidence.

Example: Hydrogen Cyanide

The final example shown here is hydrogen cyanide (HCN). Hydrogen cyanide is an extremely toxic gas with an IDLH value of 50 ppm.

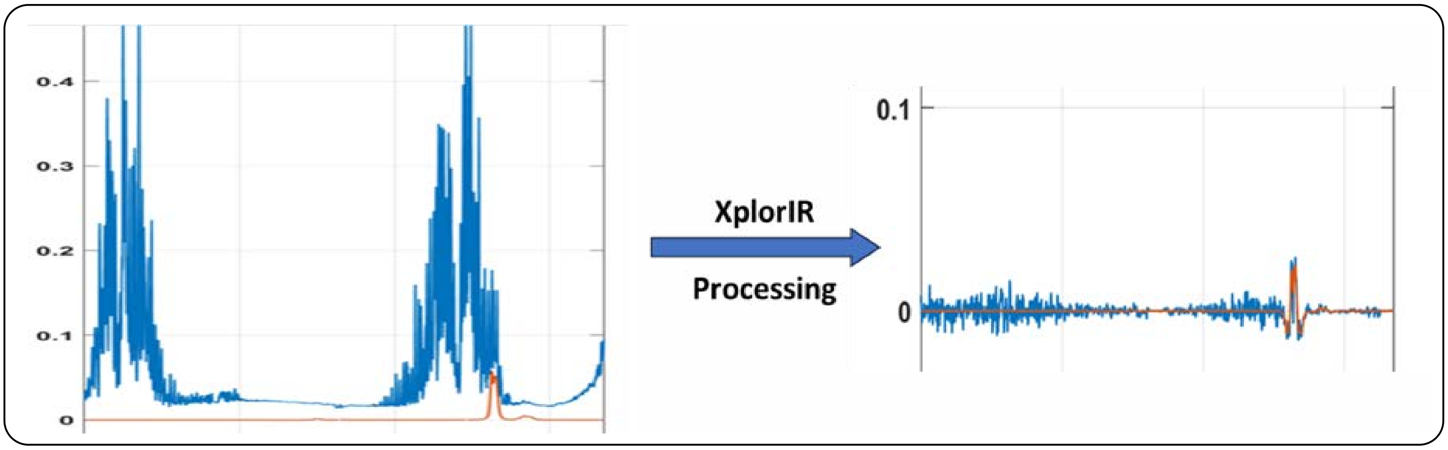

Figure 3 – Infrared absorbance spectrum of 30 ppm sulfur dioxide processed with conventional processing (left) and new XplorIR processing (right) showing the advantage of Adaptive Atmospheric Correction.

Cyanide has several industrial applications including gold plating, polymer manufacturing, and fumigation. It's also a fire gas; it is generated in the burning of synthetic materials. Cyanide has a strong infrared spectrum, but the strongest band is relatively narrow allowing the spectrum to be easily dominated by multiple bands from water vapor. Figure four shows the raw data from an XplorIR measurement of 15 ppm HCN on the left and the same data processed through the XplorIR's Adaptive Atmospheric Correction algorithm on the right. The sample spectrum is shown in blue and the library spectrum of hydrogen cyanide in red. After the correction, HCN can easily be identified by the XplorIR. Even at the low concentration of 15 ppm, a match confidence of 0.88 or 3 stars is obtained.

Limit of Identification Tests

As shown in the three examples above, XplorIR's Adaptive Atmospheric Correction allows identification of low concentrations of toxic gases at low concentrations. To characterize the overall performance, a series of tests were conducted using 8 different gases. Each gas was collected at a range of concentrations and with a humidity range from 20 to 80% RH at 72° F. Analyte concentrations ranged from 1 to 300 ppm; in that range of concentrations, approximately 20% of the samples were at concentrations lower than the estimated limit of detection, based on spectral intensity. Each sample foreground was compared to each background, producing close to 4,000 spectra to evaluate with widely varying humidity between the background and samples.

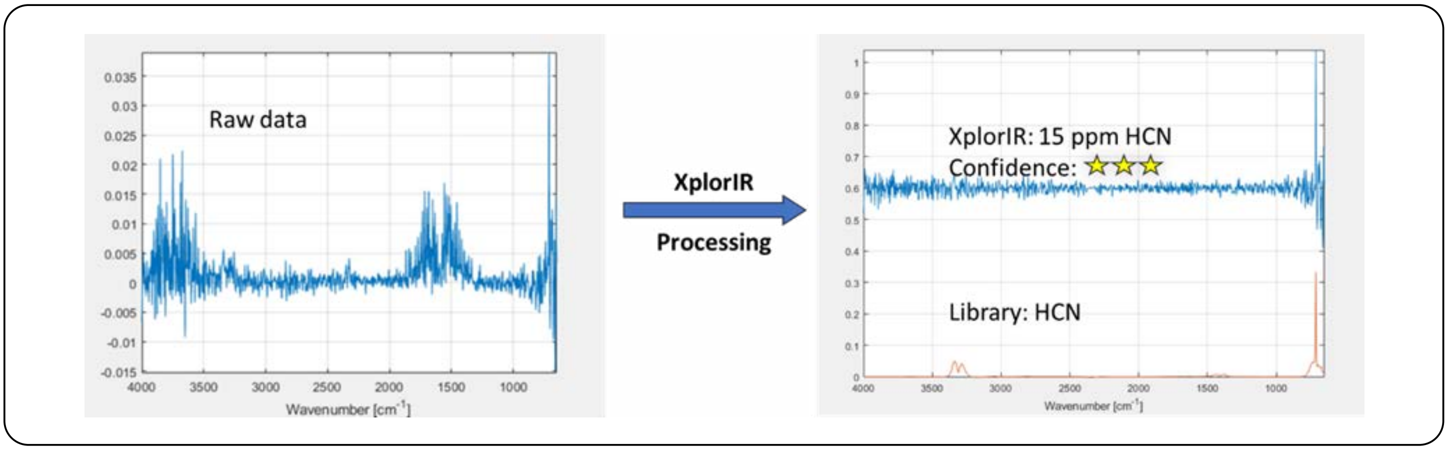

Figure 4 – Infrared absorbance spectrum of 15 ppm hydrogen cyanide processed with conventional processing (left) and new XplorIR processing (right) showing the advantage of Adaptive Atmospheric Correction.

Using a threshold of 0.8 and above for match confidence, the testing produced no false positives and only 10% false negatives. Compiling all of the data, limits of identification were estimated for the 8 gases tested and are shown in Table 1.

Sample	XplorIR LOI	IDLH	PEL (TWA)
Ammonia	**21**	300	50
Methane	**20**	2100	1000
Isobutylene	**31**		250
Sulfur Dioxide	**21**	100	5
Carbon Monoxide	**62**	1200	35
Nitrous Oxide	**6**		50
Toluene	**30**	500	200
R-134a	**~2**	40000	10000

Table 1: XplorIR Limit of Identification (LOI) calculated from laboratory testing compared to IDLH and PEL values of common gases.

Conclusion

FTIR provides emergency responders positive identification of unknown materials every day; Redwave's new Adaptive Atmospheric Correction used on the XplorIR now allows the same positive identification for unknown gases. For the first time, gases can be identified with a simple-to-use, lightweight, handheld instrument, allowing for accurate site characterization and increased community safety.

XPLORIR

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