APPLICATION NOTE

Breaking New Ground: Gas Mixture Analysis with XplorIR

The Problem

Mixed chemical products are a reality of everyday life for emergency responders. No matter if an unknown is a solid, liquid, or gas, pure chemicals are rarely encountered in the field. To that end, responders rely on chemical identification technology that can handle the messy product presentations and dirty environmental conditions they typically face. Most field-based chemical identifiers incorporate some level of mixture analysis and/or atmospheric compensation methods to address this problem. Though we don't purport to know the details of how other device manufacturers address mixtures in their software, methods utilizing legacy approaches certainly fall short of being reliable in the myriad situations encountered in the real world. RedWave Technology has developed a new approach for the XplorIR which looks at the problem from a different perspective. The underlying science and some exemplary results of this approach are the topic of this Technical Note.

Key Takeaways

Before delving into details of the XplorIR mixture analysis technique, we will summarize the salient points which make the RedWave Technology approach beneficial to emergency responders. Those points are:

- No user background collection is required as the process is automated
- The automated background adapts to changes in environmental conditions
- Continuous monitoring detects evolving products even during system clear out
- Numerous statistical metrics are used to determine which results are displayed
- Up to 6 mixture components† can be identified

That being noted, we will now explore the unique XplorIR mixture analysis algorithm and present some representative examples. For the studious reader, we will later delve into the fundamental science behind Fourier transform infrared (FTIR) spectroscopic mixture analysis and some of the important factors which must be considered.

Chemometrics at Work

It is common for device manufacturers to keep the proprietary details of their hardware and software very close to the vest. We will do the same here, but we will describe some characteristics of the XplorIR mixture analysis approach which make it unique. First, let's consider the background against which the device must be able to detect the chemical products of interest. When it comes to gasses and vapors in the atmosphere, a mixture is always present. Even a pure gas released into the environment is mixed with air, and fortunately for the XplorIR, the primary components of air (N_2, O_2, Ar) are invisible in the infrared. However, H_2O vapor and CO_2 are strong infrared absorbers and are also present at varying amounts. The traditional method of accounting for this is for the user to record a background prior to sampling. But when the background signal invariably changes over time, the resulting sample spectra are replete with uncompensated artifacts in the H_2O and CO_2 spectral regions. For this reason, the XplorIR uses a novel Adaptive Atmospheric Compensation (AAC) algorithm[1] to model the device response outside of the hotzone and then to refine the model when background conditions change. In short, the XplorIR treats ***every*** sample as a mixture with H_2O and CO_2 being ever-present. All of this is done behind the scenes without user intervention. And recent testing by RedWave Technology has shown that even abrupt changes in humidity (from 30% - 80% and vice-versa) have no impact on the quality of library matches generated by the XplorIR software.

In terms of library hits, many users are familiar with match quality scores normally ranging from 0 - 100%.

This is born out of a standard dot product correlation approach that simply compares a measured sample spectrum to a library spectrum and produces a Hit Quality Index (HQI) number. Anecdotally, most field users are comfortable with the notion that a 95% match is a “good hit.” The XplorIR software goes much deeper than that. In its Continuous Mode of operation, the XplorIR creates and validates a baseline model each time an analysis is started. Once this ~ 2-minute process is complete, the XplorIR starts measuring by looking for the appearance of spectral peaks above its baseline. But the software doesn’t just look for peaks. It continuously seeks out spectral features which are consistent with one or more library entries. If such features are detected, the device shuts off the gas cell to capture the product, and the algorithm records a few more scans for good measure.

With high-quality data in hand, the algorithm goes further by scaling the relevant spectral regions to maximize discrimination potential and then models the entire sample spectrum until a sufficient amount of the statistical variance within the sample spectrum is explained. Furthermore, the XplorIR assesses all the scores within a hit list of multiple components by giving each hit an estimated probability of significance before making a final decision. In the end, if one or more library entries have a statistically high probability of being present in the sample spectrum, the results are displayed with a “star rating” as listed in Table 1 to indicate match confidence.

Search Score Range	Star Rating Displayed
0.80 - 0.85	★★
0.85 - 0.90	★★★
0.90 - 0.95	★★★★
≥ 0.95	★★★★★

Table 1. Search score ranges and associated star ratings as generated by the XplorIR library search and mixture analysis algorithm.

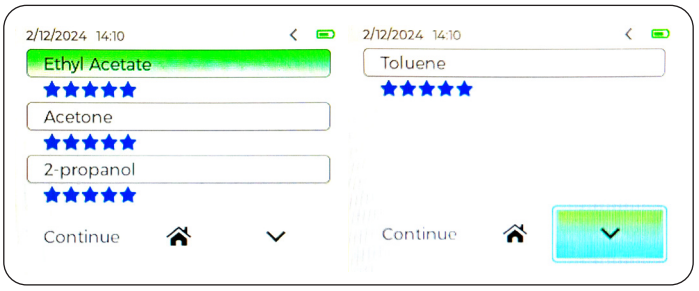

Figure 1. XplorIR result for a mixture of Ethyl Acetate, Acetone, 2-propanol, and Toluene.

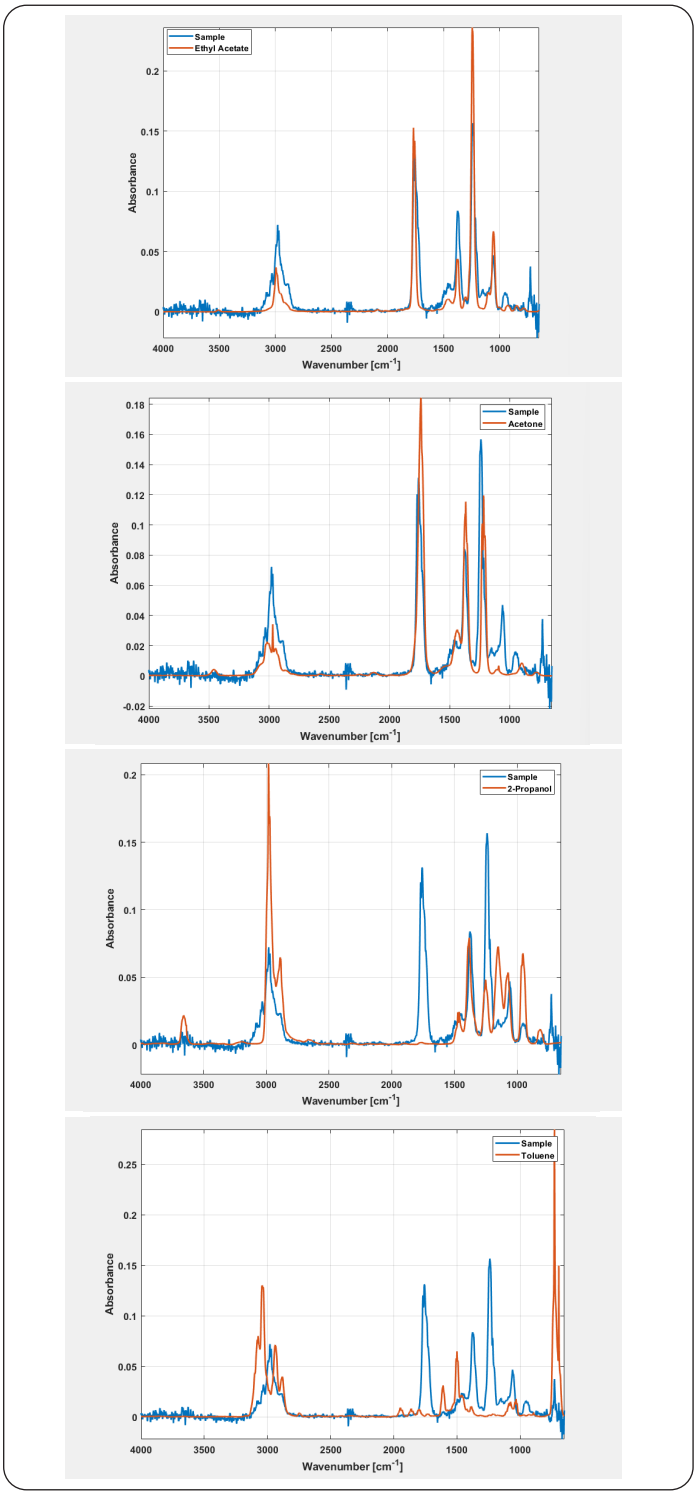

Figure 2. Measured spectral data and modeled spectral fit associated with the result in Figure 1.

For this discussion, we are focusing on gaseous mixtures as identified with the XplorIR. This is largely because such mixtures are easier to approach from a fundamental chemistry perspective. However, the underlying mathematics can be applied to condensed phase mixtures with some additional considerations, and they certainly will be deployed on other RedWave products including the ThreatID and ProtectIR. But for a deeper dive into the science, let's consider a chemical product containing a mixture of gaseous components.

Mixtures and Spectroscopy

Let's start at the first principles of infrared spectroscopy. For an FTIR spectrum, the measured absorbance (A) of a given chemical at a given wavenumber (cm^{-1}) is fundamentally expressed by ***Beer-Lambert Law*** as shown in Equation 1,

$$A = \varepsilon\, c\, b \quad (1)$$

where ε is molar absorptivity (how strongly the chemical absorbs infrared radiation), c is concentration, and b is the pathlength of the measurement (the distance over which the infrared radiation interacts with the sample). Molar absorptivity is a fundamental chemical property and is a function of wavenumber. Pathlength is fixed for a given device, and for the XplorIR it is 2 meters within a multipass sample cell volume of 35 mL. Concentration is where things start to get tricky. When two or more (or infinitely n) components are mixed within a sample, the measured absorbance (Amix) at a given wavenumber is the sum of the absorbances of each component weighted by their respective concentrations as shown in Equation 2,

$$A_{mix} = A_1 c1 + A_2 c_2 + \ldots An \quad (2)$$

where the molar absorptivities of the components and the pathlength are constant. Note here that the concentrations in Equation 2 are ***relative fractions*** in the mixture (ranging from 0 - 1). Simply put, the FTIR spectrum of a mixture can be mathematically modeled using the spectra of its constituent components. This principle lends itself to quantitation, but the focus here is on qualitative analysis of spectral data. Another important note is that Equation 2 assumes that the components in a mixture do not chemically react to form any new species. This is often the case of gaseous products, though any emergency responder can attest that some gasses can indeed be reactive in the field. Fortunately, that situation merely leads to the device needing to identify the new species as another mixture component. Math doesn't care about chemistry.

Mixtures in the Field

Equation 2 establishes that the spectrum of a mixture represents a weighted sum of the spectra of its constituents. But for a gaseous mixture, what components are present inside the gas cell when the measurement is taken? This brings us to the critical topic of ***vapor pressure***. In addition to molar absorptivity, this fundamental chemical property greatly influences how much of the sample spectrum will be attributed to each component. For a liquid mixture liberating vapors, the highest vapor pressure constituent will dominate the gaseous makeup of the target measurement regardless of the relative concentrations within the native liquid. Consider a simple 2-component mixture of 50% acetone and 50% m-xylene, both of which have relatively strong and distinct infrared spectral features. As shown in Figure 3, the temperature-dependent vapor pressures of these products are vastly different[2].

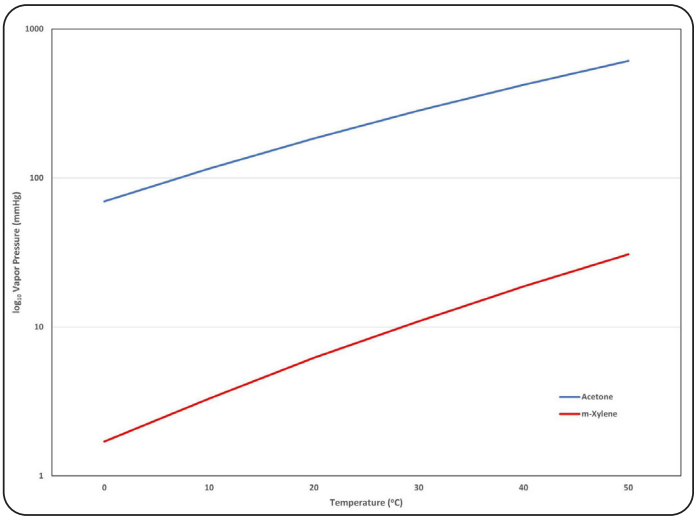

Figure 3. Vapor pressure as a function of temperature for two common chemicals.

On average, acetone has a vapor pressure that is 30× higher than that of *m*-xylene at all temperatures. Therefore, in an equal liquid mixture of these two products, the amount of acetone in the ***gaseous*** mix should be correspondingly higher as well. This would result in the FTIR spectrum being dominated by acetone peaks though both components would be identified by the XplorIR software. Just bear in mind that the result presented for a mixture on the XplorIR screen represents what is present in the gas cell and not necessarily everything in the condensed phase product.

But Wait, There's More...

At the risk of belaboring a point relative to mixtures and spectroscopy, we must further clarify the star ratings associated with the XplorIR library hits as listed in Table 1. The algorithm assigns a rating to each compound identified via the mixture search. The number of stars given to each match indicates the ***quality*** of each hit... but ***there is no correlation to spectral contribution or chemical composition***. We presented how multiple compounds mathematically contribute to a measured spectrum in Equation 2, and this information is used by the algorithm to model the sample data. But when you see a list of compounds on the XplorIR result screen, just know that all of those compounds are likely present within the device gas cell. How likely each one is present is based on the number of stars below its name. How much of each one is present is another topic altogether.

And finally, get this. If you are using the XplorIR and a gaseous product is identified, that's great. But the identification algorithm is unique in that it continuously looks for the presence of any new chemical species even after identifying one or more products. This is because in the field, responders can encounter situations where multiple gasses can be found within a complex environment depending on where the measurements are taken.

Again, nothing has to be done by the user. Once a background model is built in Continuous Mode, the XplorIR looks for the presence of any gasses or vapors it can identify the entire time it is sampling. With a nominal battery life of 6 hours, that is a lot of detection capability! Indeed, the XplorIR AAC, mixture analysis algorithm, and general monitoring approach represent significant advancements in field-based FTIR gas identification. This reflects the RedWave Technology mission of helping those who keep us all safe to do their jobs more efficiently and reliably than ever before.

REFERENCES:

1. *Infrared Gas Identification in Any Conditions: XplorIR's Adaptive Atmospheric Correction," RedWave Technology Technical Note (2023)*
2. https://www.ddbst.com/calculation.html, Vapor Pressure Calculation by the Antoine Equation (Accessed 29 January 2024)

† Limiting the display of 6 mixture components is related to what can be reasonably seen on the XplorIR screen. In principle, the mixture analysis approach can identify as many compounds as are in the library provided that the search confidence criteria of all components are met.

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