On-Scene Mixture Analysis with DecisionEngine™ MX

Introduction

Ahura Corporation, with the introduction of the ***First* Defender** handheld Raman material identification system, has taken spectroscopic software with embedded chemical intelligence to a new level. The operating characteristics (true and false-positive rates and search precision) of the built-in algorithms for pure material identification are unparalleled. In many practical situations users are confronted with materials that are mixtures of multiple materials. In the recently released FirstDefender software version 2.0—a free upgrade for previous versions—users will have access to the new DecisionEngine™ Mixture Extensions (MX). Recognizing that users are not always able to contact instrument manufacturers 24 hr support lines for spectral mixture analysis, and that there are a number of dangerous flaws in the traditional spectral subtraction approach, scientists at Ahura developed a reliable, rapid and fully automated alternative. This application brief gives an overview of the limitations of spectral subtraction for mixture resolution, and the new capabilities that DecisionEngine™ MX brings to the scene.

Mixtures and Spectral Subtraction

In most instances, the spectrum of a non-reacting mixture of two or more substances will be a simple sum of the spectra of the individual substances.[1] An example is shown in **Figure 1 a)**, where component A and B have been mixed, and the resulting spectrum of the mixture is the sum of the individual spectra. When mixtures are analyzed using traditional spectral library search methods, the 'hit quality index' (HQI, or similar score) of the *actual* components of the mixture will often indicate a very poor match, making it difficult for the user to confirm or refute the presence of a material in the mixture outright.

There have been two historic approaches to on-site resolution of mixtures using spectroscopic identification systems. The first was to incorporate certain mixtures of particular interest in the library prior to deployment, usually very common household products (*e.g.*, windex, cake mix) or sometimes mixtures indicative of specifically troublesome activities (*e.g.*, ephedrine and isopropyl alcohol). But since spectroscopy is quite sensitive to the proportions of the components of the mixture, the proportions of the unknown mixture would have to be extremely similar to the proportions used for the library spectrum for positive identification; that is, a library spectrum of 20% isopropyl alcohol and 80% methanol would almost certainly not match the spectrum of a mixture of 50% isopropyl alcohol and 50% methanol. To approximately cover any mixture of ephedrine and isopropyl alcohol, for example, upwards of 15-20 different library spectra covering the range of possible proportions would need to be created. To cover mixtures of 3 components with a similar degree of resolution would require 20x20x20 (8,000) library spectra, just for one specific triplet.

[1] In some cases of liquid mixtures, a phenomenon termed hydrogen bonding can lead to an exception to this statement.

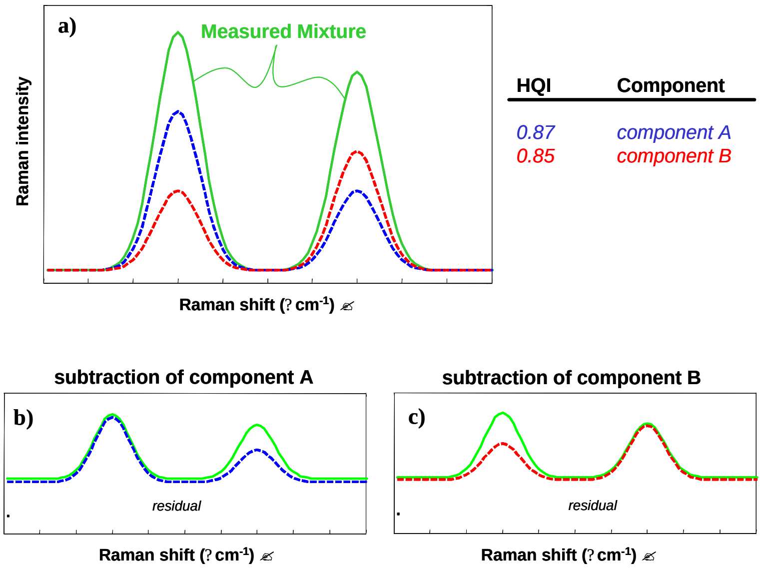

Figure 1. Illustration of a spectroscopic mixture. a) The spectrum of a mixture (green) is merely a sum of the individual component spectra (red and blue) weighted by the proportion of the material present. b) Attempt at spectral subtraction starting with component A to find the second component. c) Attempt at spectral subtraction starting with component B to find the second component.

Since this library-driven approach becomes impractical for all but the simplest of systems, system vendors have suggested that advanced users can perform a spectral subtraction procedure in software to aid in resolving mixtures. This approach is currently deployed for mixture analysis on a number of field-portable FTIR and Raman units. In short, it entails taking a measurement of the unknown mixture, subtracting the top library hit spectrum from the unknown, and re-searching on the portion of the unknown spectrum that remains after the subtraction.

Upon acquiring a spectrum of a suspected mixture, an advanced user can subtract the signature of one library hit from the mixture spectrum, and search the remaining (residual) spectrum against the library. If the correct amount of the initial library spectrum has been subtracted, what remains should be the spectrum of the remaining component (or components). The success of this approach depends on two critical factors: identification of one of the components of the mixture with which to start the subtraction, and subtraction of the correct amount of that component's library spectrum. Both of these requirements are difficult to fulfill.

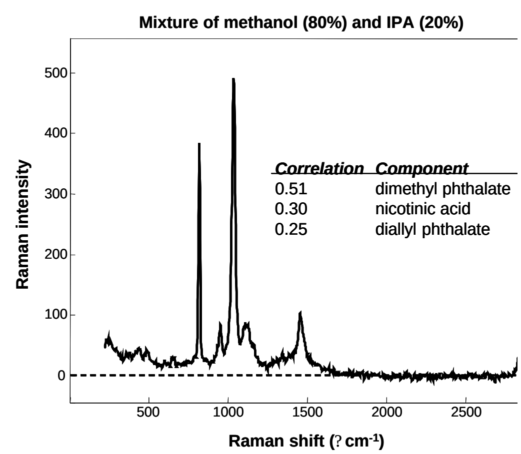

Figure 2. Raman spectrum of a mixture of methanol and 2-propanol (80/20 v/v%). Inset are the top ranking matches based on a traditional correlation search used in other spectroscopic ID systems.

Consider the second requirement for the simple case presented in **Figure 1 a)**. If we knew (or presumed) component A was in the mixture, how much of it should we subtract from the mixture? The usual recommendation is to subtract enough so that there are no negative features in the residual spectrum; the result of this is shown in **Figure 1 b)**. Clearly the residual spectrum will not match component B, the other component of the mixture. In **Figure 1 c)**, we've initially presumed component B is present and arrive at the same failure for component A. In fact, this sequential subtraction procedure only arrives at the correct solution in a very limited number of simple mixtures.

The other requirement, identification of one of the mixture components to start off the subtraction procedure, is also far from trivial in general use. Usually the software recommendation is to subtract the top hit from the initial library search, but there are a great many cases in which the top hit (or even top hits) is not a component of the mixture. One real example is shown in **Figure 2**. While the components of this organic mixture are actually methanol and isopropyl alcohol (IPA), the ranked top hits using a correlation search are:

1. *dimethyl phthalate*
2. *nicotinic acid*
3. *diallyl phthalate*

An especially diligent user may recognize that the mixture is unlikely to contain any of these three components, and refer the data to supporting staff, but the issue remains that the system procedures have failed to resolve the mixture on-site. Worse, the results might have misled the user into believing one or more of these top hits are components of the mixture, and the ensuing spectral subtraction could lead to a completely erroneous judgment.

Mixtures and DecisionEngine MX

DecisionEngine™ MX abandons the spectral subtraction procedure as a route to resolving mixtures. This is in part because of the critical flaws in the procedure discussed above, but also because of the demands on the user – in an emergency situation there are enough things to worry about. If, in the course of its analysis, the system can not establish a positive match for the observed material based on its spectral library of pure materials, it will automatically invoke the mixture extensions. These algorithms will attempt to find combinations of library materials (as many as five) that could account for the spectrum of the unknown material. This, in essence expands the system library exponentially, as illustrated in the following: There are approximately 2000 pure materials in the system library, this results in

1,999,000 *combinations of two materials*
1,331,334,000 *combinations of three materials*
664,668,499,500 *combinations of four materials*
265,335,665,000,400 *combinations of five materials*

These numbers are further multiplied because the system can solve for combinations of materials in any proportion. (In contrast, if one incorporates the spectrum of a mixture into the system library it is only characteristic of the mixture in that single proportion.)

In order to come to a reliable solution, the algorithms must not only determine *what* components may be present, but also *how much* of their spectrum is present, and *how well* the proposed solution accounts for the spectrum of the unknown material. If a plausible solution is found, the user will be presented with a blue screen titled "mixture", the proposed components, and the proportion of the unknown spectrum that can be accounted for.

Figure 3 a) shows the results screen when our methanol/IPA mixture is evaluated with the mixture extensions. The system has found strong evidence of a mixture of methanol and IPA. **Figure 3 b)** shows the proposed solution in terms of the spectroscopic evidence, and one can see that the system has very effectively 're-created' the measurement of the unknown by mixing methanol and IPA in the correct proportions.

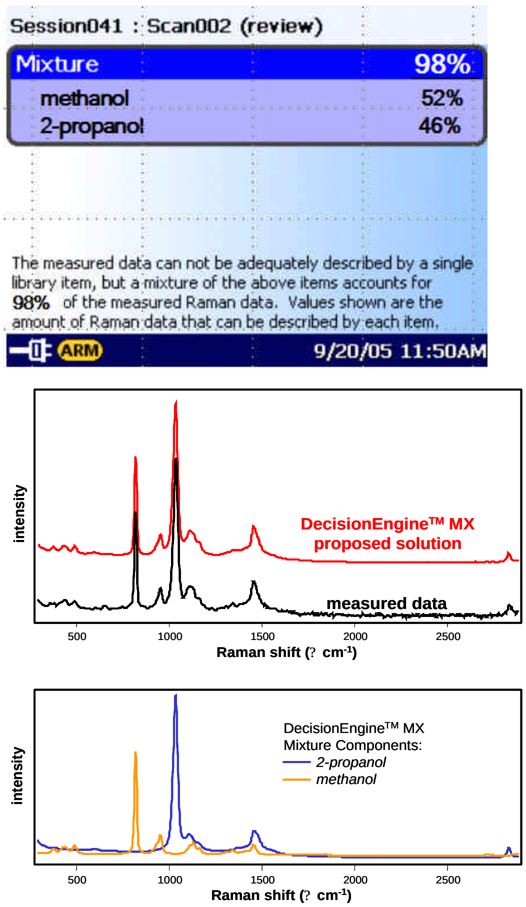

Figure 3. Top panel. Screen shot of the presented results if the system has found a plausible mixture solution. **Middle Panel.** Plot

Figure 4 shows another example of the DecisionEngine^{TM} MX at work. This was a measurement of over-the-counter Excedrin®, which contains acetaminophen, aspirin, and caffeine. Since the system could not find a positive library match for the tablet measurement, the mixture extension has proposed a mixture of acetaminophen, aspirin and caffeine as the likely composition.

We believe that with the release of DecisionEngine^{TM} MX, many complex mixtures will be resolved in real-time while on-scene, avoiding the complications and delays of extended support. But as always, if FirstDefender fails to resolve the identity of an unknown material Ahura Extended spectral analysis support is available 24/7/365.

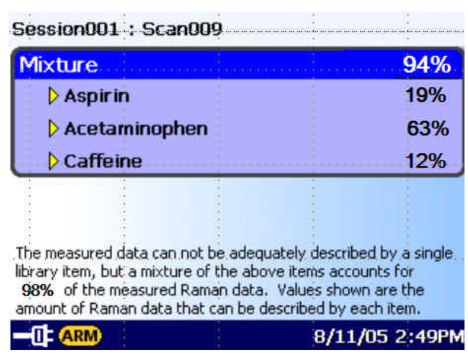

Figure 4. Mixture results for a measurement of an Excedrin tablet while it was still its commercial packaging.

Summary

The latest release of the FirstDefender embedded analysis software adds significant capabilities and speed enhancements to earlier versions. This application brief introduced our industry-first mixture extensions that enable the FirstDefender systems to automatically, and reliably resolve mixtures of multiple components without error-prone and time-consuming user intervention.

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