Mixture analysis in hand-held NIR instrumentation

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Introduction

Practical handheld instrumentation was first introduced for general use in 2005 by Polychromix.[1] Although applications for the handheld unit include classical PCA and PLS prediction models, the majority of commercial applications currently being used utilize a spectral matching model for pure material identification.[2] As we have explored potential uses for handheld NIR instrumentation over the last few years, it has become apparent that there are many applications not just for pure material identification, but also for determining the presence of multiple materials in mixtures. This need was the driving force for the development of a mixture analysis algorithm for the Polychromix handheld instrument.

Materials and methods

The computing platform used for this work was the Polychromix Micro-Phazir NIR analyzer (1000–1800 nm or 1600–2400 nm) running a 200 MHz ARM processor with a Linux OS (Figure 1).

Twenty different ternary mixtures of lactose, caffeine, and APAP were created in triplicate and each sample was measured 9 times resulting in over 500 sample spectra. Each sample was mixed by weight and then processed in a "ball mill" to maximize homogeneity. The concentrations were chosen to span various regions of the 3-dimensional concentration space.

Results and discussion

Analysis method

The mixture algorithm takes up to four passes through the library. Each pass modifies an initially "null" synthetic spectrum for a best match to the sample spectrum. The amount of the sample spectrum that is accounted for by a pass through the library is referred to as the "contribution". The contribution is analogous to the "hit quality index" or "HQI" used by other researchers[3,4] and may be determined by correlation, or Euclidian distance, as well as other proprietary algorithms. Analysis speed was enhanced through "smart" searching schemes combined with careful use and rearrangement of programmed equations to minimize processor load and maximize computational efficiency.

Figure 1. Micro-Phazir Analyzer (2.75 lbs, waterproof, self referencing).

Analysis Speed

A test library of 2681 spectra was created from the Polychromix Pharmaceutical data base. Combined scan and analysis times for this large library ranged from 3.1 to 11.8 seconds, depending on sample. For the narcotics library which contains 80 materials (drugs and cutting agents) and less than 500 spectra, the combined scan and analysis times are less than 3 seconds.

Analysis accuracy

The 500 ternary mixture sample spectra were processed using a mixture analysis library containing only the spectra of the three pure materials.

After noting a trend in the differences between the concentrations by weight and "contribution" predictions, the pure powder samples were inspected with optical microscopy and their powder densities were measured. Volume fractions were determined by combining the relative powder density measurements with known weight percent. The mixture set volume fractions are plotted in Figure 2 (large circles) along with the mixture algorithm "contribution" results (small circles).

The *RMSEP*'s for caffeine, lactose, and APAP are .052, .052, and .054 (vol-fraction) respectively.

Interference from other library components

The library of the three pure components was added to the Polychromix spectral library of narcotics and cutting agents, increasing the number of materials from 3 to 80 and the number of library spectra from 27 to 450. The ternary mixture samples were re-analyzed to test for

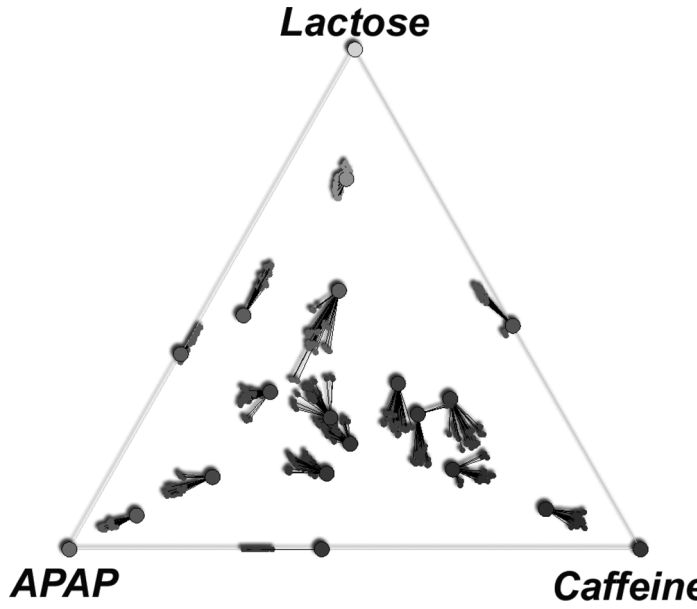

Figure 2. Ternary plot of APAP, Caffeine, and Lactose sample set. (Large circles: actual volume percents, Small Circles: mixture analysis predictions).

interference from other narcotics library compounds. Only one ternary mix (vol. Caffeine:11%, lactose:74, APAP:15) out of 540 sample scans resulted in a false negative for APAP. There were a number of false positives for materials in the narcotics library not in the ternary mix. However, none of these were identified in concentrations greater than 2% by volume. Figure 3 shows the

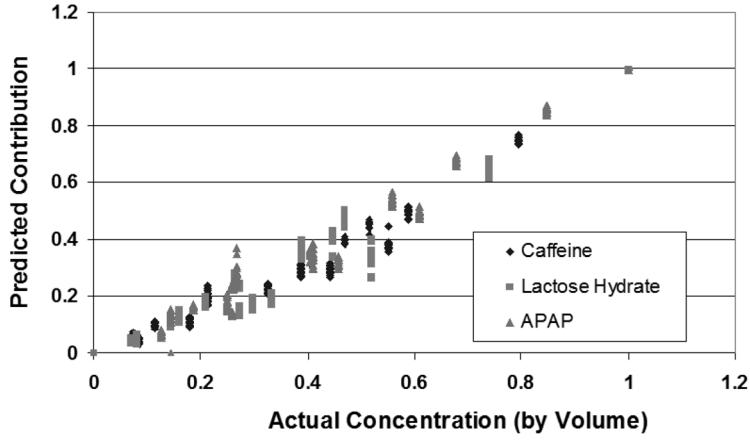

Figure 3. Predicted "contribution" vs actual concentration by volume after searching the narcotics library containing 80 compounds and over 400 spectra.

Table 1. Street narcotics test results from the National Forensic Technologies Center of Excellence.

Sample #	Sample	Methodology	Phazir Result	Identified	Comments
46	Cocaine	GC/MS	High/Cocaine Base	YES	
43	Cocaine	GC/MS	High/Cocaine Base	YES	
11	Cocaine	GC/MS	High/Cocaine Base	YES	
927	Cocaine HCL	IR	High/Cocaine HCL	YES	
930	BZP	GC/MS	Unknown Material	NO	Not in Library
940	Cocaine Base	IR	High/Cocaine Base	YES	
40	Heroin	GC/MS	High/Heroin	YES	
8	Fake Crack	?	Unknown Material	NO	Not in Library
31	Heroin	GC/MS	High/Heroin	YES	
950	Hydrocodone/ APAP	GC/MS	High/APAP	YES/NO	Narcotic <5%
955	Oxycodone in bag	GC/MS	High Polyethylene, Med Lactose Hyd, Low Oxycodone	YES	
960	Xanax	GC/MS	High Lactose Hydrate	YES/NO	Not in Library
965	Clonazepam	GC/MS	High Lactose Hydrate/Low Borax	YES/NO	Narcotic <5%
966	Morphine in bag	GC/MS	High Polyethylene, Med Lactose Hyd, Low Morphine	YES	
970	Propoxyphene/ APAP	GC/MS	High APAP	YES/NO	Narcotic <5%
975	Hydrocodone/ APAP	GC/MS	High APAP	YES/NO	Narcotic <5%
977	Hydrocodone/ APAP	GC/MS	High APAP	YES/NO	Narcotic <5%
33	Heroin/Caffeine	GC/MS	High Heroin	YES	
15	Cocaine	GC/MS	High Cocaine Base	YES	
45	Cocaine	GC/MS	High Cocaine HCL	YES	

Tests by FTCoE at Manatee's Office Forensic Laboratory (Adjudicated Case Samples) using the Polychromic Phazir, Sept. 2009.

predicted ternary mix fractions versus actual volume fractions as determined using the narcotics mixture library.

Threshold and range usage

Mixture analysis in the field presents many uncontrolled conditions. Unknown sample materials often contain compounds not in the library. Sample morphology and moisture levels may be greatly different from library samples. The mixture algorithm will do the best it can to find matches from the library, even if the sample contains nothing at all from the library. For this reason, after each pass through the library, identified materials below preset contribution thresholds are excluded. An additional threshold is used to reject all identification if the sum total contribution is too low.

It has been found useful to classify identified materials into High, Medium, and Low Range categories since the contribution values can be influenced by a wide variety of sample conditions and make up. Thresholds are also used to define the limits for these ranges.

From initial testing, it has been found that ideal libraries contain good quality pure scans of the materials likely to be present in a given application field (like narcotics) and exclude unnecessary items or low probability materials. Having too many materials in a library will increase the chance for false positives, while too few materials may lead to missed identifications. Even with the ideal library, there is also a trade off in setting thresholds. By increasing or decreasing threshold values, the likelihood of false negatives and false positives can be reduced at the expense of the other. The Polychromix library creation tool uses a default set of thresholds but allows the user to adjust them depending on performance preferences.

Results from the field

Over the last six months the Polychromix narcotics mixture analysis library has been trial tested in several locations. Except for instances where certain drugs were not present in the library, or when concentrations were below 5%, identification of narcotics in street samples has been extremely successful. Table 1 is a chart of testing performed by the National Forensic Technologies Center of Excellence on street narcotic samples from the Manatee County Sheriff's Office Forensic Lab's in Florida.

The Phazir has also recently been tested and successfully qualified at two other institutions including the U.S. Federal Law Enforcement Training Center in Brunswick, Georgia.

Summary

A mixture analysis algorithm has been developed for handheld NIR instrumentation. While it is well known that NIR does not have the specificity and narrow peak features of mid infrared and Raman spectroscopy, this work has demonstrated that with a properly constructed library, pre-processing, and search algorithm, very accurate mix analysis can be reliably carried out. A large advantage of handheld NIR mixture analysis over other instrumentation is the lack of need for sample preparation, ease of sample presentation, no anomalies due to sample florescence (Raman), no danger of sample ignition (Raman) and very high speed analysis (< 3 seconds typical).

References

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