Kirk M. Grates[1] BA, *Senior Forensic Specialist – Chemistry*, Joan Ring[1] MS, *Chemistry Technical Services Manager*

Objective

In today's post-9/11 environment, it has become increasingly important for first responders to have the tools necessary to probe unknown bulk materials for the presence of explosives, controlled substances and other hazardous materials while in the field.

Field-portable near-infrared (NIR) spectrometers have been well established and proven successful in material identification for various industrial applications, including pharmaceutical manufacturing, polymer recycling, agriculture, environmental monitoring and petrochemical production. However, it was unknown whether such a handheld device would be suitable for the rapid identification of forensically relevant materials like controlled substances and explosives.

To investigate this potential, a performance evaluation was conducted on the handheld microPHAZIR™ NIR spectral analyzer manufactured by Polychromix, Inc.* The evaluation objectives were as follows:

- Build a single chemometric model for controlled substances, cutting agents, non-controlled (over-the-counter) substances and explosives.

- Objectively assess and determine the relevance of the microPHAZIR™ analyzer for the analysis and identification of the aforementioned substances and explosives.

- Perform experiments to determine conformity, specificity, sensitivity, portability, reproducibility and the effects of environmental factors on performance.

- Provide user feedback to the forensic community, law enforcement and defense agencies as well as to the manufacturer regarding assessment findings.

* Since the time of this evaluation, Polychromix has become a division of Thermo Scientific. The microPHAZIR™ is currently manufactured with an RX model for pharmaceuticals, a PC model for plastics and an AS model for asbestos.

Introduction

The microPHAZIR™ is a handheld NIR-based spectrometer that has a semi-rugged, ergonomic and lightweight design. This instrument uses a safe Tungsten lamp as the excitation incident light source, which is focused onto the unknown sample after the microPHAZIR™ trigger has been activated by the user.

When the sample is exposed to the electromagnetic radiation emitted from the light source, that radiation is reflected, absorbed and/or transmitted. The interaction between this harmless radiation and the compound(s) contained within the sample causes molecular excitation as well as vibrational energy changes. These vibrational changes cause functional groups, especially O-H, C-H, C-O, C=O, C=C, S-H and N-H if they are present within the sample compound(s), to stretch and bend.

During the analysis, the instrument collects digitized data of the corresponding overtones and combinations of vibrations that result in a spectra or unique chemical "fingerprint" of the material. This is graphically represented by plotting the spectral reflectance versus the wavelength. The microPHAZIR™ model used in the evaluation was capable of scanning a wavelength range from 1600 to 2400 nm with an optical resolution of 11 nm.

Materials

- Controlled substance standards (58)
- Common over-the-counter medication standards (6)
- Common cutting agent standards (8)
- Explosive standards (5)
- Controlled substance training samples (9)
- Adjudicated forensic case samples (20)
- 20-mL scintillation vials with caps
- microPHAZIR™ NIR handheld chemical analyzer
- PC interface cable
- microPHAZIR™ Method Generator (MG) model-building software

Methods

To properly assess the application of the portable microPHAZIR™ NIR analyzer for use in controlled substance and explosive identification, experiments were specifically designed to test the analyzer's performance in traditional and non-traditional laboratories as well as a field-type environment. To accomplish these goals and maintain scientific objectivity, the evaluation was divided into the following parts:

Part I

In order to develop a chemometrics model for the classification/identification of controlled substances, cutting agents, non-controlled (over-the-counter) substances and explosives:

- Reference samples were placed into appropriately labeled 20-mL disposable scintillation vials and capped.

- The reference samples of pure controlled substances, cutting agents, and non-controlled substances were analyzed as reference spectra.

- A background reference was automatically taken as needed using the white reference standard positioned within the instrument.

- A minimum of five spectra were collected for each reference standard.

- During the evaluator's training session, the microPHAZIR™ MG software and the previously ascertained spectra were used to build a chemometrics drug model with minimal assistance from a Polychromix representative during training.

Note 1: When a chemometrics model is constructed properly, it will account for most of the molecular variability occurring within the collection of reference spectra for each of the compounds of interest, thus statistically reducing the occurrence of unknown sample misidentification errors.

Note 2: Due to the limited amount of explosive standards, the manufacturer's explosive model was used during the assessment instead of developing a new one for explosive identification. The Polychromix mathematically enhanced narcotics model was also evaluated.

Part II

In order to determine conformity, specificity, sensitivity, portability, reproducibility and environmental effects:

- Test samples consisting of pure analytes as well as mixtures with ratios ranging from 80:20 to 5:95 of analyte of interest to diluent were used. Training samples consisting of forensic street samples obtained from various police agencies were also used to assess specificity. All samples were placed into appropriately labeled 20-mL scintillation vials and capped.

- Conformity, specificity, sensitivity, portability, reproducibility and environmental effects were assessed by analyzing test samples in triplicate*.

* Portability and environmental effects test samples were analyzed in duplicate only.

Part III

The PHAZIR analyzer was tested on 20 real case samples as follows:

- The instrument was transported to the Manatee County Sheriff's Office Forensic Chemistry Laboratory.

- Recently adjudicated forensic drug case samples were transferred to appropriately labeled 20-mL scintillation vials, capped and then analyzed in triplicate.

- The forensic laboratory sample number, laboratory results, lab methodology used for identification and the microPHAZIR™ results were recorded for all 20 samples.

microPHAZIR™ NIR spectral analyzer manufactured by Polychromix, Inc.

Results and Discussion

Conformity: With the appropriate chemometric model selected for identification during the conformity portion of the evaluation, the microPHAZIR™ was able to accurately identify all 19 pure standard samples containing either a controlled substance, cutting agent or explosive with a "High" confidence level in 57 of 57 trials (100%).

Specificity: The microPHAZIR™ was able to accurately identify the analyte of interest in 18 of 27 samples composed of a controlled substance training sample (multiple component), controlled substance standard, cutting agent, over-the-counter medication or explosive with a "High" confidence level. Of the 138 trials conducted, 91 trials or 66% identified the analyte of interest; the secondary analyte(s) was identified in 25.4% of the remaining trials, followed by 4.4% as "Unknown material" and 4.4% sample misidentification.

Determination for Limit of Detection for Commonly Abused Illicit Drugs Cut with a Caffeine Diluent

Sensitivity: Using a "Med." confidence level as the cut-off, the sensitivity of the microPHAZIR™ was determined to be at a concentration range from 20 to 30% for heroin, 10 to 20% for methamphetamine, and 30 to 40% for both cocaine base and cocaine HCl.

Portability: The mobile laboratory environment had no noticeable effects on the functionality of microPHAZIR™ during testing.

Reproducibility: The NIR device performed extremely well during the Inter-day and Intra-day Reproducibility Studies using the 50:50 ratio sample of cocaine HCl to caffeine, which was analyzed each day in triplicate over the ten-day period. Results showed a "High" confidence for both cocaine HCl and caffeine in all replicates except for Days 3, 4, and 6, which had a "Med." confidence level for caffeine.

Environmental Effects: This portion of the study indicated that there is no statistical difference between the results of the sample set run in a laboratory at a temperature of 25.1°C (47% humidity) and the results obtained outside at 27.9°C (64% humidity).

Summary

microPHAZIR™ NIR Evaluation Data Summary

microPHAZIR™ NIR Performance Summary

Note: Chart percentages were calculated out of 433 total trials.

Conclusions

Analysis of portable spectroscopy tools is critical to the advancement of forensic science, homeland security efforts and military operations. These types of devices hold the promise of empowering first responders with crucial forensic intelligence to make quick, actionable, on-site decisions to preserve public safety.

Strengths

- The microPHAZIR™ NIR analyzer was noted to provide the user with extremely quick, reliable results within 8–10 seconds after trigger initiation. Most other portable spectroscopy-based devices using Fourier transform infrared (FTIR) or Raman technology take 2 minutes or more to accomplish this.

- Samples containing mixtures of multiple components can be easily deconvoluted from one another and identified, provided the individual components make up at least 25–30% of the mixture and the sample is homogenous in nature.

- The instrument uses a non-destructive, point-and-shoot analysis technique that requires no sample preparation.

- Analysis can be performed through the original or primary container (polyethylene bags, amber or glass bottles) just like most portable Raman based instruments. *Note: Container thickness can be a factor.*

- This device can be used to identify powders, solids, and liquids.

- A very minimal amount of training is required to operate this instrument. The user need only know which chemometric model to select, be able to place the analyzer in direct contact with the sample, squeeze the trigger, and remain relatively motionless for ten seconds.

- The analyzer possesses a built-in internal white reference for background correction measurements; these are automatically performed by the unit when required.

- Adding a compound to an existing chemometrics model was fast and accomplished using an easy two-step process. The user must first "collect" spectra of the reference material using the analyzer, then upload those spectra into the user-friendly microPHAZIR™ MG model-building software. Most commercially available NIR analyzers on the market require the use of complicated chemometrics model-building software (e.g., Grams AI software) as well as the knowledge and experience of a spectroscopist.

- Fluorescent or dark-colored compounds are not a problem for NIR spectroscopy as they are for other spectroscopy-based technologies such as Raman.

Areas for Improvement

- Any slight movement of the microPHAZIR™ during analysis can be problematic and produce an inaccurate result (false negative or false positive). During sample analysis, the unit should have the capability to determine and prompt the user of any discrepancies regarding varying signal strength as a result of disruptive movements that have occurred during collection.

- The unit needs to be more rugged to meet military 810 F specifications for harsher field environments. Per the manufacturer, the unit is only dust- and splash-resistant.

- The device's current design resembles a gun-style type of handheld analyzer, where the majority of the instrument's weight is on the top of the grip handle holding the rechargeable battery. A more compact design capable of fitting into the user's entire hand or into the cargo pocket of their tactical wear would be more suitable for field applications and transport.

- Customizable sample entry information fields should be made available to the user for quicker text entry than those currently provided via the navigation keys.

Limitations of Technology

- Some NIR spectroscopy devices require a thorough understanding of complex chemometric software and statistics to build model(s) that meet specific needs and cutoffs for the detection and identification of compounds of interest. Although the microPHAZIR™ does not require expertise in spectroscopy to develop a model for use, users may find advanced knowledge of spectroscopy required for model optimization and verification.

- Mixtures can be problematic if the major component(s) are fillers, binders, diluents, excipients, APAP, etc., and the compound(s) of interest are minor component(s) at low concentrations. For example, the NIR analysis of a crushed 2.0 mg Xanax® would most likely not be able to identify the benzodiazepine alprazolam, a Schedule IV drug, present within the tablet. Only the fillers, binders, diluents, and/or excipients may be seen. A crushed 5 mg oxycodone/500 mg APAP tablet would also present some difficulty. The NIR would identify as having a "High" confidence level only for the APAP and maybe a few binders or fillers, but not the Schedule II drug oxycodone.

- NIR spectroscopy has limited specificity compared to other spectroscopy-based technologies due to its narrow scan range.

The microPHAZIR™ NIR analyzer was noted to provide the user with extremely quick, reliable results within 8–10 seconds after trigger initiation.

Portable spectroscopy tools hold the promise of empowering first responders with crucial forensic intelligence to make quick, actionable, on-site decisions to preserve public safety.