SAND2014-16252C

# Laboratory and Field Testing of Commercially Available Detectors for the Identification of Chemicals of Interest in the Nuclear Fuel Cycle for the Detection of Undeclared Activities

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## ABSTRACT

Traditionally, IAEA inspectors have focused on the detection of nuclear indicators as part of infield inspection activities. The ability to rapidly detect and identify chemical as well as nuclear signatures can increase the ability of IAEA inspectors to detect undeclared activities at a site. Identification of chemical indicators has been limited to relatively low-tech methods during inspections such as visual observation of chemical container labels and chance detection of odors or post-inspection analysis of environmental samples for actinide elements. Although IAEA analytical laboratories are highly effective, environmental sample processing does not allow for immediate or real-time results to an IAEA inspector at a facility. During Complementary Access under the Additional Protocol, the use of fieldable technologies to quickly provide accurate information on chemicals that may be indicative of undeclared activities can increase the ability of IAEA to effectively and efficiently complete their mission.

The Complementary Access Working Group (CAWG) is a multi-laboratory team with members from Brookhaven National Laboratory, Idaho National Laboratory, Los Alamos National Laboratory, and Sandia National Laboratory. The team identified chemicals at each stage of the nuclear fuel cycle that may provide IAEA inspectors with indications that proliferation activities may be occurring. The group eliminated all indicators related to equipment, technology and training, to obtain a list of by-products/effluents, non-nuclear materials, nuclear materials, and other signatures and observables (S&Os). These proliferation indicators were prioritized based on detectability from a conduct of operations (CONOPS) perspective of CA (for example, whether an inspector actually can access the S&O or whether it is in process with no physical access), and the IAEA's interest in the detection technology in conjunction with radiation detectors. The list was consolidated to general categories (nuclear materials from a chemical detection technique, inorganic chemicals, organic chemicals, halogens, and miscellaneous materials). The team then identified commercial off the shelf (COTS) chemical detectors that may detect the chemicals of interest.

Three chemical detectors were selected and tested in laboratory and in field operations settings at Idaho National Laboratory. The instruments selected were: Thermo Scientific TruDefender FT (FTIR), Thermo Scientific FirstDefender RM (Raman), and Bruker Tracer III SD (XRF). Functional specifications, operability, and chemical detectability, selectivity, and limits of detection were determined. Results from the laboratory and field tests are presented in this document.

## INTRODUCTION/BACKGROUND

The International Atomic Energy Agency (IAEA) is responsible for monitoring Member States (180 States) and partners worldwide to promote safe, secure and peaceful nuclear technologies. Traditional safeguards are used to verify nuclear material and nuclear material activities performed at facilities and locations that Member States declare through the safeguards programs.

Complementary Access is part of the Additional Protocol that was endorsed by IAEA Board of Governors in 1992 (approved in 1997). The intent of Complementary Access is to provide IAEA an additional tool to draw safeguards conclusions about the diversion of declared nuclear materials and the absence of undeclared nuclear material and activities in the States (119 States have Additional Protocol) as well as the decommissioned status of facilities. “Additional protocols require States to provide access to any place on a nuclear site and to other locations wherever nuclear material is, or may be, present. States are required to provide access to all locations that are, or could be, engaged in activities related to the nuclear fuel cycle and in cases where such access may not be possible to make every reasonable effort to satisfy IAEA requirements without delay through other means” [1]. Inspections are used to verify States’ nuclear material accounting reports, and design information verification is used to ensure that facilities operate in the manner declared by the State. The IAEA would like to consider the use of in-field chemical detection during Complementary Access. The commercial off the shelf equipment described and tested would provide chemical detection of possible proliferation indicators as described within this document.

The Complementary Access Working Group (CAWG) is a multi-laboratory team with members from Brookhaven National Laboratory, Idaho National Laboratory, Los Alamos National Laboratory, and Sandia National Laboratory. The team was brought together in response to a call for proposals from the Next Generation Safeguards Initiative, National Nuclear Security Administration. The team was tasked with identifying indicators at each stage of the nuclear fuel cycle that would provide IAEA inspectors with indications that proliferation activities may be occurring. The group eliminated all indicators related to equipment, technology and training, to obtain a list of by-products/effluents, non-nuclear materials, nuclear materials, and other observables. These proliferation indicators were prioritized based on detectability from a conduct of operations (CONOPS) perspective of a CA inspection (for example, whether an inspector actually can access the indicator or whether it is in process with no physical access whether the indicator is detectable with tools in the current CA toolkit, particularly the HM-5 (FLIR IdentiFinder) gamma ray detector/identifier. After selecting indicators that were not detected and identified by the current CA tool kit, the team found that most were chemical indicators. The list was consolidated and organized by general categories (nuclear materials from a chemical detection techniques, inorganic chemicals, organic chemicals, halogens, and miscellaneous materials.

The team then identified commercial off the shelf (COTS) chemical detectors that may detect the chemicals of interest. An ideal detector is one that can detect chemical signatures selectively within an acceptable time; sensitive enough to detect concentrations at or below levels which the proliferation indicators are expected to be found, not affected by other factors in the environment, rapid reaction and recovery times and yet be portable, easy to operate and produce data that is easily interpreted. Many of the commercially available detectors use technologies that are adapted from classical analytical chemistry techniques. An open source literature review was performed to evaluate instrumentation based on x-ray fluorescence (XRF), infra-red (IR) spectroscopy, Raman spectroscopy, gas chromatography (GC), high pressure liquid chromatography (HPLC), nuclear magnetic resonance (NMR), laser induced breakdown spectroscopy (LIBS), mass spectroscopy (MS), ion mobility spectroscopy (IMS), colorimetric and electromechanical detection. Three chemical detectors were selected based on the ability to detect the chemicals of interest and the cost and maturity of the instrumentation. These instruments: Thermo Scientific TruDefender FT (FTIR), Thermo Scientific FirstDefender RM (Raman), and Bruker Tracer III SD (XRF), were tested both in laboratory and in field operations settings at Idaho National Laboratory. Functional specifications, operability, chemical detectability, selectivity, and limits of detection were determined.

## INSTRUMENT DESCRIPTIONS

**Thermo Scientific TruDefender FT (FTIR):** In infrared (IR) spectroscopy, IR radiation is passed through a sample and some of this radiation is absorbed while some is transmitted. The result is the production of a spectrum which represents the molecular absorption or transmission, creating a unique molecular fingerprint of the sample. Infrared instruments measure the amount of light absorbed at a specific wavelength to look for a characteristic chemical group, such as the phosphate group in organic phosphates. The intensity of this IR absorption is proportional to the concentration of the targeted chemical. Fourier transform infra-red (FTIR) spectrometers simultaneously collect spectral data in a wide spectral range, the spectra are combined into one spectrum resulting in a lower detection limit than if one spectrum were collected. This detector requires the substance of interest to be placed in the crusher (powders) or on the diamond sensor (liquids). The detector cannot identify chemicals through a container. FTIR is a good detector for non-water liquids; however, water may confuse the signal. It cannot see metals, elements, or ionic compounds, and ionic acids in water. It is a good detector for simple oils and fuels and complex anions in ionic compounds. It is also unaffected by colored solutions.

**Thermo Scientific FirstDefender RM (Raman):** In Raman spectroscopy, a sample is illuminated with a monochromatic laser light and the scattered light is then detected as a function of wavelength. The scattered light results from both elastic collisions, known as Rayleigh scatter, of the photons with the sample molecules and inelastic collisions, known as Raman scatter. Raman spectroscopy uses the molecular light scattering phenomena to selectively detect the presence of chemicals by way of spectral fingerprinting. A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation and is usually expressed in units of wavenumbers ($cm^{-1}$). The detector can be used to look through closed transparent containers, either by placing a small vial in the interior chamber of the instrument or holding the instrument sampling tip to the container. Raman may generate heat in darker samples and one must be extremely careful analyzing unknowns that may be ignitable or explosive in nature. Raman cannot see metals, elements, ionic compounds, or purely ionic acids in water. However, it is good for looking at complex anions in ionic compounds, and chemicals in water solutions. Raman cannot see water solutions and may be blinded by heat or dark colors which tend to fluoresce.

**Bruker Tracer III SD (XRF)**: X-Ray fluorescence is an analytical method used for solids and powders. In XRF, x-rays are produced by an x-ray tube or radioactive source to irradiate the sample. The elements present in the sample will emit fluorescent X-ray radiation with discrete energies that are characteristic of these elements. X-rays from the analyzer bombard the atoms of the target sample. Some of the generated photons collide with K (and L) shell electrons of the sample, dislodging them from their orbits, leaving a vacant space in the shell which is immediately filled by any electron from the L, M, or N shell. This is accompanied by a decrease in the atom's energy, and an x-ray photon is emitted with energy equal to this decrease. Since the energy change is uniquely defined for atoms of a given element, it is possible to predict definite frequencies for the emitted x-rays. The x-rays are analyzed and the quantity of K shell and/or L shell x-rays detected will be proportional to the number of atoms of the particular element or elements present in the sample. Although the XRF can see through containers, the container makeup will appear within the spectrum, sometimes overshadowing the signal from the sample within the container. Mylar can be used to prepare samples to decrease container background signals; however, the best results are obtained when a metal is placed directly on the analyzer.

## EXPERIMENTAL SECTION

**Laboratory Testing:** The instruments were tested in an analytical laboratory prior to field testing. The functional specifications were evaluated for each of the three instruments as defined in Table 1. Each sample of interest was analyzed in neat form. If the sample was already in the vendor-provided instrument library and a positive detection was made, the sample was analyzed ten times to ensure statistical performance of the instrument. If the instrument library did not contain the sample of interest, it was added to the library if the chemical showed that there was a sufficient signal for the instrument and the library addition time was less than one hour. Once the sample spectral information was added to the library, the sample was analyzed ten times by removing from the instrument and resetting with FTIR and Raman to ensure statistical performance of the instrument. The x-ray system is set to the number of analyses to perform and therefore the sample is not repositioned. The instrument sampling conditions are listed below for each instrument.

- **Raman:** All samples were placed in clear glass vials and inserted directly into the internal sample vial holder. Samples were not analyzed external to the instrument.
- **FTIR:** All liquids were pipetted directly onto the diamond detector crystal. If the sample has a high vapor pressure and will evaporate during the analysis, it needs to be continually replenished during analysis. The other option is to put the liquid in the crusher and provide enough liquid that the sample did not evaporate during analysis. All powders were placed in the crusher and analyzed.

- **XRF:** All samples were analyzed in “lab rat” mode, which is a screening mode that allows for 1-40 keV x-ray energies to reach the sample, thereby exciting all the elements from magnesium to plutonium, although not optimally. This mode is not ideal for trace elements. In “lab rat” mode, no filter is used, voltage is set to 40 KeV, amperage is set to 35 µamps for non-metallic samples or 9 µamps for metallic samples, and the vacuum is used and should be less than 15 Torr. To optimize for particular elemental groups, you would need to use filters and settings that “position” the x-ray energy impacting the sample just above the absorption edges of the element(s) of interest.

**Lower Limits of Detection**: Once the chemical spectra were added to the library in the neat (pure, undiluted) chemical form, dilutions were made of chemicals that are normally found as mixtures within the fuel cycle Each of these sample dilutions were analyzed a minimum of five times (same sample with repositioning between analysis. If the instrument appeared to be inconsistently detecting chemicals, the samples were analyzed more than five times. No lower limits of detection were identified for the XRF due to the difficulty in identifying liquids. The mixtures were 50% of the organophosphorous (TBP) and 50% of the aliphatic hydrocarbon (hexone, dodecane, or kerosene). The TBP percentage was ½ of the previous amount, so the second dilution was 25% TBP/75% hydrocarbon, etc. The lowest dilution was 6.25%TBP/93.75% hydrocarbon.

**Detection of Chemical Spills:** An attempt to determine if the instrumentation could identify spills was performed during laboratory testing. Samples of ferrous sulfamate (both new and degraded) as well as a transuranic extraction (TRUEX) process mixture ((Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) mixed with TBP) sample were spilled onto petri dish surfaces and analyzed to determine if the spill components were identifiable. The ferrous sulfamate spills dried to form a hard crystalline substance with what appeared to be separation of the sulfamic acid from the ferrous compounds. The TBP/CMPO mixture remained as a liquid in the petri dish. The ferrous sulfamate spills were analyzed by all three instruments while the TRUEX spill was analyzed with the FTIR and Raman.

**Field Testing:** The instruments were tested in operating nuclear facilities once the chemicals of interest had been added to the libraries. The instruments were taken to the operating facilities and samples were taken of visible chemicals associated with the nuclear fuel cycle activity in that facility. For example, samples that would identify the facility as an electrorefiner were measured in the facility that houses the electrorefiner, materials associated with nuclear fuel fabrication were measured in the facilities where fuel fabrication occurs, and any chemicals associated with nuclear fuel support operations were measured in the analytical laboratory facilities. Samples were analyzed as they were found in the facility, which was generally in their neat form prior to process makeup. Most samples were analyzed while remaining in their existing bottles/containers at various process stages and in storage cabinets. Some sampling was done for spills as discussed below. Some point-and-shoot sampling was done at other areas inside of the facilities, such as floors or piping. Most samples were analyzed only once due to time constraints in each facility. Some samples were analyzed multiple times with the XRF. In most cases, the FTIR was not used since this particular instrument requires contact with the sample which does not appear to be acceptable in normal CONOPS. The instrument sampling conditions are listed below for each instrument.

- **Raman:** All samples were analyzed external to the instrument unless they were already present in sample vials that would fit into the integrated sample area on the instrument.
- **FTIR:** Liquid samples were pipetted directly onto the diamond detector crystal. Powder samples were placed in the crusher and analyzed. However, most samples were not analyzed because the facilities would not allow radioactive material containers to be opened.
- **XRF:** All samples were analyzed in "lab rat" mode. Liquid metallic dilutions were analyzed in their poly bottles directly on top of the instrument.

**Table 1: Functional specifications for the TruDefender, FirstDefender and Tracer III SD**

| Functional Specifications | Thermo Scientific TruDefender FT (FTIR) | Thermo Scientific FirstDefender RM (Raman) | Bruker Tracer III SD (XRF) |
|---|---|---|---|
| Proliferation Indicators | Limited to liquids and powders | Limited to liquids and powders | Metals, powders, can do liquids and gases but require additional sample preparation, limited to elements with atomic numbers ≥ 12 |
| Weight | 2.9 lbs (1.3 kg) | 1.8 lbs (816 g) | 4.49 lbs (2 kg) with batteries, 3.9 lbs (1.77 kg) base weight, |
| Size | 7.8" x 4.4" x 2.1" (19.8cm x 11.2 cm x 5.3 cm) | 7.6"x4.2"x1.75" (19.3 cm x 10.7 cm x 4.4 cm) | 30 cm (L) x 10 cm (W) x 28 cm (H) |
| Spectral Range | 650 $cm^{-1}$ to 4000 $cm^{-1}$ | 250 $cm^{-1}$ to 2875 $cm^{-1}$ | |
| Spectral Resolution | 4 $cm^{-1}$ | 7 to 10.5 $cm^{-1}$ (FWHM) across range | Elements with atomic numbers ≥ 12, typical resolution 145 eV at 100,000 cps |
| Collection Optics | ATR Diamond Crystal | NA=0.23. 17mm working distance; 0.14 to 1.8 mm spot size | NA |
| Data Export Formats | SPC file, text file or JPEG | .jpg, .spc, .txt, .arb | S1 PXRF and Artax |
| Power Requirements | Removable and rechargeale 3.7V lithium ion battery or 123a (e.g. SureFire) batteries >4 hours | Removable and rechargeale 3.7V lithium ion battery or 123a (e.g. SureFire) batteries >4 hours | Removable and rechargeable battery or plug in wall adapter |
| Sample Collection | Sample must be directly in contact with instrument | Sample can be analyzed through translucent containers: point and shoot or placed in integrated vial holder | Sample can be analyzed directly or through containers or mylar sampling containers, point and shoot mode |
| Sample Analysis Time | Requires background analyzed between each sample then sample analysis (~1-1.5 minutes) | | Set by user (~30 seconds) |
| Sample Preparation Time | Minimal | Minimal to none | Minimal to none |
| Training Require/Ease of Use | Vendor training provided/easy to use | Vendor training provided/easy to use | Vendor training provided/moderately easy to use |

| | | | |
|---|---|---|---|
| Laser Output | Not applicable | Power Adjustable 75 mW, 125 mW, 250 mW | Not applicable |
| Survivability | Independently tested for MIL-STD-810G and IP67 certification | Independently tested for MIL-STD-810G and IP67 certification | Unknown |
| Scan delay | None | Optional; user-configurable delay up to 120 seconds | Can be set by user |
| Operating Temperatures | -4°F to 104°F (-20 °C to +40°C | -4°F to 104°F (-20 °C to +40°C | Unknown |
| Storage Temperatures | -30 to 60°C | -30 to 60°C | Unknown |
| Library Size | ~9000 | ~8550 | ~1000, User can set up library using their own standards |
| Software | Internal | Internal | Software driven voltage and current control included: Full laboratory XRF analyses capability utilizing S1 PXRF and Artax Software |
| File Identification | Chronological by session (user named) results list numerical identifier unless changed by user | Chronological by session (user named) results list numerical identifier unless changed by user | Identified by user |
| On-instrument data review | Yes, only by session | Yes, only be session | Yes |
| Detector | Not applicable | Not applicable | 10 square mm XFlash SDD, peltier cooled |
| X-ray tube | Not applicable | Not applicable | Rh target, max voltage 40kV |
| Filter changer | Not applicable | Not applicable | Manual filter for optimum flexibility, 4 filter kit supplied |
| Vacuum pump | Not applicable | Not applicable | Yes, allows for enhanced light element sensitivity |
| Gas flow chamber | Not applicable | Not applicable | Yes, allows for the measurement of gases down to Ne |

## RESULTS AND DISCUSSION

Sample spectra were added to the instrument libraries during laboratory testing. The instruments were then taken into operating facilities to determine chemical detectability. The x-ray fluorescent (XRF) system generally identified metals in the chemicals. However, the detection is limited to chemicals that have an atomic number >12. In addition, the instrument requires filters to be changed and voltage and amperage to be adjusted to optimize results. The transition metals provided the best signal under the "lab rate" mode conditions as tested. When the XRF is used to interrogate through glass bottles, the bottle components are often more significant in the spectra than the material inside the bottle.

The Raman system successfully identified many of the chemicals that were interrogated. However, depending on the concentration of the sample and the thickness of the poly bottle container, the results are more indicative of the container than the material inside the container. The FTIR system also successfully identified chemicals that it interrogated; however, the number of samples that were presented to the FTIR was limited due to the inability to open the bottles in the field.

Figures 1 and 2 are examples of results from the Raman, FTIR, and XRF instruments. Figure 1 depicts a sample of hexone (4-methyl-2 pentanone) analyzed on both the Raman and the FTIR, while Figure 2 is the instrument setup for a zirconium sample on the XRF through a poly bag.

**Lower Limits of Detection**: Once the chemical spectra were added to the library in the neat chemical form, dilutions were made of chemicals that are normally found as mixtures within the fuel cycle. Three concentrations of nitric acid were analyzed. The FTIR identified all three concentrations while the Raman identified that the chemical is a nitrated solution. It should be noted that all of the metal nitrates appear to have similar chemical signatures with the Raman (i.e. only sees the nitrate signature) and therefore are generally identified as various nitrated metals, without a specific metal identified.

In the nuclear fuel cycle aqueous reprocessing facilities, mixtures of organic phosphates and hydrocarbons are common. Therefore, a series of dilutions were made with various organic phosphates (tributyl phosphate and di-2-ethylhexyl phosphoric acid (HDEHP) and hydrocarbons (hexone, dodecane, and kerosene). When TBP is mixed with dodecane, FTIR can identify that there is a mixture of the two components at concentrations of ~6% TBP/~94 dodecane while Raman can only identify the mixture to a 30% TBP/70% dodecane concentration.

Similar dilutions of TBP and hexone were made. FTIR can identify mixture concentrations of 12.5%TBP/87.5% hexone while Raman correctly identifies the mixture at a 50%TBP/50% hexone concentration. When the concentration is 25%TBP/75% hexone, the Raman system identified the hexone and also identified what appeared to be dibutyl phosphate, a breakdown product of the TBP. As the concentrations decrease, both instruments identified only the hexone component of the mixture.

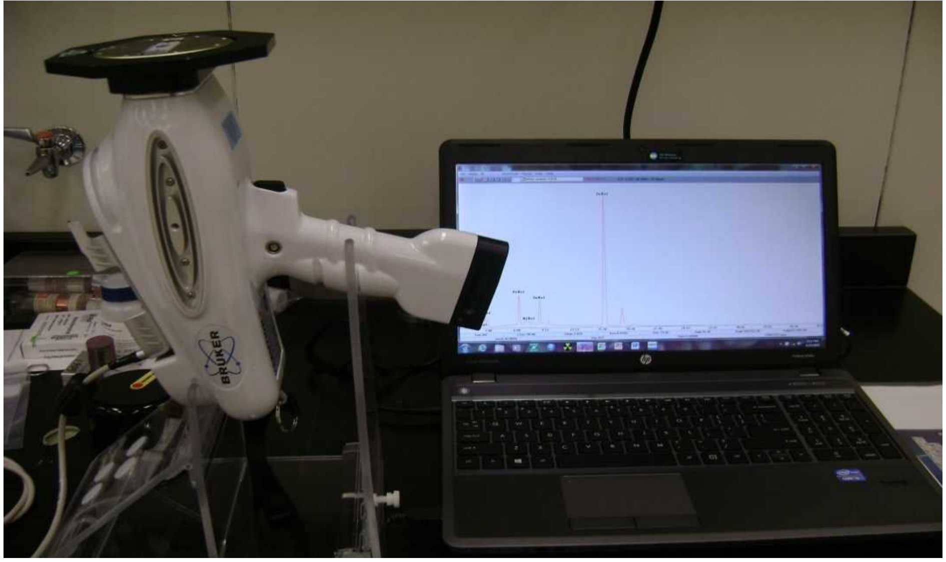
Similar dilutions of TBP and kerosene were made. However, in this case the Raman readily identified the mixture combinations correctly at mixture concentrations of 12.5%TBP /87.5% kerosene. At the lowest TBP level of 6%TBP/94% kerosene, the Raman system could only identify the kerosene. However, the FTIR had a more difficult time identifying this mixture from concentrations of 50%TBP/50% kerosene to the lowest mixture level. Similar dilutions of HDEHP and hydrocarbons were made with similar varying results.

**Detection of Chemical Spills**: The older ferrous sulfamate had ferrous materials settling in the bottom of the poly bottle prior to the spill. Degradation of the material had occurred. The dried spill sample was not broken and placed in the crusher on the FTIR. The diamond sampling tip was placed on the surface of the hardened material; however no detection could be made. This was also the situation with another, newer ferrous sulfamate spill using the FTIR. The Raman system was used to look at both the thinner and thicker parts of the chemical spills. Five of the 11 samples attempted at varying thicknesses from the aged ferrous sulfamate spill did not match any signature in the library. The Raman system did identify six of seven samples as a metal carbonate plus sulfamate or sulfuryl chloride from the newer ferrous sulfamate solution spill. The XRF identified iron peaks in the ferrous sulfamate spill at all of the varying sample thicknesses.

Analysis of a TRUEX spill with FTIR was performed by putting the diamond sampling tip directly into the solution. However, there was no match found although both TBP and CMPO and TRUEX are in the chemical library of the FTIR after being added by the user. There were no matches found in the library when holding the Raman tip into the liquid TRUEX spill although all the components are located in the Raman library. The XRF was not used to identify the liquid spill.

**Figure 1: A comparison of the hexone sample results as seen on the TruDefender FT and the FirstDefender RM**

**Figure 2: The instrument setup for the Bruker XRF. The system can be operated using either a PDA or a laptop.**



## CONCLUSIONS

Fourier transform infrared spectroscopy and Raman spectroscopy are complementary techniques for identifying liquid and powder samples. For this application, the Raman system was more useful because the system can see through containers, especially glass. Unfortunately many of the chemical compounds were in poly bottles and the Raman signal was often blocked therefore the results registered as the components of the container rather than the material inside.

This particular FTIR system was chosen by the CAWG but had limited usefulness in the field applications because the facility did not allow the bottles to be opened, which renders this system unusable. However, many commercial FTIR systems have attachments that can be used for analysis of samples through containers. Using this type of attachment would enhance the capability of the instrument in environments where the instrument cannot be in contact with the sample.

The x-ray fluorescence system was the most useful system, but it too has limitations, including container interference, and is most reliable with metals that can be put in direct contact with the instrument. It is apparent from both the laboratory and field testing that the best data sets were obtained when the Raman and x-ray fluorescence system were used in conjunction with each other. Based on laboratory and field testing, the Raman Spectroscopy and the x-ray fluorescence systems demonstrated good capability for detecting a range of chemicals as potential proliferation indicators. The indicators and equipment may be considered for further evaluation for potential use in Complementary Access activities.

## ACKNOWLEDGEMENTS

This work is supported by the Next Generation Safeguards Initiative, Office of Nonproliferation and International Security, National Nuclear Security Administration.

## REFERENCES

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