ANL/NE-15/5

Technology recommendations for pre-screening of IAEA swipe samples

Progress Report

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2/9/15

Executive Summary

Argonne and Oak Ridge National Laboratories have prepared an analysis of recommended, possible, and not recommended technologies for pre-screening and prioritizing IAEA swipes. The analytical techniques listed under the recommended technology list are the most promising techniques available to date. The recommended list is divided into two sections: Argonne's recommended techniques and Oak Ridge's recommended techniques. This list was divided based upon the expertise of staff in each subject area and/or the instrumentation available at each laboratory. The following section, titled Possible Techniques, is a list of analytical techniques that could be used for pre-screening and prioritizing swipes if additional instrumentation and effort were provided. These techniques are not necessarily top priority, but should not be discounted for future or expanded efforts. Lastly, a list of not recommended techniques is provided to outline the analytical methods and instrumentation that were investigated by each lab but deemed not suitable for this task.

In addition to the recommendation list, a short procedure is provided outlining the steps followed for destructive analysis by the Network of Analytical Laboratories (NWAL) for determination of uranium concentrations, isotopic content of sample and swipe. Swipes generated for this project will be given to ORNL's NWAL laboratory for analysis after analysis by other techniques at both laboratories.

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1. Argonne Recommended Technologies

1.1. X-ray Fluorescence (XRF), handheld/benchtop instruments

The X-Ray fluorescence technique has several advantages including: short measurements times of 90 seconds or less; large detection range of elements; and known compatibility measuring elements from swipes. Argonne currently has both a handheld XRF (Figure 1) with a tabletop configuration and access to a full benchtop analytical instrument to compare the limits of detection on the handheld instrument. These will facilitate evaluation of XRF for rapid screening of swipes in plastic bags. We have proven in the past that plastic polyethylene bags have minimal impact on XRF measurements and are confident useful data can be gained by using this setup. There will be no additional cost to the program by using these instruments. There is the optional capability of upgrading our handheld XRF for a "smear detection" mode that may or may not produce better data.

Figure 1 – Handheld Olympus XRF instrument with accompanying soil foot holster.

It is important to note that the IAEA already uses a laboratory based XRF instrument to obtain a quantitative elemental analysis on "cold" swipes. Swipes that do not have any measureable radioactivity are subject to a 4-5 hour analysis, with detection limits on the order of 35 ng/cm^2 with results sent to the IAEA Network of Analytical Laboratories (NWAL) laboratories in order to determine where the swipe sample should be stored or what analysis should be completed first. The handheld XRF that we are proposing to use would measure each smear in 90 seconds or less, providing a much faster rate for prioritizing each sample. The handheld XRF is also preconfigured for a "smear detection" mode that corrects for the cotton/cellulose swipe background and provides limits of detection on the order of µg/cm^2 or less. Additionally, according to the Safeguards Techniques and Equipment 2011 edition document, IAEA inspectors do have access to a similar handheld XRF instrument for analysis of metals, alloys, and samples that cannot be removed.[1] The handheld XRF may be useful in prioritizing or obtaining a quick analysis of smears in the field if the situation warrants the analysis.

Technical Basis

A handheld/benchtop X-ray fluorescence spectrometer uses a compact anode x-ray excitation source to generate primary x-rays to interrogate the sample. The primary x-rays generated are next collimated to the sample of interest, and, if the energy of the x-ray exceeds the binding energy of a core shell electron within the sample, that electron can be ejected. This ejection causes the element to be in an unstable electronic state, which is subsequently stabilized as electrons fall from higher levels to fill the vacancy. When these electrons fall from higher to lower energy levels, a secondary x-ray (commonly referred to as a "fluorescent x-ray") is emitted, which is characteristic to the element. For handheld instruments, the energy range is limited since the power to operate the instrument must be generated from 5.2 Ah lithium Ion batteries. The typical energy range of the instrument is between 0-50 keV.

1.2. Confocal Raman Spectroscopy

It may be possible to use a confocal Raman microscope to analyze smears in plastic bags. This instrument should allow the laser focal point to be placed inside the plastic bag, therefore mitigating the potential interference from the bag itself. We will have to test this confocal Raman microscope with several swipes to assess the

[1] IAEA Safeguards Techniques and Equipment 2011 Edition. International Verification Series no. 1 (Rev 2.)

magnitude of interference from the cotton and/or cellulose contained in smears. At Argonne, we currently have a confocal Raman microscope that we are able to access and use for this project. There will be no additional cost to the program by using this instrument.

Technical Basis

Raman spectroscopy uses the interaction of a laser beam and the electronic field and bonds of a molecule to determine information about the molecule's structure and identity. These measurements are performed by examining the wavelength shift of inelastically scattered laser light as it interacts with a target material, which is dependent on vibrational transitions within the molecule. Confocal Raman uses optical components to focus the excitation laser and collection optics on a small area. This simultaneously increases the laser fluence on the sample and reduces background signal. This will require that the sample be moved in a raster pattern to adequately image the entire surface.

1.3. **Near Infrared Spectroscopy (Near IR)**

The specific near IR region (800 nm - 2500 nm) has several vibrational regions of interest for uranium fluoride, uranyl fluoride, and other uranium compounds. Other non-radioactive chemical signatures also present differentiable chemical signatures in this spectral range. There have been a few literature articles describing the interference of Ziploc specific plastic bags in the near IR region and they do not appear in the regions of interest of the uranium compounds.[2] However, we still are not confident that polyethylene and the contents of the swipe will not interfere with identifying other chemical compounds of interest. There is also some uncertainty as to the limits of detection for this technique with regard to swipe samples. A portable instrument may need to be acquired.

Technical Basis

IR spectroscopy works by using infrared light to probe vibrational transitions which result in a change of the molecular dipole moment. These specific vibrational modes will absorb radiation at characteristic wavelengths. For these measurements, a spectrophotometer measures the differential transmission of infrared radiation through the sample in comparison to a reference as a function of wavelength (Figure 2)

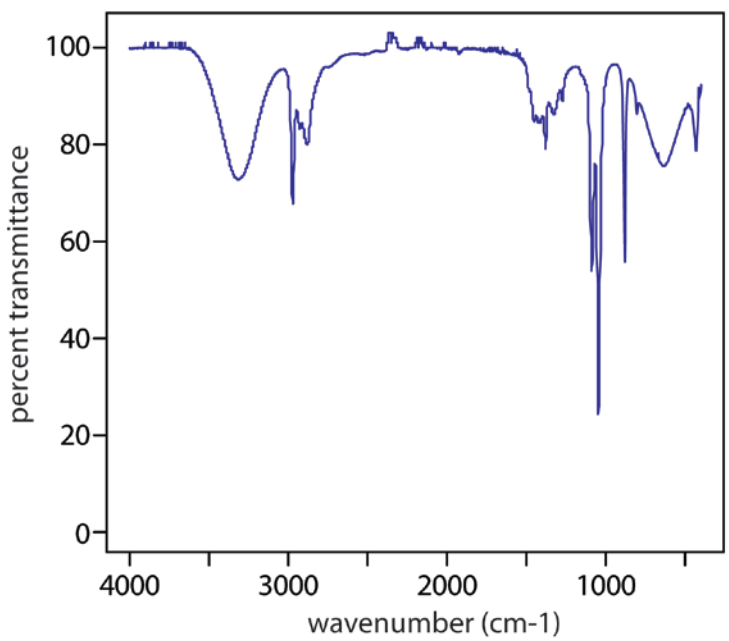

Figure 2 – Infrared spectrum of ethanol. © UC Davis, available at chemwiki.ucdavis.edu, available under a Creative Commons Attribution-NonCommercial-Share Alike 3.0 US License (http://creativecommons.org/licenses/by-nc-sa/3.0/us/)

[2] Causin, V. et al. A quantitative differentiation method for plastic bags by infrared spectroscopy, thickness measurement and differential scanning calorimetry for tracing the source of illegal drugs. Forensic Science Internationa, Vol 164 (2006) 148-154

2. ORNL Recommended Technologies

2.1. Neutron Activation Analysis (NAA)

We propose to investigate neutron activation analysis, where the delayed gamma ray energy will be measured to determine if an isotope is present on the sample. Common NAA techniques involve significant irradiation times for quantification purposes, which will alter the trace chemical components in the sample. As this technique is to be investigated as a pre-screening tool, we propose to use an atypical short irradiation time and smaller neutron flux for element identification purposes only. We propose to irradiate six to ten swipes in the University of Wisconsin Nuclear Reactor (UWNR). These samples will be irradiated and shipped back to ORNL for NWAL analysis. We will analyze the NAA samples along with control samples that were prepared in the same manner to determine if the NAA process is too destructive as a pre-screening tool.

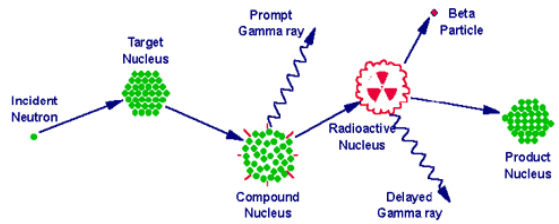

Figure 3 – Neutron Activation Analysis Schematic[3]

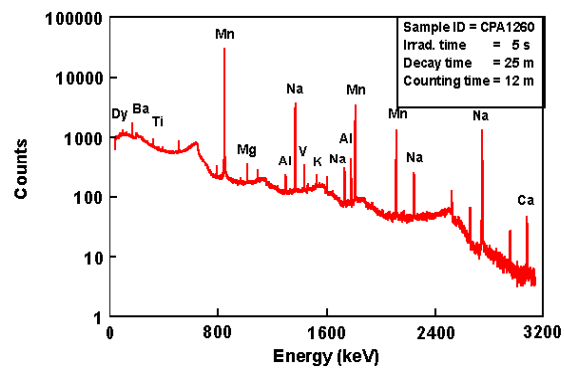

Figure 4 – Isotope Identification[3]

Technical Basis

Neutron Activation Analysis (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements (Table 1). For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods, on the order of parts per billion or better. NAA operates by irradiating target atoms with neutrons (Figure 3) and observing the decay products of resulting nuclei with gamma spectroscopy (Figure 4).

Table 1 - . Estimated Detection limits using decay gamma rays. Assuming neutron flux of $1x10^{13}$ n cm^{-2} s^{-1}.[3]

Sensitivity (picograms)	Elements
1	Dy, Eu
1–10	In, Lu, Mn
$10–10^2$	Au, Ho, Ir, Re, Sm, W
$10^2–10^3$	Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb
$10^3–10^4$	Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr
$10^4–10^5$	Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
$10^5–10^6$	F, Fe, Nb, Ne
10^7	Pb, S

[3] Permission to use Figures/Table provided by M.D. Glascock (University of Missouri). Images can be found at http://archaeometry.missouri.edu/naa_overview.html

2.2. **Handheld Raman Spectroscopy**

We recommend investigating Raman spectroscopy using a simple point and shoot probe on a majority of the swipes collected for this project. An example of this process is shown in Figure 5. The handheld probe will both supply the monochromatic excitation source, as well as collect the Raman scattered light. The Raman scattered photons will subsequently be directed into a grating spectrophotometer for analysis. For this portion of the work, swipes collected will be examined using point & shoot Raman spectroscopy. Oak Ridge has a Raman spectrometer on site; however a probe will need to be acquired for this work, as well as some supporting materials to execute the necessary measurements. Some amount of time investment is anticipated to determine the correct geometry and examine any interference which may be produced from swipe and/or bag materials.

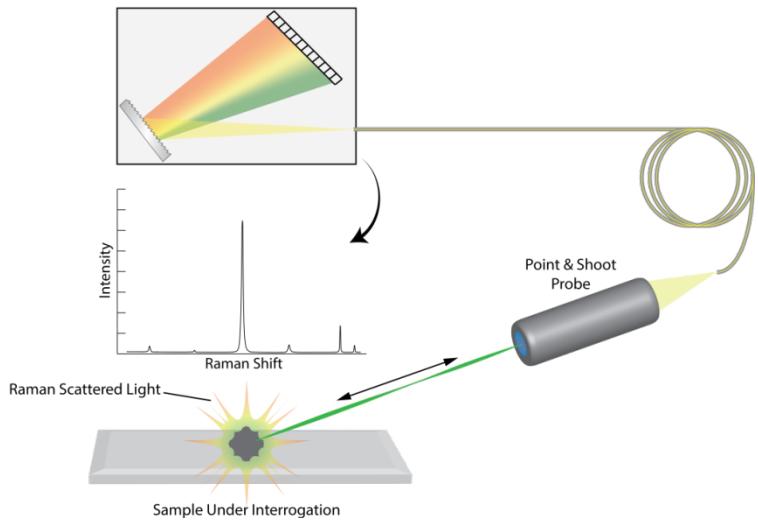

Figure 5 – Shown above is the general process for the examination of target materials using a handheld point & shoot Raman system. The probe serves to supply the excitation source, as well as collect Raman scattered light for analysis.

Technical Basis

Raman spectroscopy uses the interaction of a laser with the electronic field and bonds of a molecule to determine information about the molecule's structure and identity. These measurements are performed by examining the wavelength shift of inelastically scattered laser light as it interacts with a target material, which is dependent on vibrational transitions within the molecule. By using a self-contained, handheld probe (Figure 5), this technique may be used for non-destructive identification of Raman active materials that may be of interest for IAEA pre-screening needs either in-field or upon receipt at an IAEA facility.

2.3. **Fluorescence Microscopy**

The goal of this work is to test the feasibility of fluorescence microscopy for pre-screening purposes. While new molecular targets may be identified in future studies, this work will be mainly centered on probing the uranyl moiety. Detection limits for fluorescence microscopy can reach the single molecule level, however there are known interferences which will be present for swipe analysis. Both the bag material and the cotton of the swipe itself may exhibit fluorescence, so work will need to be performed on tailoring the imaging optics to filter out unwanted emission from these sources. While this work will not identify the species of interest outright, it may serve as an important pre-screening tool to assist in prioritizing samples for destructive analysis. Oak Ridge currently has a microscope which can be used for this task; however it will need to be upgraded to perform fluorescence measurements. In addition, there will be a time investment regarding a determination of the appropriate imaging optics to attenuate interfering signals from swipe materials.

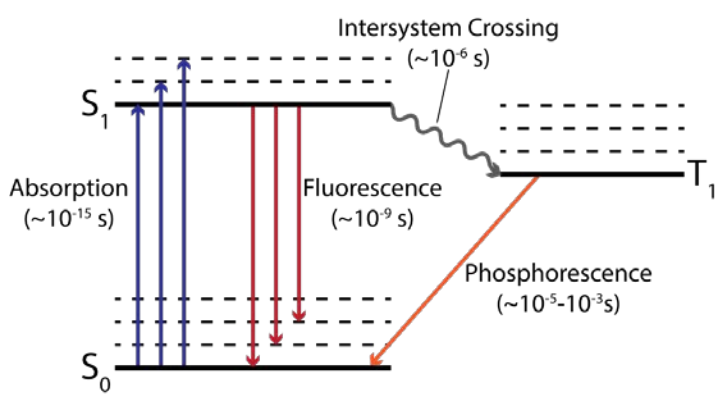

Figure 6 – Jablonski diagram illustrating absorption and emission processes in a fluorescent/phosphorescent material.

Technical Basis

Fluorescence spectroscopy is a method that

probes the emission of light from certain materials that occur as those materials undergo electronic transitions. To describe this approach, consider a simplified Jablonski diagram of the processes which can occur in a fluorescent material (Figure 6). In this technique, a target material is illuminated with a wavelength of light matching (or blue shifted from) an electronic absorption band within the substance. Upon the absorption of a photon, the material is elevated from the S0 to the S1 excited electronic state. At this point, the molecule may undergo a number of processes; the relevant event is the emission of a photon from the S1 to the S0 state, known as fluorescence. This photon will be of a longer wavelength than the excitation source (red shifted), and can be filtered and subsequently detected for quantitative or imaging purposes.

3. Potential Technologies

3.1. Terahertz wave spectroscopy

Terahertz wave spectroscopy is currently used for remote and stand-off detection of gaseous and volatile analytes of interest. Although terahertz wave in theory should be able to differentiate chemical compounds by producing unique chemical spectra, a chemical library of terahertz wave spectra for comparison and identification of an unknown sample does not yet exist. Terahertz wave, in general, is better geared towards detection of compounds in the gas phase and additional difficulty is present for the analysis of solid materials. Significant upgrades would have to be made to the instrument setup without the guarantee that the instrument could detect solids. Use of the terahertz wave spectrometer for this project is not discouraged, but would require a large amount of research that is likely out-of-scope for this project.

3.2. Infrared-micro spectroscopy

This technique will focus on a small region of the swipe and measure the full IR spectrum. This technique will have a broader range than near IR, but it is not certain if the extended range will provide any additional useful signature information. Additionally, neither Argonne nor ORNL have a micro IR spectrometer in house, with a cost of approximately $180k to procure the instrument. Depending on circumstances, ORNL may acquire an IR microscope using a separate funding source, in which the cost to investigate its feasibility would be drastically reduced.

3.3. Fluorescence lifetime analysis

Similar to the basic fluorescence spectroscopy detailed above, fluorescence lifetime analysis looks at the lifetime of fluorescence emission. While some materials (such as fibers present in swipe material) will have spectral overlap with target materials, their fluorescence decay time will likely be different, allowing temporal separation of each signal. This would yield a significant reduction in interference when screening for target actinide species. The cost of implementing such a method, however, would be quite substantial. Estimates for a confocal fluorescence lifetime analysis microscopy are at roughly $750k, and microscopes capable of taking these measurements are not currently available at either laboratory. This technique may be highly effective for pre-screening purposes, but unless substantial capital is available, it is outside the scope of this project.

4. Technologies Not Recommended

4.1. XRF/XRD portable instrument

The XRF/XRD combination instrument has the ability to provide elemental and chemical information on a sample of interest within a relatively short measurement time (30-90 seconds). Although excellent for mg or more amounts of samples, the XRD component of the instrument requires the sample to be ground into a fine power to be able to identify the chemical structure. There is evidence in the literature that with specialized sample preparation methods, chemical compounds located on a smear have been detected using XRD. But, the interferences from the amorphous structure of cellulose, cotton and other binders in the smear are severe. Therefore, we recommend that this technique is not considered for this specific project.

4.2. **Mossbauer Spectroscopy**

Several isotopes of uranium and plutonium are Mossbauer active, making this analytical technique intriguing for pre-screening. However, Mossbauer spectrometers are not generally considered to be commercially available and instruments that already exist are generally geared towards ^{57}Fe analysis. Additionally, the sample must be cast on a transparent substrate, therefore eliminating this technique from consideration for this specific project.

4.3. **Laser Induced Breakdown (LIBS) Spectroscopy**

LIBS would be an ideal analytical technique for detection of analytes on a smear if the smear could be taken out of the plastic bag. While a confocal setup (not COTS) might be possible to focus the laser inside the plastic bag, there is no guarantee that the ablation plume would not damage the bag. As chain-of-custody must be maintained and small amounts of the sample are ablated during the measurement process, this technique has been eliminated from consideration.

4.4. **Ion Mobility Spectrometer**

The IMS instrument is ideal for smear detection of chemicals and elements of interest. However, IMS only works if the smear is outside of the bag to ionize and release the chemical compounds into the detector. Chemical compounds containing uranium and plutonium will not be ionized with the soft ionization sourced typically used in IM; a hard ionization MS such as ICP-MS would be required. This technique should not be considered for this task.

4.5. **Millimeter wave spectroscopy**

Millimeter wave has considerably less active regions for unique chemical identification versus the related terahertz wave spectroscopy. For this reason alone, we eliminated this technique from consideration.

5. **NWAL Laboratory Analysis Procedure**

Swipe samples will be submitted to the Chemical and Isotopic Mass Spectrometry group for traditional NWAL destructive analysis to determine uranium concentration and isotopic content of the sample and swipe.

Samples are dry ashed in leached glass tubes in for ~12 hours in a furnace, with a ramped temperature profile reaching 600 °C.

1. After the sample is ashed, the furnace tube containing the ash is transferred to the appropriate clean room laboratory depending on the estimate of its content. Acid is added gravimetrically to the ash and the sample is heated to ensure complete dissolution.

2. ~1% of the sample is removed to screen (by ICP-MS) for U quantity and isotopics, as well as significant amounts of trace element contaminants in the sample. The result of the screen is used to select appropriate aliquot size and spike levels during further processing.

3. Chemical processing of the samples utilizes cleaned, prepared UTEVA columns to purify uranium from the remainder of the sample matrix. Typically, 60% of the sample is purified for uranium isotopic analysis, 20% is spiked with U^{233} tracer and then purified for concentration determination by isotope dilution mass spectrometry, and 20% is archived for re-analysis if required.

4. The spiked and unspiked uranium aliquots are then submitted for mass spectrometric analysis. A ThermoScientific Neptune *Plus* multi-collector inductively coupled plasma mass spectrometer is used to analyze the samples. Typically, the U^{233}/U^{238} ratio is monitored in the spiked fraction, while the U^{233}/U^{238}, U^{234}/U^{238}, U^{235}/U^{238}, and U^{236}/U^{238} ratios are all monitored in the unspiked fraction. The combination of the spiked and unspiked analysis allows the calculation of the uranium concentration in the sample. Currently, the IAEA requires the analysis of both spiked and unspiked uranium aliquots, as this is the best way to monitor for trace U^{233} which may be present in a sample.

5. The full combined uncertainty budget in both the reported concentration and isotope ratio measurements is made up of components from both the chemistry (gravimetric dissolution and weighing of spikes) and from the mass spec analysis (calibration of instrument and count rate of the sample).

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