A Reassessment of Complementary Access Tools for Chemical Indicators

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April 2016

Nonproliferation and National Security Department

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U.S. Department of Energy
NA-24

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October 2015

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<u>Background and Purpose</u>

The Complementary Access Working Group (CAWG) was set up as a multi-laboratory team with members from Brookhaven National Laboratory (BNL), Idaho National Laboratory (INL), Los Alamos National Laboratory (LANL), and Sandia National Laboratories (SNL) under the direction and funding provided by National Nuclear Security Administration (NNSA) through NA-241, Next Generation Safeguards Initiative (NGSI). During FY 13 the CAWG evaluated proliferation indicators based largely on a review of the 1996 version of the IAEA's Physical Model (Phase 1)[1]. During FYs 13 and 14, the CAWG then selected technologies and specific portable and hand-held devices that could be used by the IAEA to identify the chemical compositions of materials found during complementary access (Phase 2)[2]. [Note that in this report "chemical" is used in a broad sense to include elements, metals, and alloys as well as chemical compounds.] In November 2014, the CAWG issued its Phase 3 report[3,4] describing laboratory and field testing of three devices, each device representing a specific technology that the CAWG had selected as a result of the Phase 1 and Phase 2 activities. LANL and BNL continued measurements and analysis during FY15, leading to a reinterpretation of some of the Phase 3 results.

Separately, the European Commission Joint Research Center (JRC) Institute for Transuranium Elements (ITU) hosted a Technology Demonstration Workshop on portable and hand-held chemical identification instruments during November 2014 in Karlsruhe, Germany. This workshop had the similar objective of identifying and selecting instruments that the IAEA may employ during complementary access; JRC completed its preliminary report[5] in November 2014, but expects to release its final report by the end of 2015. According to the JRC project coordinator, further measurements and analysis are currently being conducted by ITU for the final report.

This report serves a twofold purpose. The first section of the report compares and contrasts the Phase 3 testing with presently available preliminary results of the Karlsruhe workshop. The results of Phase 3 (and the reinterpretation of some of these results) as well as the preliminary results of the Karlsruhe workshop provide the rationale for the second section of this report. In Section 2 of this report, we revisit the combinations of signatures

and technologies considered in Phases 2 and 3 of the CAWG effort. We do this to determine whether the three technologies and the matching instruments selected for the Phase 3 testing are more limited than initially thought. Based on this initial re-evaluation of the technologies considered under Phase 2, we provide a preliminary re-ranking of the suggested tools for detection of chemical indicators during complementary access.

Section 1: Comparison of CAWG Phase 3 Report with the Karlsruhe Workshop

1. Purpose of the Section

 This section of the report details for the NGSI organization the similarities and differences between the CAWG Phase 3 testing results and the preliminary results of the JRC technology demonstration workshop. Comparisons are made in four key areas:

- The basic approach and methods used in the tests;
- The devices tested;
- The sample materials used; and
- The basic conclusions of the two reports.

In addition, this section contains some limitations applicable to both projects based on research that followed CAWG Phase 3.

2. Approaches to Testing

The approaches used by the CAWG and the JRC were different but to some extent complementary. Relative to the JRC, the CAWG performed a more detailed analysis of a smaller number of devices. The CAWG evaluated three devices – one instrument for each of the three technologies X-ray fluorescence (XRF), laser Raman, and Fourier Transform Infrared Technology (FTIR), while the JRC evaluated eleven devices selected from four technologies - XRF, Raman, FTIR, and laser-induced breakdown spectroscopy (LIBS). The CAWG used a broader range and larger number of proliferation indicators and fuel cycle relevant chemicals and materials. The JRC effort appears to be what might be called a vendor demonstration (though operated by JRC). The CAWG had considered such a vendor

demonstration "bake-off" approach, since it allows examination of a large number of devices at a lower cost, but opted instead to focus on more detailed work at INL.

The preliminary JRC report describes only the general methodology used in the demonstration at Karlsruhe. The four test locations at Karlsruhe consisted of two work places in cold labs for tests with non-radioactive chemical compounds and metal samples and two places in hot labs for measurements with yellowcake. The non-metal samples at the JRC workshop included powders pelletized powders, and liquids.[*]

The CAWG study included both laboratory and preliminary field tests in contrast to only laboratory tests by JRC. In addition, the CAWG analyzed multiple samples of the same matrix to ensure analysis validity (10 analyses of each sample). The CAWG samples included metals, powders, liquids, and gases. All gas samples were in plastic bags or glass bulbs. The CAWG did not address pelletized powders or yellowcake. [The 1996 version of the Physical Model used in Phase 1 refers to "radioactive end-products of mining/milling process" and "uranium ore concentrates" as strong indicators for mining and milling but does not explicitly refer to yellowcake.]

During CAWG field-testing, the instruments were operated in a similar manner to the operation in the laboratory tests with the exception of samples that were too large to place in the Raman cuvette holder. All samples were analyzed through the container external to the instrument unless they were already present in sample vials that would fit into the integrated sample area on the instrument. No transferring of samples into vials was performed. The field test was conducted at operating nuclear facilities at INL, which included electrochemical separations, nuclear support analytical laboratories, and fuel fabrication facilities. During the field tests, instrument operators walked through the facilities and sampled chemicals/metals or piping and spill cleanup areas as allowed by the nuclear facility operations. (Note that some of the restrictions may be similar to restrictions that inspectors would find during complementary access.) During field tests, the samples were analyzed five times in whatever form or matrix they were found. For

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[*]The body of the JRC Karlsruhe workshop report states, "The sets of non-metal samples included powders, pelletized powders and liquids. The complete list of test samples is shown in Annex C." However, Annex C refers only to liquids and "pressed powder" in the list of chemical compounds.

example, if the sample was metal and lying in the open, it was analyzed directly in that form. If the sample was a liquid in a container, it was analyzed through the container wall (typically glass or polyethylene). However, because the FTIR system required opening of the containers, it was generally not used.

Neither report specifies minimum amounts of detected materials necessary for identification, which may vary both with a given chemical as well as the particular instrument. It is therefore not clear from either report what sizes of samples or concentrations of various chemicals are necessary for positive and unambiguous identification. The CAWG report acknowledges this deficiency and suggests it be part of the future work, which is currently underway at LANL in collaboration with BNL. See also the brief discussion of screening and identification in Section 2 of this report.

3. <u>Devices Tested:</u>

Table 1 below lists the devices tested in CAWG and the JRC efforts. Both efforts focused on Raman spectrometry, FTIR and XRF. The JRC test also addressed LIBS.

There are two primary differences between the devices tested by JRC and the CAWG:

- The JRC tested LIBS devices, whereas the CAWG did not test any LIBS devices
- The JRC tested several devices from different vendors within each technology area (Raman, FTIR and XRF) whereas the CAWG tested only one device within each technology area

The CAWG did consider LIBS during its evaluation of technologies in Phase 2, but field experience with commercial handheld LIBS devices was limited and the commercial hand-held LIBS technology was not sufficiently mature when the CAWG made its selection. The fact that the technology is now sufficiently mature highlights the speed of commercial development.

 Both the CAWG and JRC tested the Thermo Scientific FirstDefender and the TruDefender devices.

Table 1 Devices Tested

Complementary Access Working Group (CAWG)	Joint Research Center (JRC)
Raman:	
• Thermo FirstDefender RM	• Thermo FirstDefender RM/RMX • Rugaku Progeny • BWTEK TacticID • Snowy Range CBEX 785/1064
Fourier Transform Infra-Red (FTIR):	
• Thermo TruDefender FT	• Thermo TruDefender FTXi • Agilent 4500 FTIR Mobile
X-Ray Fluorescence (XRF):	
• Bruker Tracer III SD	• Bruker S1 Titan • Thermo Niton XL3t 980
Laser-Induced Breakdown Spectroscopy:	
N/A	• Oxford Instruments mPulse • IVEA easyLIBS • LIBS-ID Plus

4. Test materials:

For the CAWG effort, 47 specific chemicals, metallurgical and/or sample groups (e.g. uranium, thorium, or plutonium chloride, fluoride and nitrated compounds) identified in Phase 1 of the program as proliferation indicators of interest were examined. These 47 sample types were based on a prioritized list of proliferation indicators in the IAEA's Physical Model. See the Phase I report for full description of how the 47 materials were selected. In addition, the CAWG tested the devices against 46 other samples of interest in the nuclear fuel cycle that were readily available in the facilities. The preliminary JRC report indicates that tests were performed on "41 materials relevant to the nuclear fuel cycle" with no further information provided on how these had been selected.

Of the 47 materials identified as proliferation indicators by the CAWG, 11 were considered in the JRC study. Of the 46 "other" samples of interest in the U.S. study, eight were considered in the JRC study. The overlap is shown in Table 2, below

Table 2: Substances Tested

CAWG Proliferation Indicators	Additional CAWG materials	JRC
	Aluminum • 2014 • 2014 • 6061 • 7050 • 7077	Aluminum • 99.99% • AL88SI12
	Aluminum nitrate nonahydrate	Aluminum nitrate nonahydrate
	Aluminum nitrate solution	Aluminum nitrate solution
Calcium chloride		Calcium chloride
Calcium oxide		Calcium oxide
Carbon tetrachloride		Carbon tetrachloride
	Hexane	Hexane
Kerosene or paraffin		Kerosene
Lithium chloride/potassium oxide (eutectic)		Potassium oxide
Maraging steel		Steel maraging (300 and 350)
Mercury		Mercury
	Nitric acid	Nitric acid 65%
	Phosphoric acid	Phosphoric acid 85%
	Sodium carbonate (~2M)	Sodium carbonate solution
Sodium carbonate solid		Sodium carbonate solid
	Stainless steel	Stainless steel AlSl304
Tributyl phosphate		Tributyl phosphate
Titanium (IV) Chloride		Titanium Chloride
U_3O_8 (Triuranium octoxide)		NUFCOR U_3O_8

The full list of materials examined by the CAWG and JRC is contained in Appendix A of this report.

5. Comparison of Conclusions:

This section compares the main conclusions of the two reports. Each pair of conclusions below first quotes the JRC conclusion and then the corresponding CAWG conclusion or other relevant observations. In general, the conclusions of the two studies supported one another, though the CAWG's were more general, due to the broader range of materials examined.

1) Comparison of Raman Detection/Identification Characteristics

JRC: "From a detection/identification standpoint, all Raman devices perform quite similarly. Slightly better performance was demonstrated by devices with a 1064 nm incident wavelength on solid chemical compounds. Further tests of 1064 nm versus 785 nm devices on the extended set of chemicals would be desirable to validate this result."

CAWG comment: As the CAWG only tested a single 785 nm Raman device, the CAWG did not have a corresponding conclusion comparing the performance of Raman devices. It is a welcome conclusion that the JRC study indicates that all Raman devices performed similarly. If this conclusion is validated, an IAEA selection of a Raman device (if that decision is made) can be based on operational factors – for example, weight, and ease of use. [See the second part of this report for a brief discussion of trade-offs between 785 nm and 1064 nm Raman instruments.]

2) Comparison of Raman and FTIR

JRC: "On performance characteristics, form factor and implemented technological advancements, some of the Raman devices appear as promising candidates for an extended CA toolkit."

CAWG comment: The CAWG also concluded that, based on performance, the Raman device appears to be a promising candidate. For application during CA, the Raman system was more useful than others because the system can see through containers, especially glass. FTIR requires direct contact with the sample. Unfortunately many of the chemical compounds were in poly bottles and the Raman signal was often

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blocked; therefore, the results registered as the components of the container rather than the material inside.

3) FTIR and Raman as Complementary Techniques

JRC: "The **complementary nature of FTIR with respect to Raman** has been clearly demonstrated only in case of dark-colored industrial yellowcake."

CAWG comment: The CAWG reached a broader conclusion on this front, i.e., that FTIR and Raman spectroscopy are complementary techniques **for identifying liquid and powder samples, in particular dark samples and water based samples (i.e., not limited to dark-colored industrial yellowcake)**.

The FTIR system chosen by the CAWG had limited usefulness in the field applications because the facility did not allow the bottles to be opened, which renders this system unusable. However, the CAWG team during instrument evaluation and selection was aware that portable FTIR instruments typically cannot analyze gases without additional accessories. The CAWG did not obtain such accessories for these tests. FTIR with such attachments may be subject to interferences from the IR properties of the container wall materials. Raman may be able to detect a few gases and XRF can see some gases depending on atomic weight.

Both the FTIR and Raman employed in the CAWG tests were manufactured by Thermo Scientific. As of March 2015, this vendor is offering a new instrument with both FTIR and Raman capabilities, the Thermo Scientific Gemini Analyzer[6], which essentially combines the two instruments selected for this project by the CAWG.

4) Performance of Handheld LIBS

JRC: "Performance of hand-held LIBS on metal samples exceeded or was comparable to that of portable LIBS systems, and was superior to that of XRF devices (with regard to identification capability, but also because of the form factor, usability and analysis time). Further extension of the hand-held device to non-metal samples is desirable.

CAWG comment: Because the CAWG did not test LIBS devices, the CAWG cannot comment on the performance of LIBS relative to XRF. However, LIBS technology was

considered a strong candidate for future consideration largely because it had the potential to identify light elements below the detection threshold of XRF portable.

5) Capabilities of XRF

JRC: "XRF devices remain relevant for IAEA applications involving accurate in-field assay of U and Th in different matrices in support of inspections and CA missions. Capabilities of the portable XRF devices in this area shall be demonstrated in a separate workshop."

CAWG comment: The CAWG reached a broader conclusion, that t**he XRF instrument 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. The XRF instruments can provide information about elemental composition - for example, constituents of alloys - but are problematic for low-Z elements.[†] (Z is the atomic number of the element.) Furthermore, hand-held XRF instruments cannot provide information about chemical compounds; this is a particularly serious shortcoming for proliferation indicators that are organic compounds. It is apparent from both the laboratory and field testing that the **best data sets were obtained when the Raman and XRF instrument were used in conjunction with each other.** Based on laboratory and field testing, the Raman Spectroscopy and the XRF instrument demonstrated good capability for detecting a range of chemicals as potential proliferation indicators. The XRF can detect metals and some powders (detects elements within a compound) as well as gases containing heavier elements – for example, krypton, and xenon as well as the sulfur in hydrogen sulfide. The particular XRF instrument chosen by the CAWG was not optimized for CA use, as it required filters, vacuum pumps, and a computer system which increased the difficulty of use in the field. However, libraries can be created and loaded to a personal digital assistant allowing the instrument to be set as a "point and shoot" instrument without these attachments which would then make it user friendly for field applications but provide reduced spectral imaging.

[†] According to the Bruker website, hand-held XRF can detect elements from magnesium (Z=12) to uranium (Z=92). See https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/elemental-composition-analysis.html

6. Limitations and Biases of CAWG Phase 3 Report and the Karlsruhe Workshop

Based on the additional experience gained after the CAWG Phase 3 was completed (i.e., during the LANL measurement campaign aimed to quantify trace sensitivity of XRF, Raman and FTIR with respect to uranium and thorium), several significant limitations and biases in both of the projects were identified and are described in this section.

Effect of instrument setup:

Some of the instruments used in both studies can be tuned (variable settings) by the user based on the environment in which measurement takes place and the chemicals, materials or chemical elements that are expected to be found. It appears that in both studies, some devices were used with settings that were less than ideal. An improper instrument setting may result in significantly reduced sensitivity or false negative identification. The preliminary JRC report does not provide operational details of individual instruments, nor does it comment on the effect of optimized instrument settings, suggesting that the instruments were not optimized. The CAWG report does consider the effect of different settings in case of the XRF instrument (the Raman and FTIR devices have fixed instrument settings). Nevertheless, during the CAWG field trials, the XRF instrument was used in only a single setting (so called "lab-rat mode"), which is less than ideal, especially for the detection of high-Z elements. Based on subsequent experiments with different XRF settings, we now believe the CAWG report lists many materials as "not identified" (see Table 8 in CAWG report) or "difficult to identify" which would have been easily and unambiguously identifiable with optimum settings.

Positive and negative bias towards false positives:

Both reports suffer from limitations related to false positives. For example, the identification algorithm (often proprietary) of a given instrument may be more or less prone to false positive identification. Such risk strongly depends on the content and quality of the library against which the measured signal is compared.

In this regard, the JRC method of preparing devices for testing may have had the effect of obscuring the potential for false positives. The JRC report states that many instruments in the demonstration were used with libraries that were empty, except for a relatively small

number of chemical measurements that were made in the initial phase of the demonstration. Thus, in the demonstration, the "unknown" samples were screened against a very limited number of reference spectra. In this way, the chance of a false positive identification was unrealistically minimized, while the chance for correct identification was maximized. Consequently, the results listed in Table 1 in the JRC reports are biased, and likely do not reflect true capabilities of the instruments if used under the same scenario with full reference libraries, as typically provided by the manufacturer. Overall, the JRC report does not discuss risks of false positives. [Once again, see the brief discussion of screening and identification in Section 2.]

The CAWG report also contains false positive challenges. Subsequent to the completion of the CAWG Phase 3 report, LANL sought to reconstruct certain measurements performed during the CAWG Phase 3 work at INL. LANL's work revealed that a unique signal from the nitrate in a low-concentration Pu nitrate solution was incorrectly attributed to presence of Pu in the CAWG report; Pu nitrate does not have a unique Raman signature. What was unique was the Raman signature of the nitrate. When added to the library as "Pu nitrate solution," any other weak nitrate solution is identified as Pu nitrate, even though it contains no traces of Pu (more detailed discussion can be found in the "CA Tools project – Status update (June 2015)" by Henzl et al.). This example illustrates the dangers of false positives which may be difficult to avoid for certain classes of chemicals and materials.

Actually, special attention should be devoted to characterizing both false positive and false negative risks. The evaluation of false negative identification is closely tied to the quantification of detection limits of individual analytical techniques and instruments from different manufacturers and can thus be relatively easily evaluated in dedicated experiments. On the other hand the evaluation of risks of false positive identification is much more complex, but its neglect can lead to misinterpretation of the instrument usability in the field.

Section 2: Reexamining the CAWG Phase 2 Technology and Instrument Selection

1.   Purpose of the Section

 This section of the report describes for NGSI a reexamination of the selection in Phase 2 of technologies and instruments that were tested in Phase 3. The first step will be to revisit the combination of technologies and signatures by briefly summarizing the CAWG's Phase 1 and Phase 2 efforts. The next step will be to describe some concerns that have come to light about the technologies selected in Phase 2 for Phase 3 testing as a result of the additional work at LANL and the Karlsruhe workshop. Finally, a preliminary dual ranking of the technologies is proposed, accompanied by a very brief suggestion for approaching future work in evaluating COTS handheld instruments.

2.   Summary of Phase 1 and Phase 2 Efforts

The CAWG was tasked with identifying and selecting COTS hand-held instruments that could be adapted for use by IAEA inspectors during a CA.

 In Phase 1, the CAWG first identified and reviewed signatures and observables (S&Os) of interest to the IAEA in the context of identifying nuclear-fuel-cycle activities that might be indicative of clandestine nuclear weapons development – S&Os that are likely proliferation indicators. The CAWG then selected those proliferation indicators that were not adequately addressed by currently-employed IAEA inspection tools and that were deemed of high priority by the IAEA. The majority of these inadequately addressed proliferation indicators were elements (for example, metals and alloys) and chemical substances.

Phase 2 began with a systematic survey by the CAWG team of technologies that could potentially detect and identify the proliferation indicators of concern and that were also available as portable COTS instruments readily adaptable to or customizable for practical inspector use. The team first evaluated an initial list of COTS technologies that appeared to be relevant, adding to and removing technologies from that list as the team's assessment progressed. The list of COTS technologies for further consideration at this stage included the technologies mentioned earlier in this report [LIBS, laser Raman, FTIR, and XRF] as well

as ion mobility spectrometry [IMS], mass spectrometry [MS], nuclear magnetic resonance [NMR], colorimetric techniques, and electrochemical methods.

The team then conducted a functional evaluation of these technologies by systematically correlating the technologies with the proliferation indicators of concern. This was followed by a performance evaluation of those technologies based on the number of proliferation indicators each technology could address. The result was the following ranking of the nine technologies mentioned in the previous paragraph, ordered from the highest ranked (greatest number of proliferation indicators addressed) to lowest ranked (smallest number of proliferation indicators addressed):

LIBS > Raman > FTIR > XRF > IMS > MS > NMR > Colorimetric > Electrochemical

LIBS is sensitive enough so that only picograms to nanograms of the sample substrate are ablated from the sample surface by the laser beam.[7] LIBS would, in principle, allow a more sensitive analysis – at least elemental and perhaps chemical, as well – of surface composition of solids, both of the substrate and of adsorbed contaminants. However, despite its highest ranking in the performance evaluation and its sensitivity, the team felt it was necessary to consider the maturity of the technologies in the evaluation, thereby removing LIBS from further consideration at that time. In addition, as mentioned in the Phase 2 Addendum, despite the small amount of ablated material, there is residual damage to the surface on a microscopic scale, namely, craters with dimensions of tens of nanometers or even tens of micrometers.[8] This is a topic that should be clarified further by the IAEA, since LIBS was one of the technologies tested at the Karlsruhe workshop.

3. Concerns about the Technologies Selected in Phase 2 for Phase 3 Testing

The results of the Phase 3 testing as well as the results of the Karlsruhe workshop indicate that a performance evaluation of technologies based only on the number of proliferation indicators that a specific technology can detect is overly simplistic, although useful as a zeroth-order approximation.

For instance, FTIR can, in principle, detect and identify a vast number of chemical compounds, including many that cannot be detected or identified by Raman spectroscopy.

However, COTS handheld FTIR field instruments generally employ attenuated total reflectance (ATR) to direct the infrared radiation through a sample in intimate contact with the ATR surface of the instrument; for example powders may be crushed against the crystal surface and a liquid may be brought into contact with the crystal – for example, by immersing the crystal into the liquid or by pipetting the liquid onto the surface of the ATR crystal. This leads to many practical limitations on the use of FTIR in realistic field situations in which chemical substances of interest may be in containers or in process lines where there are safety or procedural considerations preventing direct contact between the FTIR instrument and the substance of interest. For example, the facility staff may say, "No, we can't provide a sample of the liquid in the process line because it will disrupt our operations." Or, "No, we can't open the bottle of liquid due to safety considerations." [See the Phase 2 Addendum for additional consideration of these limitations as well as a brief discussion of the molecular basis for infrared and Raman activity; note that a chemical substance may be either infrared active or Raman active or both or neither.]

Raman instruments have the advantage of being able to function in a stand-off "point-and-shoot" mode. However, they have other limitations. The incident radiation may generate heat in darker samples and thus result in potential safety problems when dealing with ignitable or explosive unknowns. Also, the identification of colored materials is subject to interference from fluorescence, especially with the 785 nm laser excitation from the FirstDefender® RM. Portable systems are now available with a lower-energy excitation employing 1064 nm radiation (as indicated by their availability for the Karlsruhe workshop). There is a trade-off, however; the lower-energy excitation reduces the fluorescence problem but requires longer scan times.[9]

Certain categories of S&Os were effectively deferred as a result of the ranking process and by the exclusion of LIBS. The Phase 2 analysis of the chemical detection technologies available as COTS instruments led to the conclusion that Raman, FTIR, and XRF technologies subject to the limitations mentioned in the previous two paragraphs collectively address most of the proliferation indicators except for gases, volatiles, vapors, and suspended particulates. Such airborne indicators are not addressed by the three technologies selected for testing except perhaps by means of specialized attachments that

are being developed by the vendors.[10] However, gas analysis capabilities of the next two lower ranked technologies, IMS and MS, are probably more sensitive. In any case, time and resources constraints limited the number of instruments that could be purchased for the Phase 3 testing, so the CAWG deferred further consideration of these technologies. Table 3 on the next page summarizes the preceding discussion of the pros and cons of COTS handheld technologies for different physical states of indicators.

Technologies such as IMS and MS should be investigated as tools for the detection and identification of these types of proliferation indicators, if it is determined that these additional indicators are important. Note that the Karlsruhe workshop did not consider detection and identification of gas phase or other airborne indicators.

4. Re-ranking of COTS Handheld Chemical Detection Technologies for CA

Based on the testing conducted during Phase 3 and during the Karlsruhe workshop, there is a need to reassess the initial ranking of technologies based on the number of indicators that, in principle, a given technology will address. Realistic field scenarios that incorporate the real-world constraints on employing the instrumentation should be incorporated into the ranking methodology; these constraints include interferences (*e.g.*, fluorescence, container walls), instrument requirements (*e.g.*, contact between ATR surface and sample), physical state (*e.g.*, solid, liquid, gas, vapor, airborne particulate), and procedural limitations at a facility. [It is assumed here, perhaps naïvely, that procedural restrictions by facility staff are the result of safety and operational considerations.] The methodology for readily deriving a quantitative re-ranking of technologies that incorporates realistic field scenarios is unclear at this time. However, a preliminary re-ranking of technologies is possible based on a qualitative examination of the results of the Phase 3 testing as well as from the results of the Karlsruhe workshop. This preliminary re-ranking is actually a dual ranking, with two separate rankings, each ranking applicable to a different category of samples.

Table 3 Pros and Cons of COTS Handheld Technologies for Different Physical States of Indicators

	Solids		Liquids		Gases and Airborne	
	pro	con	Pro	con	pro	con
LIBS	Stand-off point-and-shoot mode			Problematic		
Raman	- Stand-off point-and-shoot mode - Wide range of indicators detectable in principle - Can detect and identify through many [but not all] container materials	- May generate heat in darker samples, leading to ignitable or explosive hazards. - Subject to interference from fluorescence	- Stand-off point-and-shoot mode - Wide range of indicators detectable in principle - Can detect and identify through many [but not all] container materials	- May generate heat in darker samples, leading to ignitable or explosive hazards. - Subject to interference from fluorescence		Possible in principle. Capability not demonstrated for COTS handheld
FTIR	Wide range of infra-red active indicators detectable and identifiable in principle	- Intimate contact with ATR surface needed. - Indicator must be or contain an infra-red active chemical compound	Wide range of infra-red active indicators detectable and identifiable in principle	- Intimate contact with ATR surface needed. - Interference from container wall		Special attachment under development by vendor
XRF	Wide range of chemical elements detectable and identifiable in principle	Cannot identify chemical compounds; can only identify elements with Z>11	Should be possible in principle		Special attachment available from vendor	
IMS		Reportedly possible with swipe samples on cloth		Reportedly possible with swipe samples on cloth	Useful as "sniffer" for identifying gases	
MS		No		No	Useful as "sniffer" for identifying gases	

The Phase 2 ranking of technologies based on the number of indicators addressed in principle by each technology did not take into account whether the COTS handheld instruments could address indicators with different physical states. A reexamination of instruments available as COTS handhelds leads to the conclusion that Raman, FTIR, and XRF technologies collectively address most of the proliferation indicators except for gases, volatiles, vapors, and suspended particulates. The airborne indicators are better addressed by IMS and MS. Therefore, let us consider two separate rankings of the technologies based on the capabilities of the COTS handheld instruments. For one group of technologies, the COTS handhelds are best suited for bulk condensed phases, namely, solids (including powders) and liquids, while for the other group of technologies the COTS handhelds are best suited for gases and other airborne indicators.

For solids and liquids, we have the following ranking of technologies:

LIBS > Raman > XRF> FTIR > NMR > Colorimetric > Electrochemical

LIBS and Raman still rank first and second, based on the number of solid and liquid indicators each technology can address, as in the Phase 2 Interim Report. However, FTIR is demoted to the fourth rank technology based on its limitations discussed earlier in this report. As a result, XRF is promoted to the third ranked technology. As indicated in the Phase 2 and Phase 3 reports as well as in the Karlsruhe workshop report, XRF provides information about elemental composition and not about chemical compound composition, which is the reason it is not further promoted to second place. The remaining three technologies – NMR, colorimetric, and electrochemical – are provisionally ranked lower than FTIR; the CAWG did not investigate them after the Phase 2 technology selection process because project resource constraints did not permit further examination of the lower priority technologies.‡ Similarly, project resource constraints did not allow consideration of small swipe samples on paper or cloth in conjunction with IMS, which as noted in the Phase 2 Addendum, is feasible in some implementations of the technology, so IMS is not included in this ranking of technologies for solids, powders, and liquids.

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‡ It should also be noted that the JRC did not address NMR, colorimetric techniques, or electrochemical methods during the Karlsruhe workshop.

For gases and other airborne indicators, the following ranking of technologies may be considered:

$$IMS > MS >> Raman > FTIR > XRF$$

With gas identification adaptation

IMS and MS rank first and second, based on the number of gases and other airborne indicators each technology can address, as in the Phase 2 Interim Report. Gas-phase elemental and chemical identification capabilities are available or are under development for handheld Raman, FTIR, and XRF, but these three technologies have typically been employed for solids and liquids.[§] Until comparisons of these three technologies with IMS and MS are available, they are provisionally ranked much lower than IMS and MS.

An alternative way of considering the technologies is to group the proliferation indicators by chemical or structural composition before considering their physical state. For example, metals and metal alloys are solids and miscellaneous inorganics such as actinides are encountered in solids and liquids. Based on LANL experience, XRF is the best instrument for determining the composition of such materials and is the easiest to use. (LIBS may be a good choice here as well, but it was not one of the technologies selected by the CAWG.) The remaining proliferation indicators are largely chemical compounds, which XRF cannot identify and for which the other technologies may be more suitable. This alternative re-ranking has XRF (and possibly LIBS) as highest rank, with the other technologies ranked lower. The ranked order of the other technologies will depend on the requirements of the user, namely an IAEA inspector during complementary access. The IAEA will need to provide its priorities – for example, metal alloys over organic solvents, solids and liquids over gases, etc.

[§] As mentioned in Section 1 of this report, the CAWG Phase 3 effort did address a limited number of gas samples in plastic bags or glass bulbs. The XRF was able to detect gases containing heavier elements such as krypton, and xenon as well as the sulfur in hydrogen sulfide.

5. <u>User Requirements: Screening and Identification</u>

As indicated above, the (re-)ranking of technologies and instruments should be considered in the context of what the instrument is required to do and who is using it. Additional considerations include ease of use by the IAEA inspector as well as the potential for procedural opposition by the inspected facility. User requirements consist of screening for and identification of proliferation indicators in realistic situations involving target materials and interferents of interest.

The following discussion of screening and identification algorithms from a paper authored by the staff from one of the vendors, Thermo Fisher Scientific, focusses on handheld Raman instruments.[11] However, similar considerations will apply to data analysis for the other technologies [and also for handheld radiation detectors such as the HM-5 (FLIR IdentiFinder®)].

IAEA inspectors are not the typical end users targeted by the vendors of the COTS instruments. The targeted end users represent a diverse user community who must detect and identify substances that might be encountered when dealing with hazardous materials, illicit drug enforcement, contraband identification, environmental contamination, and chem/bio agent detection. These users typically do not have extensive technical or scientific backgrounds – think TSA screening for explosives at airports – so computational analysis by the instrument and/or by remote expertise provided by the instrument vendor is necessary. Accordingly, these users generally rely on the instrument software to extract useful information from the raw spectral data. Furthermore, many of the vendors provide 24/7 "reach-back" services for field users. The deployment constraints for these users are different from the constraints on their use by IAEA inspectors during complementary access. However, even users from the IAEA have at times requested instruments that provide binary pass/fail results.

Generically, the end user needs to know the answers to one or more of the following three questions:

- Authentication: Is the measured test material consistent with substance X?

Is the measured spectrum consistent with the stored reference spectrum of material X? Authentication algorithms are typically used for raw material confirmation. During complementary access, this might arise if the identification of a chemical in a labeled container is in question.

- Screening: Does the measured test material appear to contain substance X?

  Screening algorithms may be used to assess whether certain of the features in an unknown spectrum indicate the presence of one or more substances of interest. User input is required about the potential presence of specific materials.

- Identification: What material was measured?

  Identification algorithms involve searching a library of spectra of known materials to determine whether the unknown spectrum is consistent with any stored spectrum in the database. This includes a mixture analysis to ascertain whether a combination of stored spectra corresponds to a significant portion of the unknown spectrum. Identification algorithms have the potential for identifying the constituents of an unknown material. [They also have the unfortunate possibility of misidentification, especially if end-user additions to the library are allowed. Note LANL's discovery of a false positive of Pu due to the Raman signature of the nitrate ion resulting from the addition to the instrument library of spectra from plutonium nitrate solutions.]

A combination of screening and identification algorithms may provide an optimal way of proceeding if a user-defined list of target materials of interest is formulated. Ideally, the IAEA inspector during a complementary access should not go into the situation "blind" and expect the instrument to do all the work; the inspector instead should have a list of possible chemical proliferation indicators based on information about the facility. The IAEA inspectors do have technical, engineering or scientific training, although not necessarily identification of substances by means of spectroscopy.

More generally, as a result of the Phase 1 effort, the CAWG recommended to the IAEA which of the proliferation indicators of concern during complementary access did not have COTS

handheld instruments readily available – in other words, where the "gaps" were in the technologies being used by the IAEA. As a result of the Phase 2 effort, the CAWG made some preliminary suggestions about which COTS technologies might be suitable addressing those indicators. The intent of the CAWG effort from the beginning has been to recommend multiple appropriate approaches to the IAEA for its consideration.

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Appendix A: List of Substances Examined by CAWG and JRC

CAWG	JRC
Aluminum • 2014 • 2014 • 6061 • 7050 • 7077	Aluminum • 99.99% • AL88SI12
Aluminum nitrate, nonahydrate	Aluminum nitrate nonahydrate
Aluminum nitrate solution	Aluminum Nitrate solution
Ammonia	
Ammonia Gas	
	Ammonium Diuranate (ADU)
	Ammonium hydroxide
Argon	
	Beryllium (99.0%)
Bismuth phosphate	
	Brass (Cu63Zn37)
Boric acid	
Boron 10 compounds • Boron carbide • Boron containing steel • Boron nitride • Boron oxide	
	Cadmium (99.99%)
Calcium	
Calcium chloride	Calcium Chloride

Calcium Fluoride	
Calcium oxide	Calcium Oxide
Carbon Tetrachloride	Carbon Tetrachloride
Chlorine Trifluoride	
Chloroform	
	Copper (99.9%)
	Dawn (ADU)
Deionized Water	
Deuterium	
Deuterium oxide	
di-2-ethylhexylphosphor acid (HDEHP)	
	El Mesquite (UO$_4$)
Ferrous Sulfamate	
Fluorine	
Graphite	
Hafnium nitride	
Hafnium oxide	
Hastelloy C	
Helium	
Hexachloroethane	
Hexane	Hexane
Hexone (4 methyl-2 pentanone)	

Hydrochloric acid	
Hydrofluoric acid	
Hydrogen sulfide	
Inconel 492	
Kerosene or paraffin	Kerosene
Krypton	
Lithium	
Lithium chloride/lithium oxide (eutectic)	
Lithium chloride/potassium chloride (eutectic)	
Lithium hydride	
	Macassa (UH)
Maraging Steel	Maraging Steel (300 and 350)
Mercury	Mercury
Monel 400	
n-dodecane	
Nitric acid	Nitric Acid 65%
Nitrogen	
Nitrogen Dioxide	
Octyl(phenyl)-N-N-diisobutylcarbamoylmethylphosphine oxide (CMPO)	
Octylphenyl phosphoric acid (OPAP)	
Phosphoric acid	Phosphoric Acid 85%
Plutonium metal	
Plutonium nitrate	

Potassium amide	
Potassium chloride anhydrous	
Pu (IV) chloride	
Pu (IV) fluoride	
PuO$_2$ (Plutonium oxide)	
	Potassium Chloride
Sodium carbonate solid	Sodium carbonate solid
Sodium carbonate solution (~2M)	Sodium carbonate solution
	Sodium Diuranate (SDU)
Solvesso 150 (C10 aromatics)---(Orform SX12 was used)	
Stainless steel	Stainless Steel (AISI304)
	Steel 1.2379
	Steel 1.5916 (15CrNi6)
	Steel 1.7227 (42CrMo24)
	Steel CK45
	Steel ST37
	Steel ST52
Sulfur dichloride	
Th (IV) chloride	
Th (IV) fluoride	
Thionyl chloride	
ThO$_2$ (Thorium oxide)	
Thorium metal	
Thorium nitrate (tetrahydrate)	

Titanium	
Titanium (IV) chloride	Titanium chloride
Tributyl phosphate	Tributyl phosphate
Tritium	
Tungsten	
U (IV) chloride	
U (IV) fluoride	
U_3O_8 (Triuranium octoxide)	NUFCOR (U_3O_8)
UO_2 (Uranium oxide)	
UO_3 (Uranium trioxide)	
Uranium metal	
	Uranyl Hydroxide (UH)
	Uranyl Peroxide(UO_4)
Uranyl nitrate	
Used TRUEX solution (CMPO/TBP)	
UTEVA solid (resin bead with CMPO coating	
Xenon	
Xylenes	
	Yankee Yellow (SDU)
Zinc bromide	
Zirconium	