IAEA
International Atomic Energy Agency

Experts and Users Advisory Meeting on

Laser Induced Breakdown Spectroscopy

Convened at IAEA Headquarters
Vienna, Austria
7-11 July 2008

Scope

This preparatory paper is intended to initiate discussion and identify issues to be addressed at the forthcoming Experts and Users Advisory Meeting on *Laser Induced Breakdown Spectroscopy (LIBS) for Safeguards Applications*. The meeting will provide the International Atomic Energy Agency (IAEA) Department of Safeguards with an opportunity to bring together LIBS experts and safeguards specialists to investigate the full range of use of LIBS based techniques for safeguards applications, including verification, complementary access, environmental sampling and monitoring.

The meeting participants will:

- Review end-user needs for detection, measurement and monitoring of materials;
- Review concepts and techniques for LIBS use in IAEA safeguards verification and detection applications;
- Discuss the latest developments in (safeguards-related) LIBS research and assess the relevance to IAEA safeguards;
- Define the most appropriate uses of LIBS for safeguards applications;
- Formulate an essential set of user requirements for each specific application;
- Devise effective strategies to manage LIBS development tasks from concept to implementation;
- Establish an estimated development time-frame and resource requirements for each application and safeguards scenario.

The Division of Technical Support (SGTS) within the Department of Safeguards will review the outcome of the meeting and will recommend the most promising techniques for further development or evaluation. Where necessary, new research and development (R&D) tasks will be defined and undertaken through the IAEA's Member States Support Programme (MSSP) system.

Table of Contents

1 Introduction

A principal recommendation resulting from the experts and Safeguards departmental staff attending the September 2006 Technical Meeting on *Application of Laser Spectrometry Techniques in IAEA Safeguards* was to “pursue the development of [a] novel complementary access instrument based on laser induced breakdown spectroscopy (LIBS) for the detection of gaseous and solid signatures and indicators of nuclear fuel cycle processes.” To implement that recommendation, a task was initiated with the Canadian Member State Support Programme (MSSP) to develop a prototype transportable LIBS system for safeguards applications

Over the course of the task, NTU has become increasingly aware of the extensive body of work that has been undertaken on the use of LIBS for industrial detection, measurement and monitoring applications, as well as its wide range of operating methodologies. Given the potential Safeguards benefits that LIBS-based equipment can deliver and the current state of the art generally, NTU now seeks direction from its end-users and advice from LIBS experts through the MSSP system.

This paper will introduce proposed working methodologies for LIBS systems and it will set priorities and guidelines for discussion allowing experts participating in the meeting to provide recommendations for further, targeted, R&D. Experts will work in cooperation with Department of Safeguards representatives from the Division of Technical Support (SGTS), the Division of Concepts and Planning (SGCP), the Division of Information Management (SGIM), the Safeguards Analytical Laboratory (SAL) and Safeguards Inspectors from the Operations Divisions.

At present, it is envisaged that LIBS systems could be used under a number of scenarios, these are listed below:

- Complementary Access (CA)
- In-line monitoring
- Pre-screening for environmental samples

The following sections outline these in further detail and define the basic need for each scenario.

2 Complementary Access

Under the Model Additional Protocol (AP) States must provide information about, and allow IAEA inspector access to, all parts of their nuclear fuel cycle - including uranium mines, fuel fabrication and enrichment plants, and nuclear waste sites - as well as to any other location where nuclear material is or may be present. Furthermore, the State must provide information on, and IAEA short-notice access to, all buildings on a nuclear site[1].

When undertaking a CA inspection a number of defined activities can be carried out under the Model Additional Protocol. These include, inter alia, collection of environmental samples and utilization of radiation detection and measurement devices. It is envisaged that an appropriate LIBS system would be capable of being used in this circumstance to provide the inspector with immediate identification of unknown material, thereby allowing appropriate and timely modification of the inspection process to resolve any anomalies.

At present, we envisage two operational scenarios under complementary access: the first being the identification of *accessible* materials with a portable instrument e.g identification of yellowcake powder (we shall define this as 'handheld identification'); the second being identification of *inaccessible* materials with a portable instrument e.g. the identification of items within a hot cell ('standoff identification'). These scenarios are outlined further below.

2.1 The Need for Handheld Identification

A Needs Gathering Workshop was hosted by the Novel Technology Unit in late 2007, in cooperation with the Department of Safeguards Division of Concepts and Planning (SGCP), with the purpose of soliciting needs directly from the user community (IAEA Safeguards Inspectors). During the workshop participants were clear in voicing their desire for instrumentation that will improve their ability to undertake in-field sampling, analysis and measurements and which will improve on-site inspection efficiency. A small selection of some of the many comments expressed is reproduced below:

- Need for detection capability for Np & Am (to ensure that they are not being diverted out of the reprocessing process streams)
- Need for in-field quantative measurements (general request covering all materials)
- Need for in-field isotopic composition measurements (general request covering all isotope)
- Need onsite method to screen content/use of safeguards related items, such as pipes, drums, liquids, rags, laundry, stacked items, etc.

[1] For general background on IAEA Safeguards and the Model Additional Protocol, participants are direct to Appendix A where a brief overview is given

These comments reinforced one of the principal recommendations from the 2006 ‘Technical Meeting on Application of laser Spectrometry to IAEA Safeguards’ to “pursue the development of [a] novel complementary access instrument based on laser induced breakdown spectroscopy (LIBS) for the detection of gaseous and solid signatures and indicators of nuclear fuel cycle processes”. This need and recommendation led to the tasking of the the Canadian MSSP to develop a prototype transportable LIBS system for safeguards applications.

At present, this task is at the stage of moving from laboratory prototype to miniaturization and more information on the current status of the task and results obtain thus far will be given during a presentation at the meeting.

It is expected to refine the end-user needs and formulate the essential set of user requirements for this capability during the meeting.

2.2 The Need for Standoff Identification

As was mentioned in the Introduction, during the course of the above task, NTU has become increasingly aware of the extensive body of work that has been undertaken on the use of LIBS for industrial detection, measurement and monitoring applications, as well as its wide range of operating methodologies. Of interest to the Department of Safeguards is the use of LIBS for standoff detection using either open path geometry or a fibre optic cable.

For example, results from the previously referenced Needs Gathering Workshop demonstrated a clear issue with the efficient verification of the use of hot cells. A selection of comments from end-users is given below:

- Need easier, quicker, cheaper method to determine if medical isotopes have been produced or some other proliferant used in a hot cell.
- Would like hot cell sample screening in real time
- Request capabilities that enable inspectors to confirm what is in rabbits or experimental ports
- Require improved detection and measurement methods and/or instruments for inside hot cells
- Request capabilities to verify the use or absence of use of hot cells for “low-tech” reprocessing

The Novel Technologies Unit is aware of previous work undertaken in verifying material within a hot cell using either open path or fibre optic methods and would like to take the opportunity of the meeting to collate available knowledge on the subject.

During the meeting it is expected to develop the end-user needs for the use of LIBS in the verification of hot cells and formulate the essential set of user requirements for this capability. It will also be necessary to address safety

aspects of the system and to establish the estimated development time-frame and resources requirement to bring the system to a Category A safeguards instrument.

The NTU is also aware of other work undertaken to verify the contents of a spent fuel pond using LIBS with an umbilical fibre optic, again we would like to take the opportunity of the meeting to collate available knowledge on the subject and match this against the needs of the end-user.

3 In-line Monitoring

A further area of interest which was highlighted by end-users at the Needs Gathering Workshop was the need for improvements to the Agency's real time process monitoring abilities. Comments were received regarding the enrichment, reprocessing, conversion and reactor areas of the nuclear fuel cycle and a selection of these are given below:

- Need improved ability to measure/monitor reprocessing plant waste stream
- Need real time monitoring of flows through a reprocessing plant facility
- Require clear process monitoring and verification of feed, intermediate and final production in conversion plant

The NTU is aware of the availability of LIBS systems for on-line process control in the metals production industry and work undertaken on using LIBS as a continuous emissions monitor at incinerators. We intend to discuss the applicability of LIBS to continuously monitor target materials relevant to safeguards.

During the meeting it is expected to develop the end-user needs for the use of LIBS for continuous monitoring of target material for various stages of the nuclear fuel cycle and to match this to current state-of-the-art LIBS techniques. If possible solutions are envisaged then it will also be necessary to establish the estimated development time-frame and resources requirement to bring the system to a Category A safeguards instrument.

4 Environmental Sample Screening

Since 1996, the IAEA has been implementing environmental sampling for Safeguards as a strengthening measure designed to detect clandestine or undeclared nuclear activities in countries subject to full-scope safeguards.

4.1 Current Sampling procedure

In general, samples are taken by trained inspectors using standardized sampling kits and approved sampling protocols according to the facility-specific sampling plans; these samples are then forwarded to Clean Laboratory for Safeguards for analysis. The Clean Laboratory facility, based at the Safeguards Analytical Laboratory, Siebersdorf near Vienna is specifically designed for clean handling of sampling materials and samples which significantly reduces the risk of cross contamination which might lead to incorrect safeguards conclusions. The Clean Laboratory consists of over 200 m^2 of laboratory space, with approximately 100 m^2 at Class-100 cleanliness level.

Upon arrival at the facility the samples are given a code number to maintain confidentiality about their origin. The samples are then measured by low-background gamma spectrometry to detect the presence of actinide elements (primarily U and Pu) and fission or activation products (such as ^{60}Co, ^{137}Cs, ^{106}Ru, etc.); the samples are then measured by X-ray fluorescence spectrometry to detect the presence of U, Pu or other important elements. Alpha/beta counting is applied to radioactive samples to detect actinides or beta-emitting isotopes such as ^{3}H, ^{90}Sr or ^{99m}Tc. Scanning electron microscopy is used to examine small particles removed from environmental samples. The size and morphology of these particles can be examined at high magnification and their elemental composition can be measured with X-ray fluorescence spectrometry using the electron probe attachment.

Following the screening measurements, sub-samples are distributed to laboratories of the IAEA Network of Analytical Laboratories (NWAL) for more detailed analyses. Selected samples are chosen for measurement in the Clean Laboratory by isotope dilution thermal ionization mass spectrometry, using a highly-sensitive instrument equipped with pulse-counting detection. The ultimate sensitivity of this method is in the femtogram range (10^{-15} grams) for Pu and the picogram (10^{-12} grams) range for U.

Upon completion of analysis the results are evaluated by the Inspection Measurement Quality section of SGIM which prepares an evaluation report that is supplied to inspectors to allow them to compile a report that can be fed into the final State Evaluation.

Turnaround time from sample collection to analysis and reporting varies according to circumstances; however, it is of the order of 2-4 months, with the shipping of samples accounting for a significant proportion of this time, taking on average 45 days for U samples and 58 days for Pu samples.

4.2 The Need for a Screening Tool

There are 2 specific instances which require enhanced screening tools to improve efficiency.

- Pre-screening of ES on site before they are submitted for analysis, to ensure that the number of sparse samples entering the system is reduced to a minimum
- Pre-screening of ES at the laboratory to provide higher sensitivity or selectivity compared to those screening methods already in operation.

During the meeting it is expected to present the end-user needs for the use of LIBS for the pre-screening of environmental samples and to match this to current state-of-the-art LIBS techniques. If a possible solution is envisaged then it will also be necessary to establish the estimated development time-frame and resources requirement to bring the system to a Category A safeguards instrument.

5 Preparation and Issues for the Experts Meeting

While LIBS promises to increase the Agency's capabilities in the areas of nuclear safeguards verification and undeclared activity detection, there are issues requiring expert attention and guidance that need to be addressed, both prior to, and during the meeting.

Participants are kindly requested to undertake the following prior to the meeting:

- If necessary, become familiar with the safeguards system of the IAEA; using open source and other available information;
- If necessary, become familiar with the stages of the nuclear fuel cycle; using open source and other available information;
- Suggest other useful safeguards applications based on LIBS for both on-site and remote detection other than those described in preceding sections.

The following links are provided for information purposes

Department of Safeguards Website
http://www.iaea.org/OurWork/SV/Safeguards/index.html

The Safeguards System of the International Atomic Energy Agency
http://www.iaea.org/OurWork/SV/Safeguards/safeg_system.pdf

Topical Booklets & Articles on IAEA Safeguards
http://www.iaea.org/Publications/Booklets/sv.html

IAEA Safeguards Glossary
http://www-pub.iaea.org/MTCD/publications/PDF/nvs-3-cd/Start.pdf

The Nuclear Fuel Cycle – From Ore to Waste, ed. P.D. Wilson, OUP, 1996
http://www.oup.com/uk/catalogue/?ci=9780198565406

The Nuclear Fuel Cycle: Analysis and Management; R. Cochran, ANS, 1999
http://www.ans.org/store/vi-350015

During the meeting, participants will be requested to contribute to general discussions, and will be requested to deliberate upon specific findings and issues.

Appendix A – Possible Indicators and Signatures

The following is a list of some of the important materials associated with some key nuclear processing stages that you may find useful. For purposes of discussion we define 'indicators' as *entities that go into making the process operative*, such as resources, materials, related R&D etc. and 'signatures' as *entities produced by the process when it is in operation*, such as, process by-products, end material, energy emanations etc.

- Uranium
- Plutonium
- Thorium
- Uranium metal or alloys
- Uranium compounds
- Uranium dust
- UF_5
- UF_6
- Uranium chlorides
- Fission and activation products
- Noble gases
- Special steels
- Special oils for centrifuges (e.g. fomblin)
- Centrifuge test gases (e.g. heavy freons, SF_6)
- Graphite
- Freon, Glycol, Dry nitrogen
- Fluorinating agents (F_2, ClF_3)
- Ni powder
- Ti salts
- Be, Zr oxide
- Na, Mg or K metal or alloy
- Tantalum
- Neutron poisons (B, Cd, In, Sm, Eu, Gd, Hf)
- Nitric acid
- Gd nitrate
- Al nitrate
- Methyl isobutyl ketone
- Dibutoxi diethyl ether
- Tri-n-butyl phosphate
- Thenoyltrifluoracteone
- Tri-lauryl amine
- Boron carbide
- Hydrazine
- Hydroxylamine
- Formic acid
- Oxalic acid
- Hydrochloric acid
- HDO (semiheavy water)
- HTO (partially tritiated water)

Appendix B - IAEA Safeguards Overview[2]

In order to ensure that all meeting participants are familiar with IAEA Safeguards the following text is provided for information purposes.

What are safeguards and what role do they play?

Safeguards are activities by which the IAEA can verify that a State in compliance with its international commitments not to use nuclear programmes for nuclear-weapons purposes. The global Nuclear Non-Proliferation Treaty (NPT) and other treaties against the spread of nuclear weapons entrust the IAEA as the nuclear inspectorate. Today, the IAEA safeguards nuclear material and activities under agreements with more than 140 States.

Within the world's nuclear non-proliferation regime, the IAEA's safeguards system functions as a confidence-building measure, an early warning mechanism, and the trigger that sets in motion other responses by the international community if and when the need arises.

Over the past decade, IAEA safeguards have been strengthened in key areas. Measures aim to increase the likelihood of detecting a clandestine nuclear weapons programme and to build confidence that States are abiding by their international commitments

What verification measures are used?

Safeguards are based on assessments of the correctness and completeness of a State's declared nuclear material and nuclear-related activities. Verification measures include on-site inspections, visits, and ongoing monitoring and evaluation. Basically, two sets of measures are carried out in accordance with the type of safeguards agreements in force with a State.

- One set relates to verifying State reports of declared nuclear material and activities. These measures – authorized under NPT-type comprehensive safeguards agreements – largely are based on nuclear material accountancy, complemented by containment and surveillance techniques, such as tamper-proof seals and cameras that the IAEA installs at facilities.

- Another set adds measures to strengthen the IAEA's inspection capabilities. They include those incorporated in what is known as an "Additional Protocol" – this is a legal document complementing comprehensive safeguards agreements. The measures enable the IAEA not only to verify the non-diversion of declared nuclear material but also to provide assurances as to the absence of undeclared nuclear material and activities in a State.

---

[2] Taken from http://www.iaea.org/Publications/Factsheets/English/sg_overview.html

What kinds of inspections are done?

The IAEA carries out different types of on-site inspections and visits under comprehensive safeguards agreements.

- *Ad hoc* inspections typically are made to verify a State´s initial report of nuclear material or reports on changes thereto, and to verify the nuclear material involved in international transfers.

- *Routine inspections* - the type most frequently used - may be carried out according to a defined schedule or they may be of an unannounced or short-notice character. The Agency´s right to carry out routine inspections under comprehensive safeguards agreements is limited to those locations within a nuclear facility, or other locations containing nuclear material, through which nuclear material is expected to flow (strategic points).

- *Special inspections* may be carried out in circumstances according to defined procedures. The IAEA may carry out such inspections if it considers that information made available by the State concerned, including explanations from the State and information obtained from routine inspections, is not adequate for the Agency to fulfil its responsibilities under the safeguards agreement.

- *Safeguards visits* may be made to declared facilities at appropriate times during the lifecycle for verifying the safeguards relevant design information. For example, such visits may be carried out during construction to determine the completeness of the declared design information; during routine facility operations and following maintenance, to confirm that no modification was made that would allow unreported activities to take place; and during a facility decommissioning, to confirm that sensitive equipment was rendered unusable.

What is the Additional Protocol to safeguards agreements?

The Additional Protocol is a legal document granting the IAEA complementary inspection authority to that provided in underlying safeguards agreements. A principal aim is to enable the IAEA inspectorate to provide assurance about both declared and possible undeclared activities. Under the Protocol, the IAEA is granted expanded rights of access to information and sites.

An overview of the strengthened safeguards measures under Additional Protocols and comprehensive safeguards agreements follows:

Measures under Additional Protocols

- State provision of information about, and IAEA inspector access to, all parts of a State's nuclear fuel cycle - including uranium mines, fuel fabrication and enrichment plants, and nuclear waste sites - as well as to any other location where nuclear material is or may be present.

- State provision of information on, and IAEA short-notice access to, all buildings on a nuclear site. (The Protocol provides for IAEA inspectors to have "complementary" access to assure the absence of undeclared nuclear material or to resolve questions or inconsistencies in the information a State has provided about its nuclear activities. Advance notice in most cases is at least 24 hours. The advance notice is shorter - at least two hours - for access to any place on a site that is sought in conjunction with design information verification or ad hoc or routine inspections at that site. The activities carried out during complementary access could include examination of records, visual observation, environmental sampling, utilization of radiation detection and measurement devices, and the application of seals and other identifying and tamper-indicating devices).

- IAEA collection of environmental samples at locations beyond declared locations when deemed necessary by the Agency. (Wider area environmental sampling would require IAEA Board approval of such sampling and consultations with the State concerned).

- IAEA right to make use of internationally established communications systems, including satellite systems and other forms of telecommunication.

- State acceptance of IAEA inspector designations and issuance of multiple entry visas (valid for at least one year) for inspectors.

- State provision of information about, and IAEA verification mechanisms for, its research and development activities related to its nuclear fuel cycle.

- State provision of information on the manufacture and export of sensitive nuclear-related technologies, and IAEA verification mechanisms for manufacturing and import locations in the State.

Measures under Comprehensive Safeguards Agreements

- IAEA collection of environmental samples in facilities and at locations where inspectors have access during inspections and design information verification (with sample analysis at the IAEA Clean Laboratory and/or at certified laboratories in Member States).

- IAEA use of unattended and remote monitoring of movements of declared nuclear material in facilities and the transmission of authenticated and encrypted safeguards-relevant data to the Agency.

- IAEA expanded use of unannounced inspections within the scheduled routine inspection regime.

- IAEA enhanced evaluation of information from a State's declarations, IAEA verification activities and a wide range of open sources.

- State provision of design information on new facilities and on changes in existing facilities as soon as the State authorities decide to construct, authorize construction or modify a facility. The IAEA has the continuing right to verify the design information over the facility's lifecycle, including decommissioning.

- State voluntary reporting on imports and exports of nuclear material and exports of specified equipment and non-nuclear material. (Components of this reporting are incorporated in the Model Additional Protocol).

- Closer co-operation between the IAEA and the State (and regional) systems for accounting for and control of nuclear material in Member States.

- Provision of enhanced training for IAEA inspectors and safeguards staff and for Member State personnel responsible for safeguards implementation.