ELSEVIER

Journal of Alloys and Compounds 271–273 (1998) 11–18

Journal of ALLOYS AND COMPOUNDS

Strengthening IAEA safeguards through environmental sampling and analysis

D.L. Donohue*

Safeguards Analytical Laboratory, International Atomic Energy Agency, P.O. Box 100, A-1400 Vienna, Austria

Abstract

The IAEA conducts nuclear safeguards world-wide to verify countries' compliance with international agreements such as the Treaty on the Non-Proliferation of Nuclear Weapons (NPT). For the past 25 years, the traditional safeguards tools of materials accountancy, containment and surveillance were focused on the declared nuclear materials in a country's fuel cycle. Following events in Iraq in 1991 and elsewhere, the IAEA initiated 'Programme 93+2' with the goals of strengthening the safeguards system, making it more cost-efficient and providing an enhanced ability to detect undeclared nuclear activities in States subscribing to comprehensive IAEA safeguards agreements. Environmental sampling and analysis are one important new feature introduced to aid in the detection of undeclared nuclear activities. This paper will describe the rationale behind this programme, the sampling and analytical methodology used, and the relevant quality assurance measures. The IAEA's Class-100 Clean Laboratory in Seibersdorf will be described along with the highly sensitive analytical techniques which will be employed there to determine the uranium and plutonium content and isotopic composition in environmental swipe samples collected during routine safeguards inspections. The analytical contribution of a Network of Analytical Laboratories in the Member States will also be described. © 1998 Elsevier Science S.A.

Keywords: Safeguards; Uranium; Plutonium; Environmental sampling

1. Introduction

International safeguards have been applied for over 25 years in order to verify that nuclear materials declared by a State to the IAEA are used for peaceful purposes only. Under the provisions of the Treaty on the Non-Proliferation of Nuclear Weapons (NPT), signatory States are obligated to declare all their stocks of special nuclear materials, principally uranium and plutonium, and to allow the IAEA to independently verify the declarations by applying materials accountancy techniques as well as containment and surveillance measures (such as applying seals and mounting surveillance cameras).

A watershed occurred for safeguards in 1991 when, in the wake of the Gulf War, it was discovered that Iraq—although an NPT signatory state—had mounted a large-scale clandestine programme to produce nuclear weapons. The UN Security Council passed Resolution 687 as part of the cease-fire settlement, designed inter alia to neutralize Iraq's infrastructure for producing weapons of mass destruction (chemical, biological and nuclear, and delivery systems). The Security Council set up a Special Commission to monitor compliance with UNSC Resolution 687 and, in parallel, tasked the International Atomic Energy Agency with the investigation and ultimate dismantling of Iraq's nuclear weapon programme. The IAEA Action Team which was set up within a month of the cease-fire was given the job of gathering evidence concerning what emerged as a multi-billion dollar research and development project to produce an Iraqi nuclear weapon (the Petrochemical 3 project). This project was carried out both in violation of Iraq's obligations under the NPT and notwithstanding the application of IAEA safeguards for many years to Iraq's declared nuclear materials at the Tuwaitha Research Centre south of Baghdad.

The revelations that Iraq had been engaged in illicit activities both at Tuwaitha and elsewhere throughout the country had two important consequences: the IAEA gained experience in conducting more aggressive inspections aimed at detecting undeclared or clandestine activities, and the Member States accepted the need to see IAEA safeguards strengthened and made more effective at verifying both the *correctness* and the *completeness* of States' declarations. Therefore, following recommendations by the Standing Advisory Group on Safeguards Implementation (SAGSI), the Department of Safeguards initiated 'Pro-

---

*Tel.: +43 1 206028566; e-mail: donohue@rial1.iaea.or.at

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0925-8388(98)00015-2

gramme 93+2' to study a number of proposed strengthening measures and to report its findings to the IAEA Board of Governors before the NPT Review and Extension Conference in April/May of 1995.

One of the principal strengthening measures studied under this programme was the use of environmental sampling and analysis to detect nuclear signatures which might reveal undeclared activities. In this context, a series of 12 environmental sampling field trials was carried out in and around nuclear facilities in 11 Member States. These trials sought to quantify the nuclear signatures which are released into the environment by various nuclear activities, as well as to test the sample handling and analysis protocols appropriate to such sampling. The successful outcome of these field trials led to the decision by the Board to implement environmental sampling as part of routine safeguards inspections beginning in early 1996.

In parallel with 'Programme 93+2' and based on the advice of Member State experts, the IAEA designed and built a special Class-100 Clean Laboratory for Safeguards in Seibersdorf, Austria, for the preparation of clean sampling materials and the handling, distribution and analysis of environmental samples collected by inspectors. This Laboratory, which began operation in early 1996, serves as a focal point for a Network of Analytical Laboratories (NWAL) in several Member States.

2. Experimental

2.1. Sampling kits

The Field Trials of environmental sampling which were carried out in 1993–1995 focussed on sampling inside nuclear facilities and at distances of up to 20 km away. The principle sample types taken were cotton swipes (inside and around process buildings) as well as soil, vegetation, water, sediment and biota (from outside the site boundaries). Standard sampling equipment was developed in conjunction with Member State experts, as were the protocols for sample taking and subsequent handling. The implementation of environmental sampling as part of routine safeguards inspections was started in 1996, with the collection of swipe samples in enrichment and hot cell facilities where the IAEA has existing rights of access. The other types of sample (soil, vegetation, etc.) will not be taken until additional access rights have been granted by the State authorities under a new draft legal agreement.

In any case, swipe sampling has a number of advantages over these other sample media: (1) swipe samples from inside process buildings give the highest probability of detection for undeclared activities carried out there; (2) the use of certified clean swipe media virtually eliminates the background (especially of U) which may dilute or obscure the anthropogenic nuclear signatures present; (3) swipes are small, lightweight and can be shipped and stored easily; (4) swipes are well suited to the particle analysis technique (described in a later section) which gives the maximum amount of useful information about the nuclear materials and activities present in the sampled location.

The IAEA standard cotton swipe sampling kit is shown in Fig. 1. The kits are prepared in the Class-100 area of the Clean Laboratory, and the swipes in them are chosen at random and destructively analyzed to certify that they are free of U and Pu at the nanogram level or below. In addition to the kit supplied, the inspector also needs a roll of aluminum foil to establish a clean working surface in the sampling location. Each standard kit contains seven cotton swipes and mini-grip bags for double bagging. These are used for taking a number of replicate subsamples from the same location along with a 'control' swipe of the sampler's hands to check for possible cross-contamination. The replicate subsamples are double-bagged at the time of sampling and are not opened again until they reach the analytical laboratory, which has a clean area to handle them. Stringent precautions are taken to prevent cross-contamination of the swipe samples which could lead to false safeguards conclusions. Fig. 2 shows swipe sampling in a process location.

A different swipe sampling kit is used to sample inside hot cells where remote manipulators must be used. Such swipes can be heavily contaminated with radioactivity and must be transported in special Pb-lined containers. The analysis of such samples is more limited than that applied to cotton swipes because of the restrictions on bringing radioactive materials into clean-room laboratories.

2.2. Screening measurements

Swipe samples from inspections are transported under seal to the IAEA Clean Laboratory for Safeguards and opened by a representative of the Department of Safeguards in the presence of a Health Physics technician. The samples are then given an analytical code number, and all other labeling and documentation is removed in order to preserve the confidentiality of the country and facility of origin. The first action taken in the Clean Laboratory is to screen the samples for γ activity using the equipment shown in Fig. 3. This is a low-background γ-spectrometer with a coaxial Ge detector and 10 cm of Pb shielding. The system is equipped with an automatic sample changer which can accommodate 15 Marinelli Beakers. Typical measurement time is 1 h. The raw counting results are reported (corrected for background) in counts per second. Provided that enough counts are collected, the spectrum is evaluated and a report is produced of the radioisotopes found and their activity in Bq/sample, corrected for detector efficiency.

For samples from enrichment facilities, a second type of screening is carried out which involves radioisotope-excited X-ray fluorescence measurements of the U present. This technique uses a 20 mCi ^{109}Cd excitation source and

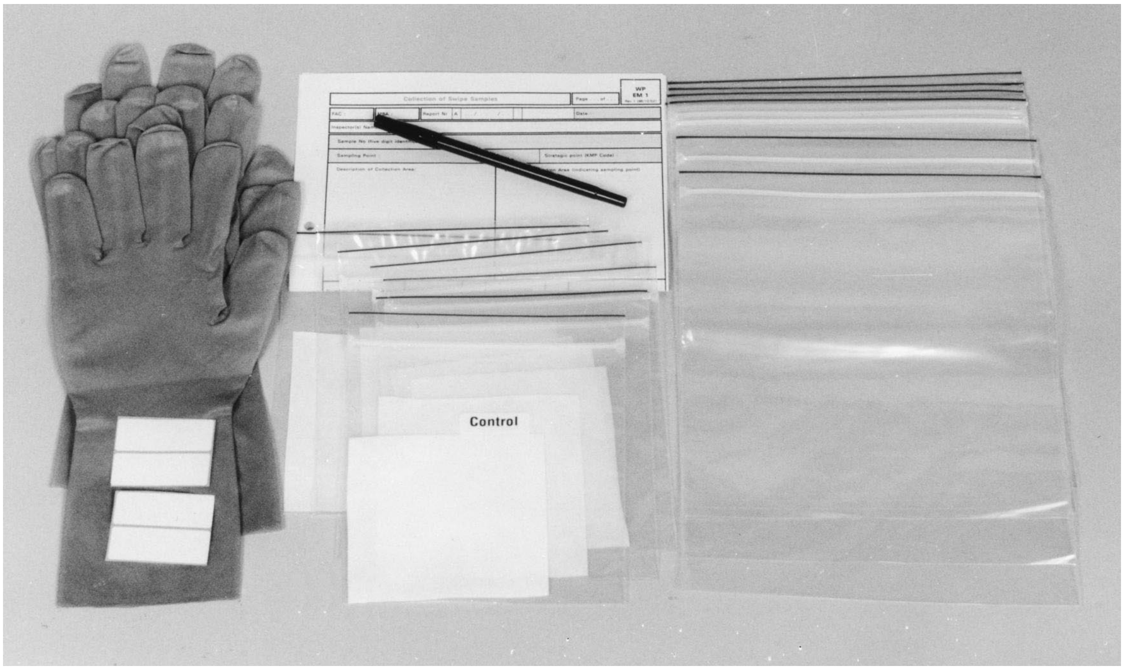

Fig. 1. IAEA cotton swipe sampling kit.

a 100-mm^2 Si(Li) detector. The measurement time is approximately 10 min and the detection limit for U is 1 μg cm^{-2}. The results of this measurement are used to decide on the further treatment or analysis of the samples—certain particle analysis techniques such as secondary ion mass spectrometry (SIMS) require a sample which is relatively rich in U.

Alpha/beta screening measurements are not routinely performed on swipe samples because of the need to expose them to the detector, thus leading to possible cross-con-

Fig. 2. Swipe sampling in a process location.

Fig. 3. High-resolution γ-spectrometer for screening swipe samples.

tamination. Measurement equipment exists in the Clean Laboratory in the form of a gas proportional counting system and a low-background liquid scintillation spectrometer. In addition, a scanning electron microscope is available with both energy and wavelength-dispersive X-ray fluorescence capability which could be used to screen for the presence of U- or Pu-containing particles and for measuring the elemental composition of such particles (in the electron-probe mode). The SEM with its XRF detectors is shown in Fig. 4.

2.3. Mass spectrometry

For more detailed measurements of U and/or Pu in environmental samples, the Clean Laboratory is equipped with a high-sensitivity thermal ionization mass spectrometer (Finnigan-MAT 262 RPQ), as shown in Fig. 5. This instrument has multiple Faraday-cup detectors, as well as an ion-counting system and high abundance sensitivity energy filtering system (reverse potential quadrupole filter). Samples are electrodeposited on Re filaments and overcoated with Pt [1] for increased ionization efficiency. An ion-counting detector system is used for small samples or minor isotopes and the Faraday collection system can be used for larger ion signals. The correction factor for mass-dependent fractionation is calculated from the measurement of certified isotopic reference materials. The ultimate detection limit for this method is governed by the cleanliness of the blank and the sample preparation chemistry, but we have demonstrated sub-pg levels of detection for U.

2.4. Sample preparation

The normal swipe samples consist of a square piece of cotton cloth which is 10×10 cm and weighs about 1 g. Depending on the analytical request, either the entire swipe is treated or it is subsampled by cutting with a clean pair of scissors into several pieces. If isotope dilution mass spectrometry is chosen as the final measurement method, a separated isotopic spike (typically ^{233}U or ^{244}Pu) is added before further treatment. Pieces of swipe smaller than 0.5 g can be dissolved in a high-pressure microwave digestion system using nitric acid. Larger pieces are ashed in an oven at 800°C in a quartz beaker, and finally dissolved in nitric acid. Separation of the U and Pu from other elements is accomplished with anion exchange in a nitric acid medium. Small amounts of perchloric acid may be used to eliminate residual organic matter. The separated U and Pu fractions are finally dried and re-dissolved in hydrochloric acid before electrodeposition on the mass spectrometer filament, using a buffered electrolyte and followed by overplating with platinum.

2.5. Measurements in the network laboratories

The laboratories in the IAEA Network of Analytical Laboratories (NWAL) are designated by the various

Fig. 4. Scanning electron microscope with X-ray fluorescence attachments.

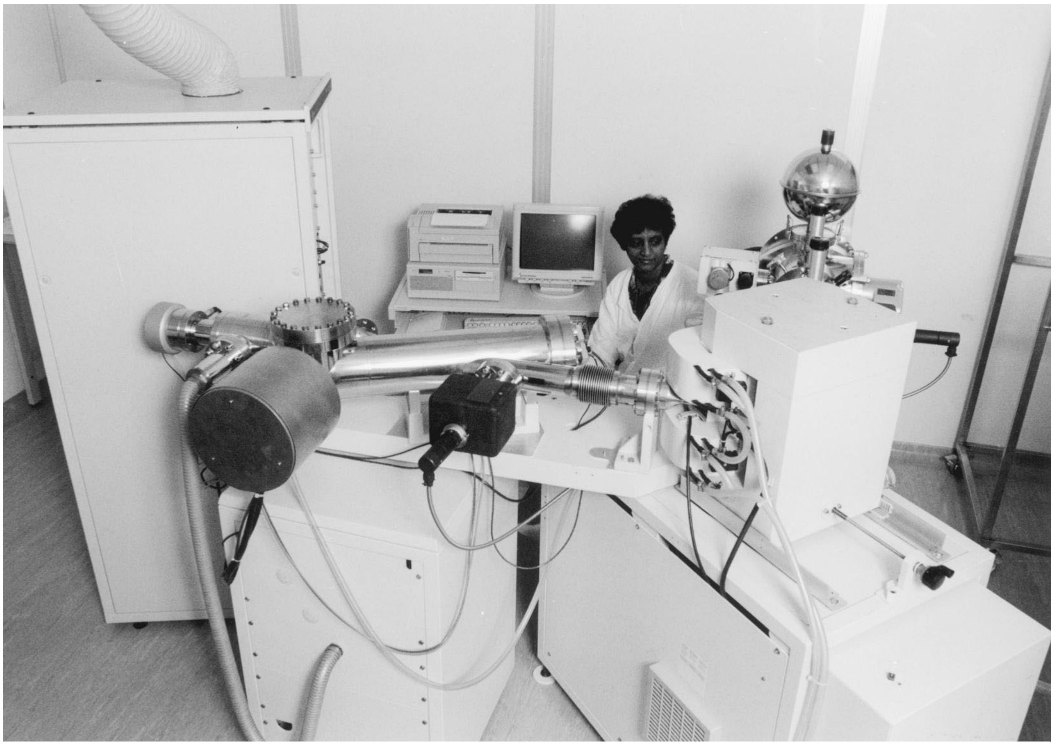

Fig. 5. High-sensitivity thermal ionization mass spectrometer.

Member States and must have a Quality Assurance system which is audited by the IAEA. These laboratories apply standard operating procedures for the handling, treatment and measurement of IAEA environmental samples. Each laboratory has its own treatment and measurement scheme, but these can be broadly divided into *bulk* and *particle* analysis methods. Bulk analysis implies the dissolution and measurement of the entire subsample; most NWAL participants use thermal ionization mass spectrometry similar to that described above.

Particle analysis involves the chemical or isotopic measurement of individual micrometer-sized particles containing U and/or Pu. In the traditional particle analysis scheme, particles of interest are located by using the fission track method, following which the individual particles are loaded onto Re filaments and measured by thermal ionization mass spectrometry. This method can be highly selective for particles containing significant amounts of fissile isotopes (^{233}U, ^{235}U, ^{239}Pu) and provides highly precise isotopic abundances for the major and minor isotopes of U and Pu. Typically, 10–20 particles are measured for each sample.

An alternative method, secondary ion mass spectrometry (SIMS) operating in the microscope mode can be used to measure large numbers of particles loaded on a conducting substrate. Ion images are formed using the isotopes of interest (^{235}U and ^{238}U, for instance) which can then be merged to obtain the isotopic ratio for each particle in the field of view. Repeating this process for many hundreds of fields results in the measurement of thousands of particles. Smaller numbers of particles (10–20) can be measured in the microprobe mode to obtain information on minor isotopes (^{234}U and ^{236}U).

3. Results and discussion

The results from the Field Trials in ‘Programme 93+2’ and from inspections since 1996 can be divided into two main groups: those from enrichment facilities and those from hot cell facilities. These are sufficiently different to be treated separately below.

3.1. Enrichment facilities

Generally speaking, enrichment of U has been carried out on a large scale using a variety of processes [2]

(1) Electromagnetic isotope separation (EMIS) was used in the US during the Manhattan Project to produce high-enriched U for the nuclear weapon dropped on Hiroshima. The method was considered too inefficient for further production and was subsequently abandoned. The Iraqi weapons programme revived it in the late 1980s and succeeded in separating several hundred grams of low-enriched product before the programme was terminated. The choice of this method by Iraq reflects the difficulty they experienced in obtaining the more sophisticated enrichment technology listed below.

(2) Gaseous diffusion isotope separation was the technology used in a number of countries in the period 1950–1980 to produce both LEU for nuclear reactors and HEU for weapons. This technique consumes large amounts of electrical power and, because it operates at above atmospheric pressure, is subject to leaks and the release of significant amounts of material. The environmental ‘footprint’ of a large gaseous diffusion plant (i.e. evidence of disturbed U isotope abundances) can extend for many kilometers from the site boundary.

(3) Stationary-wall centrifuge (Vortex-Tube) and separation-nozzle methods have been used in certain countries as an alternative to gaseous diffusion separation. These have similar energy efficiency compared to gaseous diffusion, and may also operate at above atmospheric pressure and would therefore be subject to significant releases of U to the environment.

(4) High-speed gas centrifuge separation is the most energy-efficient method in regular use for commercial production of LEU for power reactors. The most modern facilities work at below atmospheric pressure and can be operated without significant releases to the environment outside the process buildings.

3.2. Enrichment signatures

The principal environmental signature of U enrichment is the change in ^{235}U abundance compared to the natural value of 0.726 at%. Facilities producing HEU have a higher probability to be found through elevated ^{235}U abundances, whereas facilities producing LEU may also show lower ^{235}U abundances resulting from the excess of depleted material which is produced. The presence of depleted U is not unambiguous evidence of enrichment, because this material has a number of commercial, industrial or even military uses (X-ray shielding, aircraft ballast, armor-piercing munitions, etc.). Bulk analysis of samples from enrichment facilities is only moderately informative, because the results obtained are the average of all U present in the sample; small amounts of enriched U can be hidden by larger amounts of natural or depleted U. After all, the isotopic inventory of the entire process (feed, product and tails) should show an average ^{235}U content very close to the feed material which is, in most cases, natural U.

Particle analysis of samples from enrichment facilities gives a more complete picture of the process and the various materials handled. A common way to display these data consists of a scatter plot of ^{234}U versus ^{235}U, as shown in Fig. 6. Each point displayed is from the measurement of an individual particle. It can be seen that the points lie along a straight line, and that the extremes (enriched product and depleted tails) are readily seen. The slope of the line is affected by the feed and tails assay; all

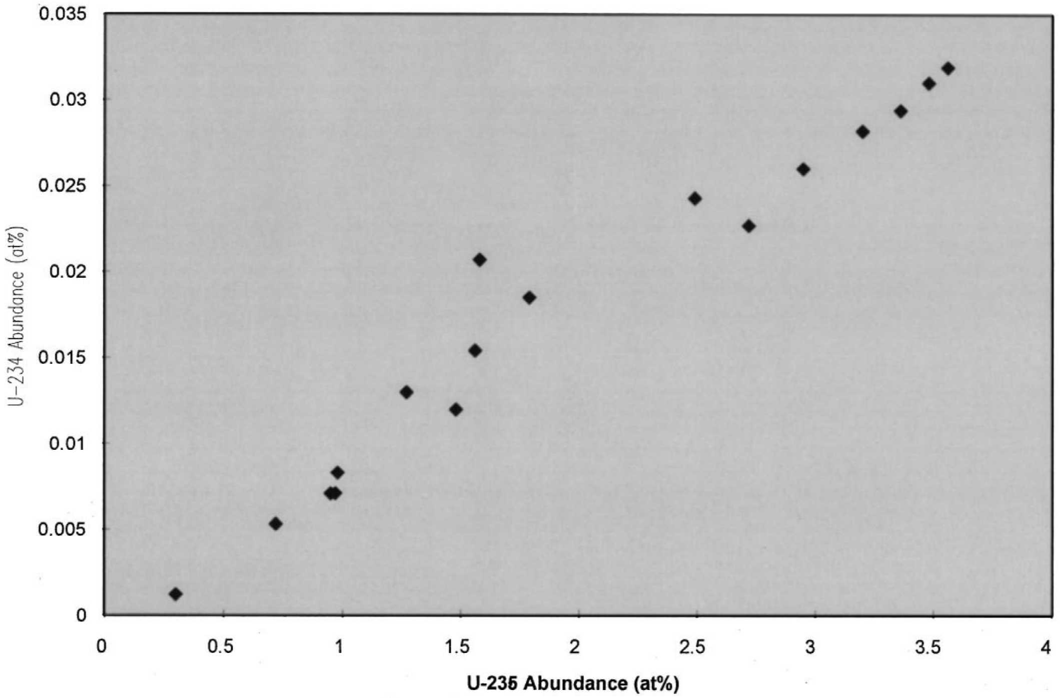

Fig. 6. Particle analysis results for an enrichment facility.

products from a given combination of feed and tails will lie on the same line. Thus, such a plot can be used to judge if all materials seen are consistent with the declared feed and tails assay, and whether the maximum declared enrichment level is exceeded. Additional information is obtained from measurement of the ^{236}U content of particles; the presence of ^{236}U in the product or tails indicates that irradiated U was used as feed material at some time in the past (recycled U from power reactors can have ^{235}U near to 0.72%, but will contain up to 0.5 at% of ^{236}U and higher than natural levels of ^{234}U).

3.3. Hot cell facilities and signatures

Hot cell facilities which have safeguards significance are used for the following purposes.

(1) Post-irradiation examination (PIE) of spent reactor fuel. The operations carried out are mechanical and microscopic testing of the cladding, as well as fission gas measurements, γ-spectrometry and other non-destructive measurements. The fuel may be physically cut, polished, etc., but there is normally no wet chemical dissolution or processing steps. The signatures of these activities consist of fission and activation products, such as ^{95}Zr/^{95}Nb, ^{106}Ru, ^{134}Cs, ^{137}Cs, as measured by γ-spectrometry, and actinides, U, Pu, Np, Am, Cm, etc., as measured by thermal ionization mass spectrometry. Reactor code modeling can be used to predict the U and Pu isotopic composition, provided that the initial fuel composition, burn-up and cooling time are given. There should, for instance, be consistency between the ^{236}U and ^{240}Pu abundances, between the Pu isotopic composition (typically ^{240}Pu>15%) and the U/Pu elemental ratio (typically U/Pu=100–200) and between the ^{241}Am/^{241}Pu ratio and the declared cooling time. The presence of short-lived fission products (^{131}I, for example) would not be expected in fuel cooled for several years.

(2) Medical isotope production, such as the manufacture of ^{99}Mo, is significantly different compared to PIE, as described above. The process involves short irradiation of U targets which may be either LEU or HEU. This is followed by dismantling of the target capsule and dissolution of the U to chemically recover the ^{99}Mo. The signatures of this operation would include certain fission products, U isotopics which show only slight changes from the target material (slightly lower ^{235}U and higher ^{236}U), very low burn-up Pu (^{240}Pu<1–2%) and no evidence of Pu separation (i.e. U/Pu ratio >1000).

(3) General-purpose hot cells attached to a research reactor would be used for irradiating various targets, for neutron activation analysis or for production of radiography or radiology sources, such as ^{60}Co or ^{137}Cs. These locations should not show the presence of fission products other than those declared, nor any actinide elements.

Table 1 shows U and Pu isotopic data from particles found in a swipe sample taken at a hot cell facility where LEU, at about 2% enrichment, was used for ^{99}Mo production. It can be seen that the ^{235}U content is as expected (2.0–2.2 at%), ^{236}U is consistent with low burn-up, as is the ^{240}Pu abundance (0.6–0.8 at%).

Table 1
Particle analysis results from a hot cell facility

Particle number	^{234}U (at%)	^{235}U (at%)	^{236}U (at%)	^{240}Pu (at%)
1	0.0185	2.096	0.0179	0.579
2	0.0190	2.105	0.0222	0.639
3	0.0207	2.115	0.0307	0.594
4	0.0189	2.142	0.0129	0.759

4. Conclusions

Environmental sampling and analysis has been shown to be a valuable addition to the traditional safeguards tools of materials accountancy, containment and surveillance. The use of highly sensitive analytical measurement methods combined with swipe sampling significantly increases the probability of detecting undeclared nuclear activities, and will help to deter such activities by the risk of timely detection. Since the implementation of these methods, the IAEA is better able to assure the world community about the correctness and completeness of States' declarations pursuant to the NPT and comprehensive safeguards agreements.

References

[1] D.J. Rokop, R.E. Perrin, G.W. Knobeloch, V.M. Armijo, W.R. Shields, Anal. Chem. 54 (1980) 957–960.

[2] Nuclear Material Safeguards for Uranium Enrichment Plants, K/ITP-524/PT1/R1, ISPO-347/R1, Martin Marietta Energy Systems, Inc., Part 1, 1994.