Bulk Analysis of Environmental Swipe Samples

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Abstract
Bulk analysis of environmental swipe samples taken within nuclear installations as part of routine IAEA inspections has proven to be a very sensitive analytical technique. The combination of chemical separations under very clean conditions with highly sensitive mass spectrometric measurements assists in the identification and characterization of uranium and plutonium signatures at ultratrace levels. The method has been applied at the IAEA’s Safeguards Analytical Laboratory in Seibersdorf, as well as many of the Network Laboratories. SAL’s Clean Laboratory Unit provides with its class-100 environment the required cleanliness to achieve unsurpassed analytical sensitivity.

1. INTRODUCTION

Environmental swipe sampling is routinely used by the International Atomic Energy Agency (IAEA) to verify the absence of undeclared nuclear activities in States subject to comprehensive safeguards. Environmental sampling and analyses probing for the completeness of facility declarations are thus complementary to the traditional safeguards activities of verifying the correctness of declared nuclear activities. Following the extensive field trial exercise during the “93+2” program, local environmental swipe sampling within facilities was determined to be the most effective method for safeguards verification purposes. Wide-area monitoring, away from specific facilities, is being explored as an additional measure for even more stringent control measures. As a result of the field trials swipe sampling (“smear tests”) in enrichment and hot-cell facilities was implemented. Repeated sampling and analysis has provided a baseline for individual facilities, allowing conclusions not only about present processes, but also historical activities that may not be related to the ongoing operations and declarations of a specific nuclear facility.

Environmental samples, including swipe samples from within nuclear facilities, cover a wide range of sample matrices as well as concentrations of possible nuclear materials. Signatures ranging from natural environmental levels to those found in nuclear installations such as enrichment, fuel fabrication, and reprocessing facilities are anticipated. To accommodate such a diverse spectrum of samples laboratory space was needed away from the traditional Safeguards Analytical Laboratories (SAL). The IAEA designed and built a class-100 clean laboratory for the preparation of sampling materials and the handling, distribution and analysis of environmental samples collected by inspectors [1]. For samples with rich nuclear signatures separate laboratory space, away from the Clean Laboratory, has been established.

Bulk analysis is one approach used to obtain detailed information of uranium and plutonium collected with environmental swipe samples. The method requires the decomposition of the swipe sample followed by chemical separation and the mass spectrometric measurement using Thermal Ionization Mass Spectrometry (TIMS) [1]. This method has unsurpassed sensitivity and can detect uranium and plutonium concentrations in the sub-picogram range.
2. Experimental

2.1 The Clean Laboratory

The IAEA’s Clean Laboratory provides about 200 m² of floor space. It houses areas for the preparation of sampling kits and control materials, the physical and chemical manipulation of samples for bulk and particle analysis, and the instrumentation areas. The facility uses particulate filtered air conditioned at 22° C and 40 – 60 % relative humidity. The pressure inside the laboratory is higher than atmospheric pressure and employs a pressure gradient from 30 to 10 Pa between the clean sample manipulation, instrumentation, and entrance area. In general, the 85 % pre-filtered air comes from the plenum through the High Efficiency Particulate (HEPA) filter down to work benches and into the room. The HEPA filters supply air of class-100 (defined as < 100 particles of < 0.5 µm per ft³ air [5]) or better to the work areas, such as work benches and clean fume hoods. Traffic areas are rated at class 100,000 without requiring additional filtration units in these areas. Figure 1 shows a cross-sectional view of the air circulation. All interior walls are made from epoxy-covered aluminum panels. Cabinets are constructed from wood and hoods from welded polypropylene. To minimize the possibility of introducing particles generated by the deterioration of floor material and their release into the air stream the flooring is from seamless PVC.

The Clean Laboratory performs several major tasks in support of nuclear safeguards administered by the Department of Safeguards. The sampling kits are assembled in a class-100 area of the clean laboratory to ensure contamination free preparation. Swipe materials are routinely analyzed for their uranium and plutonium concentration using bulk analytical
techniques, and only those devoid of the elements of interest to safeguards are used in the sampling kits. Samples returned from inspections are handled at the Clean Laboratory, including screening of all samples [4], archival storage and distribution to the Network of Analytical Laboratories (NWAL). Control samples are prepared and administered to the NWAL, to ensure continued quality of analytical results. Finally, the Clean Laboratory also participates as one of the Safeguards Network Laboratories and bulk analysis on environmental swipes is one of the main services delivered.

To ensure continued operation and cleanliness of the clean laboratory, three main control mechanisms are employed. Firstly, monthly particle counts are taken and recorded for each individual area of the laboratory, to verify compliance with the air cleanliness requirement set forward in the design specifications of the laboratory. Complementary to the low particulate concentrations the ambient levels of uranium are checked for all vital work areas by virtue of room blanks on a rotating basis at least twice a year. Room blanking refers to collecting particulates, including aerosols, that settle in beakers exposed to the laboratory environment for set periods of time. These materials are handled similar to real samples and analyzed for uranium using isotope dilution mass spectrometry. Finally, the laboratory is re-certified annually to its design specifications by an external contractor.

2.2 SAMPLE PREPARATION

Bulk analysis of environmental swipe samples is a destructive method and includes decomposition of the sample including the swipe matrix, separation and purification of plutonium and uranium, and the mass spectrometric measurement.

Environmental swipes are either taken using 10 cm x 10 cm cotton or round cellulose wipers of about 2.5 cm diameter designed for remote manipulators and used exclusively inside of hot-cells. To facilitate the separation and purification of uranium and plutonium the sample has to be dissolved and a homogeneous aqueous solution prepared. Decomposition of the organic matrix is done routinely by oxidation using either high-temperature ashing or wet-chemical decomposition. Thermal ashing is done in quartz boats under a constant flow of oxygen in a tube furnace. The ashing procedure is carried out as a two step process with a pre-ashing at 450° C and the final decomposition at 650° C. The process takes about 4 hours and leaves a residue, which readily dissolves in nitric acid. Wet chemical ashing, or dissolution, is done in quartz beakers of low uranium contents using nitric and perchloric acid mixtures. Because of the potential hazard perchloric acid is added to the nitric acid only after the wiper is almost completely oxidized.

Microwave assisted wet chemical decomposition and cold plasma ashing using a radio-frequency generated oxygen plasma have been tested but are not used routinely. The commercial microwave digestion systems are not practical for swipe samples as dissolution requires the sample to be distributed over several vessels because of limitations of the maximum amount of organic material. To decompose a 10 cm x 10 cm wiper weighing about two grams four vessels are required. Plasma ashing, on the other hand, is a very elegant method as it produces an extremely clean residue, but it is limited to one sample at a time. With several hours needed for a complete ashing procedure and cleaning in between samples this method is not well suited for high throughput, unless multiple systems, which are quite costly, are available.

Subsequent to the ashing procedure and dissolution of the residue in nitric acid, the sample solution is split into two portions. One fraction is used for the determination of the uranium
and plutonium concentrations by isotope dilution mass spectrometry (IDMS) and the other fraction for the mass spectrometric determination of the isotopic composition of the uranium and plutonium. For the IDMS technique the sample is spiked with a few nanograms of $^{233}$U, such as the IRMM 040/1 $^{233}$U = 99.70%, and a few hundred picograms of $^{244}$Pu, such as the IRMM 042a $^{244}$Pu = 97.88%, prior to the separation and purification procedure.

All major chemical separation procedures require the uranium (U) and plutonium (Pu) to be in the oxidation state U (VI) and Pu (IV). To obtain a chemically homogeneous solution prior to the separations a reduction-oxidation cycle is applied to ascertain plutonium to be in the Pu (IV) state. The addition of a few micro-moles of ferrous solution followed by the addition of a few micro-moles of sodium nitrite ascertains that the valency adjustment to plutonium (IV) is complete. Any plutonium (III) and to a lesser extent plutonium (VI) will be lost in the subsequent separations. The adjustment of the oxidation state is even more important for the successful application of IDMS, to ensure complete equilibration between the sample’s native plutonium contents and the plutonium added via the spike. The subsequent separation of plutonium and uranium from the sample matrix, as well as chemical and isobaric interferences is performed either by solid phase extraction (SPE) or ion exchange techniques.

The SPE technique uses tri-n-octylphosphine-oxide (TOPO) as a selective extractant of plutonium and uranium. The TOPO is coated onto silicagel as stationary phase and filled into plastic columns (8.4 mm inner diameter to height of 26 mm yielding a volume of 1.4 mL). After the valency adjustment, the solution is adjusted to 3M HNO3 and loaded onto a pretreated TOPO column. Americium, fission products, and most other elements such as iron are washed off the column with 10 mL 3M HNO3. The plutonium is eluted with about 10 mL of a mixture of 0.1 M hydroiodic acid in 1.7M HNO3 reducing Pu(IV) to Pu(III). Next the column is preconditioned with a few mL of water and the uranium is eluted in a volume of 4 mL 0.7 M NH4CO2NH2. The plutonium and uranium fractions are evaporated to dryness, fumed twice with concentrated nitric acid to destroy organic residue, converted to the chloride form with hydrochloric acid and redissolved in 20 µL 1.5M HCl right before the filament preparation.

The procedure using ion exchange resins to separate plutonium and uranium is based on the stability of the respective plutonium and uranium anionic complexes that form in nitric acid and hydrochloric acid. After the valency adjustment, 1 mL of 8M HNO3 is added and the solution loaded onto an preconditioned anion exchange column. The anion columns are prepared by filling 2 mL of Dowex MP-1 (50 - 100 mesh, Cl- form) into a BioRad polypropylene column with an inner diameter of 5 mm. After washing the column with another 5 mL 8M HNO3, the uranium fraction is collected in the next 20 mL 8M HNO3. Plutonium is eluted subsequently by switching to a solution of 48% hydroiodic acid dissolved in concentrated hydrochloric acid in a volume ratio of 1:9. The uranium and plutonium fractions are evaporated to dryness. The uranium fraction is redissolved in 1 mL 8M HCl and loaded on an anion exchange columns, as described for the nitrate exchange before, preconditioned with 8M HCl. The column is washed with 20 mL 8M HCl and the uranium fraction collected in 15 mL 0.5M HCl. The plutonium fraction is redissolved in concentrated hydrochloric acid in a volume ratio of 1:9. The uranium and plutonium fractions are evaporated to dryness. The uranium fraction is redissolved in 1 mL 8M HCl and loaded on an anion exchange columns, as described for the nitrate exchange before, preconditioned with 8M HCl. The column is washed with 20 mL 8M HCl and the uranium fraction collected in 15 mL 0.5M HCl. The plutonium fraction is redissolved in concentrated HCl mixed with a few drops of 30% H2O2 (1 drop H2O2 per 10 mL of HCl) and loaded on an anion exchange column. The column has been preconditioned with 10 mL HCl/ H2O2 solution. After loading the plutonium fraction, the column is washed with 15 mL of the HCl/H2O2 mixture, followed by 6 mL 8M HNO3. Subsequently, the plutonium is collected in a volume of 12 mL 8M HBr. Both uranium and plutonium fractions are evaporated to dryness and fumed three times with a drop of 70% HClO4. Right before the filament preparation, the residues are redissolved in 20 µL 1.5 M HCl.
2.3 **MASS SPECTROMETRY**

The Clean Laboratory is equipped with a high-sensitivity thermal ionization mass spectrometer (Finnigan-MAT 262 RPQ). 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). Measurement of the small amounts of uranium and plutonium isolated from environmental swipe samples, even after spike addition, are measured on the ion-counting system. The separated uranium and plutonium fractions are co-electroplated with platinum on rhenium filaments and overplated with a thin layer of platinum for increased ionization efficiency [2]. The mass spectrometer system is equipped with one ion counting system, separate masses are measured sequentially rather than simultaneously. The correction factor for mass-dependent fractionation is determined from the measurement of certified reference materials. The detection limit for this method is largely governed by the cleanliness of the sample preparation activities.

3. **RESULTS AND DISCUSSION**

The uranium and plutonium separation schemes of environmental swipe samples are designed for maximum efficiency. Chemical yields are typically between 70 – 90 % for both elements, and ion currents achieved on the mass spectrometer are comparable to standard materials in many cases. Both separation schemes discussed, the TOPO and ion exchange method, have been optimized for certain ranges of uranium and plutonium concentrations. The TOPO method accommodates plutonium and uranium contents in the microgram to milligram range, but chemical recoveries decline rapidly for lower concentrations. Slight adaptations of the method allow successful application also for contents as low as a couple of hundred nanograms. The ion exchange method has been successfully used for uranium and plutonium concentrations in the low nanogram to low picogram range. It also produces very pure fractions required for the successful filament preparation by electroplating. One minor disadvantage of the ion exchange technique is the inadequate removal of iron, if a sample’s native iron content is too high. Detailed, qualitative X-ray screening of the swipe samples prior to their decomposition provides sufficient compositional information of the samples to assist in adapting routine chemical separation schemes as necessary.

In trace and ultratrace analysis the ultimate detection of the overall analytical process is determined by the blank levels. Table 1 summarizes typical blank levels obtained by the quality control program applied at the Clean Laboratory. The results for the room blanks indicate that the work environment inside of the laboratory is kept extremely clean and well within design specification. As guidance, just one particle of UO<sub>2</sub> with a diameter of 1µm contains about $10^{10}$ atoms ($10^{-11}$g) of uranium. With a detection limit for uranium using TIMS of about $10^7$ atoms ($5\times10^{15}$g) this signal should be detectable. Loading blanks are prepared routinely by electroplating pure reference or standard material onto a filament to observe instrumental contributions to the background. Performing TIMS measurements of these loading blanks suggest that a more reasonable sensitivity is about two orders of magnitude higher than the one quoted as instrumental detection limit. This is most likely an artifact of the additional sample handling procedure. Room blanks show on average a slightly higher signal compared with loading blanks. This is attributed to isobaric interferences during the mass spectrometric measurement, rather than a true uranium or plutonium signal.
### Table 1. Average, long-term results obtained by the Clean Lab’s quality control program

<table>
<thead>
<tr>
<th>Material</th>
<th>U</th>
<th>$^{235}$U</th>
<th>$^{238}$U</th>
<th>Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[ng]</td>
<td>[at %]</td>
<td>[at %]</td>
<td>[pg]</td>
</tr>
<tr>
<td>Cotton</td>
<td>18.8 ± 17.1</td>
<td>0.776 ± 0.117</td>
<td>99.16 ± 0.25</td>
<td>3.9 ± 4.8</td>
</tr>
<tr>
<td>Processing Blank</td>
<td>2.8 ± 3.9</td>
<td>1.02 ± 0.78</td>
<td>99.0 ± 0.78</td>
<td>1.5 ± 1.3</td>
</tr>
<tr>
<td>Room Blank</td>
<td>$(2.0 ± 0.9) \times 10^{-3}$</td>
<td>---</td>
<td>---</td>
<td>$(5.0 ± 0.1) \times 10^{-3}$</td>
</tr>
<tr>
<td>Loading Blank</td>
<td>$(5.0 ± 0.1) \times 10^{-4}$</td>
<td>---</td>
<td>---</td>
<td>$(5.0 ± 0.1) \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Processing blanks and blanks prepared by analyzing the swipe materials are measures of the true background levels attainable during routine analysis. Processing blanks are good indicators for the cleanliness of equipment and chemicals used in routine analysis. Analysis of the swipe matrix is a mandatory prerequisite to assess the levels of uranium and plutonium prior to their use in routine inspections. Both types of blanks are several orders of magnitude higher than environmental type of blanks. Processing blanks can be lowered only by eliminating contamination at the pico- and nanogram level from equipment and chemicals. Considering that only costly suprapure chemicals are used in our routine analysis, this is not a trivial task. On the other hand, the uranium contents typically found in cotton wipers can be eliminated only by switching to fully synthetic wipers. However, the concentrations assessed with the blanking efforts are quite compatible with the requirements of the overall Safeguards effort. They offer, however, an analytical challenge and SAL will continue to enhance its performance by attempting to lower these blank levels.

The results from inspections can be subdivided into two groups, those from enrichment facilities and those from hot cell facilities. Detection of undeclared activities in enrichment facilities requires the identification of small quantities of (high) enriched material admixed to a variety of other enrichments, as well as the depleted signal of the tails. Bulk analysis provides an averaged signal over the entire sample and detection of a very small quantity of undeclared high enriched material is difficult, if not impossible. Particle analysis using secondary ion mass spectrometry (SIMS) has very much replaced bulk analysis for samples from enrichment facilities at SAL.

Hot Cell facilities with significance for safeguards are used for a variety of different purposes. Post-irradiation examination of spent reactor fuel will show uranium, plutonium, fission products, and other actinides. Measurement by TIMS can be cross-checked with results from reactor code modeling used to predict the uranium and plutonium isotopic composition, provided the initial fuel composition, burn-up and cooling time are given. There should be, for example, consistency between the $^{236}$U and $^{240}$Pu abundances, between the Pu isotopic composition and the U/Pu elemental ratio and the $^{241}$Am/$^{241}$Pu ratio and the declared cooling time. Medical isotope production, such as the manufacturing of $^{99}$Mo, is very much different. The process involves short irradiation of uranium targets which may be low or highly enriched uranium. Dismantling and chemical recovery of the molybdenum will release signatures such as fission products, uranium isotopics which only show slight changes from the initial target material, very low burn-up plutonium ($^{240}$Pu < 2%) and no evidence of plutonium separation (U/Pu ratio > 1000). Other hot cell facilities, such as those used for neutron activation analysis, irradiation of various targets, or production of various radiation sources such as $^{60}$Co. These facilities should not exhibit any evidence for fission products, other than those declared, nor any actinide elements.
Table 2. Results obtained from bulk analysis on inspection swipes

<table>
<thead>
<tr>
<th>Sample</th>
<th>U</th>
<th>$^{234}$U</th>
<th>$^{235}$U</th>
<th>$^{236}$U</th>
<th>$^{238}$U</th>
<th>Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[ng]</td>
<td>[at %]</td>
<td>[at %]</td>
<td>[at %]</td>
<td>[at %]</td>
<td>[pg]</td>
</tr>
<tr>
<td>Sample 1</td>
<td>47.2</td>
<td>0.012</td>
<td>0.729</td>
<td>0.011</td>
<td>99.24</td>
<td>0.2</td>
</tr>
<tr>
<td>Sample 2</td>
<td>624</td>
<td>0.015</td>
<td>1.090</td>
<td>0.280</td>
<td>98.61</td>
<td>0.4</td>
</tr>
<tr>
<td>Cotton</td>
<td>2.57</td>
<td>0.012</td>
<td>0.744</td>
<td>0.011</td>
<td>99.22</td>
<td>0.2</td>
</tr>
<tr>
<td>Processing blank</td>
<td>0.75</td>
<td>0.013</td>
<td>0.725</td>
<td>0.004</td>
<td>99.21</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2 shows some typical results obtained from bulk analysis of environmental swipes. The elemental assays were performed by IDMS using 10 ng $^{233}$U spike (CBNM 040/1) and 0.2 ng $^{244}$Pu spike (IRMM 042a). These are currently the minimum amounts necessary for a successful filament preparation and mass spectrometric measurement, using the electroplating technique. Measurements of the uranium isotopic composition were performed by TIMS on the Finnigan MAT 262. Because inspection samples arrive at SAL completely confidential and only identified by bar-code labels a detailed discussion of the results in terms of verification efforts is not possible. Nevertheless the data clearly show the capabilities of bulk analysis, in particular within the framework of sensitivity.

4. CONCLUSIONS

Bulk analysis of environmental swipe samples is a unique and very powerful technique to identify uranium and plutonium at ultratrace levels, as well as determine their isotopic composition. This information has been extensively used in the IAEA’s efforts of verifying the absence of undeclared activities within nuclear facilities.

The Safeguards Analytical Laboratory is continuously improving its analytical capabilities. Developmental work is underway in such areas as further lowering blank levels for routine sample preparation and improving separation schemes to accommodate the recovery of samples in the low pico- to femtogram range for both uranium and plutonium. As part of these efforts many tests are in progress such as miniaturizing of certain separation steps, using new separation materials, such as the UTEVA separation material (Eichrom Industries, Darien, IL, USA), employing different filament loading techniques such as drop loading of uranium for quantities as low as 1 ng, and resin bead sample loading for plutonium measurements down to the picogram level.

5. REFERENCES