

Review of Methods and Instruments for Determining Undeclared Nuclear Materials and Activities

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At present time high-sensitivity nuclear environmental sampling techniques have been recognized as a power tool for the detection of undeclared activities in the context of the growing threats of nuclear proliferation and terrorism. The International Atomic Energy Agency has proved the ability of the environmental sampling and analysis techniques to support the traditional international safeguards. This article reviews the potentially promising physical methods as well as the current methods and instruments used to analyze trace amounts of nuclear materials in environmental samples. Two types of samples analysis are distinguished: the bulk analysis and particles analysis. Techniques for sample preparation and special laboratory conditions to prevent possible contamination are considered as an essential part of the sample analysis. Detection limits achieved at present in frame of considered techniques are discussed.

INTRODUCTION

Owing to the potential threat of nuclear terrorism, scientists are now focused on developing increasingly sophisticated methods of controlling nuclear technology. In the past few years, there has been an increasing focus on nuclear material controls that complement traditional IAEA safeguards.¹ These new controls rely on the detection and measurement of trace amounts of isotopes of uranium,

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plutonium, throrium, fission products, and others. These effluents proceed to deposit on equipment surfaces within the facility, or are transported outside where they deposit on vegetation, in soil, and propagate through aquifers. Analytical techniques can detect these extremely low levels of nuclear material so as to obtain information about the present and past processes which are occurring at the facility under inspection. For enrichment plants, this may involve detecting the presence of undeclared material or enrichment to levels greater than declared. For hot cell complexes, it may involve detecting the separation of plutonium or highly enriched uranium, the handling of certain types of spent fuel, the separation of alpha-emitting isotopes, or any operation at a shut-down facility.

This article reviews the current methods and technologies used to analyze trace amounts of nuclear materials. Some of the technologies have been adapted from other fields, like environmental monitoring, and have only recently been used in the analysis of nuclear materials. Since the characteristics of these technologies, like the lower-limit of detection, are highly dependent on experience with the assay technique, their specific limitations are not yet fully understood. Other technologies are still being developed with the hope that they will soon be used to detect undeclared nuclear materials and activities. Detection limit values are summarized in the Appendix.

GENERAL PROCEDURE OF ENVIRONMENTAL SAMPLING

Samples from nuclear facilities are taken by trained inspectors using standardized sampling procedures, kits, and approved protocols in accordance to the facility-specific sampling plan.² There are two types of sample analysis: bulk analysis and particle analysis.

Bulk analysis gives information about the average concentration or isotopic composition of the whole sample, such as the average U and Pu isotopic composition, the U to Pu ratio, and the fission product ratios. From these the burn-up and type of fuel being handled can be derived.

Particle analyses are based on the measurement of elemental and isotopic composition of individual particles in the sample. Particle analysis usually includes measurement of U and Pu isotopes, which can be used to identify clusters representing materials handled at the facility and undergoing certain irradiation processes. Analysis of fissile materials and their isotopic content are the basis for estimating the technological processes occurring at a declared nuclear facility so as to enable verification of declarations made by a state.³

Analyses of samples containing trace-level amounts of nuclear material require special laboratory conditions to prevent contamination. A number of countries participating in the environmental sampling program have established such clean-room facilities.^{4,5}

BULK ANALYSIS

Radiometry

Radiometry is used to detect and identify U and Pu in samples based on measuring the alpha, beta, and gamma spectra originating from the natural decay of radioactive isotopes. The individual gamma ray energies and intensities for nuclear materials used in the identification of nuclear material are well established. The most useful gamma lines are the 143.7 and 185.6 keV gamma rays of ^{235}U , and the 1001 keV gamma rays of $^{234\text{m}}\text{Pa}$, which is a daughter of ^{238}U . It should be noted that in areas with high natural-background radiation, the 186.2 and 187.1 keV gamma lines of ^{226}Ra can interfere with the 185.6 keV line of ^{235}U . The individual plutonium isotopes have complex gamma spectra, and as a rule special high-resolution detectors are required for their identification. The gamma-ray spectrum of plutonium contains principal decay lines at 129.3 and 413.7 keV for ^{239}Pu ; 45.2 and 160.3 keV for ^{240}Pu ; and 59.5 keV for ^{241}Am (a daughter of ^{241}Pu).

Gamma spectrometry of uranium samples can be used for verification of uranium mining activities.⁶ In particular, the $^{234}\text{Th}/^{230}\text{Th}$ activities measured by HRGS (high resolution gamma spectroscopy) can be used in estimating the age of uranium. The $^{226}\text{Ra}/^{235}\text{U}$ activity ratio is equal to about 21 for undisturbed uranium ores, and it is significantly higher than this value for tails, and lower for the products.

The U and Pu detection limits for gamma spectrometry with suppression of Compton background in measured gamma-spectrum typically do not exceed tens of μg for U and tens of ng for Pu.⁷

Alpha- and beta-spectroscopy are used mainly for screening hot cell swipes. Inside a plastic glove box the hot cell swipe is removed from its carrying container and the active surface is touched to a specially prepared carbon disc with a sticky surface. The active surface of the disc is then covered by a 5-micron protective polypropylene film. The opposite side is attached to a stainless steel planchet. This type of subsampling allows measurement by systems where a conductive sample is necessary. Such instruments include a Grid Ionization Chamber, an Alpha/Beta low level counter, and an Alpha spectrometer.⁸

Because of the low sensitivity of radiometric methods, they are usually used for preliminary screening of samples before further processing by more sensitive instruments. Generally, radiometry methods are used mainly for analysis of samples of soil, water, vegetation and hot cell swipes.

Prompt Gamma-Ray Neutron Activation Analysis

Prompt gamma-ray neutron activation analysis (PGAA) is based on detection of the prompt gamma-ray spectrum originating from neutron capture and

other (n, xy) reactions.^{9,10} It is an instantaneous, nondestructive assay technique. Because gamma-rays are typically of high energy (above 3 MeV), the method can be used to survey large samples in bulk. Unique signatures for most nuclides are available on the Internet at the neutron capture prompt-gamma activation library of the IAEA.¹¹ The minimum detectable amounts of U and Pu are functions of many parameters of the PGAA set-up, such as the source strength, detector efficiency, geometry, and other factors. At present, reactor-based PGAA instruments offer the highest sensitivity. Their detection limit for Th, U and Pu is about 0.1 mg/g. The main difficulties in using PGAA are related to interference from other nuclear reactions.

X-Ray Fluorescence and Proton Induced X-Ray Emission Analysis

The X-ray fluorescence (XRF) and Proton induced X-ray emission (PIXE) can determine the total concentration of an element in samples, including U and Pu. The operating principle relies on inner shell vacancies produced in atoms when bombarded with energetic protons (PIXE) or gamma-rays (XRF). When vacancies are refilled, and X-rays are emitted, the frequency of which is characteristic of the element from which it originates, and intensity proportional to the amount of the corresponding element present. X-rays from multiple elements are simultaneously detected with the use of solid-state, energy-dispersive detectors, such as Si(Li), HPGc (EDX mode); or individually measured with spectrometers which diffract the X-rays according to their wavelength and select for particular wavelengths (WDX mode).

X-Ray Fluorescence Analyses

Usually XRF is used to screen for U, Pu, or other elements of interest on the surface of the swipe sample. This information is used to decide about the safe handling of the samples in a clean laboratory as well as in choosing the detailed analysis methods to be applied later. There are two types of XRF instruments. One relies on gamma-rays produced by radioactive source, the other uses an X-ray tube. Radioisotope or X-ray tube-excited XRF spectrometry can detect submicrogram amounts of uranium in environmental samples. In optimal conditions, the relative detection limit of X-ray fluorescence analyses with photon excitation is about 10^{-6} g/g.¹²

An energy dispersive XRF system using a 50 mCi ¹⁰⁹Cd excitation source installed at the IAEA Analytical Laboratory provides detection limits about 0.3 μ g of U or Pu per sample. A wavelength dispersive XRF analysis performed with a 3 kW X-ray tube and a Rh anode enables a detection limit below 100 ng per sample for uranium.⁷ One XRF screening device equipped with a 100 mm² Si(Li) detector and annular 20 mCi ¹⁰⁹Cd-excitation source has detection limit for U of about 4 micrograms. All the elements with $Z > 10$ can be detected. Measurement time is about 1 h.¹³

A conventional XRF technique uses a detector capable of analyzing a swipe-sample area of about 30 mm diameter. Swipes used for environment sampling are square, 10 cm per side. One automated XRF system (TRIPOD), developed at the IAEA Analytical Laboratory, overcomes this problem by measuring small areas of a swipe sequentially.⁷ The TRIPOD system is comprised of a 100W X-ray tube, a preliminary energy selection filter (PESF), Si(Li) and HPGe detectors, a robotic arm, and appropriate electronics. The PESF selects an energy range which includes the X-ray L_{α} line of U or Pu and eliminates X-rays of other energies. The Si(Li) spectra are used to evaluate the U and Pu content from the intensities of L_{α} line. The HPGe spectra are used to estimate the elemental composition of the sample. The total measurement time for one swipe is about 4 h. The uranium absolute detection limit for this system is 30 ng per sample.

Proton Induced X-Ray Emission Analyses

The PIXE is a technique widely used for nondestructive, simultaneous elemental analysis of solid, liquid, thin film, powder and aerosol filter samples.^{14–16} A proton excitation source offers several advantages over XRF. Among these are a higher rate of data accumulation, which allows for faster analysis, and better overall sensitivity. This is due to a lower Bremsstrahlung background resulting from the deceleration of ejected electrons, as compared to electron excitation (SEM), and the lack of a background continuum, as compared to the XRF analysis. In optimal conditions the relative detection limit of PIXE analyses is about 10^{-7} g/g.¹⁵

X-Ray Absorption Fine Structure Spectroscopy

X-ray Absorption Fine Structure spectroscopy (XAFS) is an elemental analysis technique that relies on the variation, or fine-structure, of the X-ray absorption at energies in the vicinity of one of the characteristic absorption edge.^{17,18} XAFS spectroscopy can be used to determine an element's concentration in complex materials.^{17,18} This technique is nondestructive, and minimal sample preparation is required apart from pulverization and homogenization of the sample.

The XAFS spectroscopy requires a high intensity X-ray available at specialized synchrotron facilities that is one million times more intense than those available from conventional X-ray tubes. There are two independent parts to the XAFS spectrum: the X-ray absorption near edge structure (XANES), which deals with the fine structure near the absorption edge of the element itself, and the extended X-ray absorption fine structure (EXAFS) which deals with the periodic oscillatory structure above the absorption edge. The XANES spectrum can be used as a fingerprint to identify a specific element in the sample. The sample may be in any form—gas, liquid, or solid, including crystalline materials, amorphous materials (e.g., glass), or complex multicomponent materials

(e.g., soils, rocks, environmental materials, etc.). Most elements can be examined by XAFS at concentrations down to the ppm (parts-per-million) level. Nevertheless at present XAFS has not proved to be particularly valuable in the interrogation of most nuclear materials. XAFS is used primarily to obtain information about chemical bonding and molecular structure in solids.

Thermal Ionization Mass Spectrometry

The thermal ionization mass spectrometry (TIMS) technique is used for accurate and precise measurements of isotopic ratios of trace nuclear materials present in samples such as soil, vegetation, tissue, and water taken in vicinity of nuclear facility.^{19–21} In particular, the $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{241}\text{Pu}/^{239}\text{Pu}$ ratios determine the presence of weapon grade material and contain information about the origin of the materials. The main method used for analyzing samples containing U and Pu isotopes is the total evaporation technique.²² Usually a tungsten filament is used for evaporation and a rhenium filament is used for ionization.

Prior to analysis, trace levels of uranium and plutonium are separated from the bulk of sample through chemical preprocessing. The sample matrix is destroyed by acid digestion, microwave digestion, or other techniques. Extraction of the target species is done by ion-exchange chromatography, extraction chromatography, or other technique. The main advantage of the TIMS technique is the almost complete consumption of the sample under investigation which results in reduced isotopic fractionation. This is one of the main sources of systematic errors. The low-level Pu measurement is usually made with addition of a calibration tracer, typically CBNM042a. Bulk measurement with TIMS can detect levels of Pu and U typically in low femtogram (10^{-15} grams) range.²¹ An automatic measurement takes about 20 min. The disadvantage of this method is that the sample preparation is time consuming and requires skills, and the overall process is quite expensive. Chemical methods used for treatment of samples have to be adjusted for each sample and must be of extremely high purity so as to not add contaminants that would be detected in the mass spectrometer. Application of the TIMS techniques for hot-cell sample analysis at NUCEF (JAERI)²³ gave the isotopic ratio values which, within uncertainties of 1%, agreed with calculated values for both uranium (5–10,000 ng) and plutonium (0.01–100 ng). The process blank was less than 0.03 ng for U and 0.02 pg for Pu.

TIMS can also be used to analyze particles as opposed to bulk samples by employing the fission track method (FT). This method identifies the location of particles of fissile material in the sample first, extracts them from the sample, and mounts each particle on a filament which is then analyzed using TIMS. Both U and Pu can be detected from the same particle with a detection limit in the pico- to femtogram range (i.e., 10^{-12} to 10^{-15} g/sample).³

Improvement of TIMS

The ionization efficiency of uranium and plutonium (ratio of element ionized to element available) for TIMS is poor. A single filament produces 1 ion for every 2000 to 8000 atoms loaded. Recent developments have improved the efficiency of TIMS. They include new loading techniques, such as absorbing the samples on a resin bead fixed to the filament, various types of carburization by drop loading colloidal graphite on the filament, saturation of the filament with carbon from a benzene vapor, or loading the samples with electroplating techniques.^{24,25} Another approach uses high-efficiency cavity source (HECS), which also reduces the sample size required.²⁶ The HECS cavity is a solid metal rod of high-purity tungsten or rhenium, 1 mm in diameter. The cavity in which the sample is placed is a hole 0.5 mm in diameter and 5–8 mm deep, drilled into one end of the rod. A thin rhenium ribbon is used as the heating filament. The heated filament produces electrons, which are used for heating the cavity. HEC sources typically produce 1 ion for every 50–100 atoms loaded. It has been demonstrated that the total efficiency in TIMS measurements can be increased to more than 10%.²¹

Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is used to measure the concentrations and the isotope ratios of U and Pu in a sample.^{27–30} ICP-MS has clear advantages in multielement analysis: speed of analysis, better detection limits than other atomic spectroscopic techniques such as flame atomic absorption, graphite furnace atomic absorption, and inductively coupled plasma–optical emission spectrometry. There are three common types of the ICP-MS instruments used for isotopic analyses of U and Pu samples: a high-resolution type (HR-ICP-MS), a multicollector type (MC-ICP-MS), and a quadrupole type (Q-ICP-MS).

General Principles of Operation ICP-MS

All of the ICP-MS types have similar components—a nebulizer, spray chamber, plasma torch, interface, and detector—but they can differ significantly in the design of the mass spectrometer.³¹ The sample, having a liquid form, is pumped into a nebulizer where it is converted into a fine aerosol with argon gas. The fine droplets of the aerosol are separated from larger droplets in a spray chamber. Then the fine aerosol is transported via a sample injector from the spray chamber into the plasma torch with very high temperature plasma of Ar. Argon is used to generate positively charged ions of analyte which are directed into the mass spectrometer via a series of electrostatic lenses. There are many different mass separation devices, each with its own benefits and limitations. Most ICP mass spectrometers use just one detector. However, specialized magnetic-sector ICP-MS instrumentation with multiple detectors (MC-ICP-MS) is available for isotopic ratio analysis. An ion detector converts the ions

into an electrical signal which is then processed by the data handling system in the conventional way and converted into concentration data using ICP-MS calibration standards. The isotope dilution method³² is used to determine the concentration using ²³³U (CRM111A, NBL) and ²⁴²Pu (CRM130, NBL), as spikes for U and Pu, respectively. The isotopic standards such as CRM U015 (NBL) for U and SRM947 (NBL) for Pu are measured in order to correct instrument bias.³³ Most detection systems used can handle up to eight orders of magnitude in dynamic range: from hundreds of ppm (hundreds parts-per-million) to low ppt (parts-per-trillion) levels.

Sample Preparation for ICP-MS. A swipe or other sample is ashed in a quartz beaker covered with watch glass in a furnace and then is digested with nitric acid, hydrofluoric acid, and perchloric acid. The U and Pu in the resulting solution are extracted by the anion-exchange method in a hydrochloric acid media. The amounts of uranium contamination during the treatment of the swipe sample can be estimated. The uranium from the quartz beaker is the largest source of contamination. Therefore many laboratories now use Teflon beakers instead of quartz to avoid the uranium contamination problem. Contamination from reagents and the atmosphere are relatively low for clean-room facilities.

Quadrupole Mass Analyzer Technology

The Quadrupole mass analyzer (Q-ICP-MS) consists of four cylindrical rods which generate both RF and DC electrical fields.³⁴ In the Quadrupole system, the mass analyzer is created by connecting the two pairs of rods in such a manner that the X plane acts as a low mass filter and the Y plane acts as a high mass filter. By carefully matching the two fields, only ions of a particular mass are able to resonate at the correct frequency allowing them to pass through the Quadrupole system at any time. This scanning process is then repeated for another analyte ion at a completely different mass-to-charge ratio until all the analytes in a multielement sample have been detected. Quadrupole scan rates are typically in the order of 2500 atomic mass units (amu) per second. In practice, 25 elements can be determined with good precision in 30–60 seconds. However, quadrupole technology can separate only masses that are approximately 1 amu apart. If there is a severe spectral interference very close to the analyte mass, the resolution will not be sufficient to resolve the interference away. Modern Quadrupole systems are able to detect trace elements at levels in the low ppb (part per billion) range and oftentimes ppt (part per trillion) range.

Double-Focusing Magnetic-Sector Technology

In the High-Resolution mass analyzer (HR-ICP-MS), the ion beam passes through a narrow slit resulting in a narrow beam of ions all traveling parallel to each other.³⁵ In the case of a double focusing mass spectrometer with forward Nier-Johnson geometry the beam enters the electrostatic analyzer, which

is effectively an energy filter allowing in a narrow range of kinetic energies to pass into the magnet. In the magnetic field, the ions are separated by their m/z (mass to charge) ratio, such that ions of different masses follow different circular trajectories. By adjusting the field strength of the magnet, it is possible to select ions of a specific m/z ratio. The ion beam then passes through a narrow collector slit situated at the focal point of the magnet. High resolutions are achieved by making both of the slits very narrow so that the beam reaching the detector has only a very narrow bandwidth of mass at any given time. Therefore, the high-resolution mass analyzer is able to focus both energy and m/z ratio of each element enabling it to be fully resolved from any interference without over-resolving an element of interest. For some applications, the instrument is capable of achieving detection limit below 1 ppq (part per quadrillion). It should be noted that there are other types of HR-IC-MS instruments in which a reversed Nier-Johnson geometry (the magnetic sector precedes the electrostatic sector) is employed.³⁶ Both configurations arrive at comparable mass resolving power.

Time-of-Flight Technology

The main advantage of the Time-of-Flight Technology (TOF) is that the ions are sampled and detected at exactly the same moment, which means that TOF systems can collect a full mass spectrum significantly faster than a scanning device like a quadrupole. Although the TOF-ICP-MS technique is relatively new and has not yet proved itself as a routine tool, its rapid, simultaneous detection capability is well suited for high-precision work and fast transient analysis that requires the best multielement signal-to-noise performance.

Difficulties in Implementation of the ICP-MS Method

There are three sources of interference when measuring isotope ratios with ICP-MS³⁷: the production of polyatomic ions, the stability of the plasma, and coexisting elements. It was found that polyatomic ions of PtAr (compound ions) interfere with the measurements of the uranium isotope ratios. The measured isotope ratio also changes with various ICP conditions, such as plasma temperature. The production of oxide ions increases with a decrease in the plasma temperature. If the coexisting elements such as Na are present in a sample solution, the observed ratio of $^{235}\text{U}/^{238}\text{U}$ tends to become larger value than true ratio. For the isotope ratio measurement of lead, thallium is a good internal standard, however, is not applicable to uranium. If calibration tracers of ^{233}U and ^{236}U are available, the effect of coexisting elements for the uranium isotope ratio measurement can be corrected. However, the best method for obtaining accurate isotope ratios is to separate out coexisting elements to levels below 1 ppm (part per million).

Improvement of the ICP-MC Method

Electrochemical flow cells (EFL) may be used for on-line pretreatment systems for ICP-MS elemental and isotopic analyses, allowing signal enhancement via preconcentration with simultaneous elimination of matrix materials.³⁸ Analyte levels range from 20 $\mu\text{g/l}$ to subnanogram per liter before preconcentration treatment. A detection limit of approximately 0.12 ng/l can be obtained under pristine conditions with a 10-min uranium accumulation time. The EFL technique permits the detection of minor isotopes of uranium, including ^{234}U , where the total uranium content is about 5 $\mu\text{g/l}$.³⁹

Accelerator Mass Spectrometry

Accelerator mass spectrometry (AMS) is an analytical technique that uses an ion accelerator and its beam transport system as an ultra-sensitive mass spectrometer for the measurements of actinides concentrations and their isotopic ratios. The element of interest is chemically separated from the original sample and loaded as a target in the sputter ion source of a tandem accelerator. Quite large samples ranging from 1 to 10 mg are used in AMS analysis. After low-energy magnetic analysis, negative ions of the radioisotope of interest are accelerated to the terminal of the accelerator where they are converted to positive ions. Then positive ions are accelerated further to ground potential. The electron stripping process breaks up molecular species that might be injected into accelerator. This effectively eliminates possible molecular interference. After subsequent magnetic and electrostatic analysis, the ions are identified in an ion detector. In order to obtain a concentration value, an appropriate stable isotope (silver or iron) is accelerated along with the sample under investigation so the rare-to-stable isotope ratio can be used to determine the absolute mass of rare isotope in the sample. In the case of long-lived actinides, isotope spikes are used in place of a naturally occurring stable isotope, analyte-to-spike counts are measured and used to determine the absolute mass of the analyte isotope. AMS is unaffected by almost all backgrounds that limit conventional mass spectrometry. Contamination effects are assessed by processing "blank" materials in parallel with unknown samples.

The AMS system developed at the LLNL's Center for Accelerator Mass Spectrometry includes a fast isotope switching capability that allows for quasi-continuous normalization to a reference isotope, and considerable flexibility in isotope selection.⁴⁰ Capabilities of the AMS technique were measured with Pu isotope samples. The observed background levels are equivalent to less than 10^6 atoms during routine ^{239}Pu and ^{240}Pu measurements. Measurements at ^{239}Pu settings of sample containing 10^{13} atoms of ^{238}U nuclide showed that the AMS system provides a ^{238}U rejection factor of more than 10^7 . Measurements of samples derived from a calibrated ^{239}Pu solution demonstrated that

the system has a linear dependence for Pu measurement in the range from less than 10^6 atoms to more than 10^{11} atoms. Comparison by a second laboratory showed that the measured content of ^{239}Pu and ^{240}Pu in “real world” sample are precise down to $\sim 10^6$ ^{239}Pu atoms.⁴¹ In the case of uranium where typical environmental samples yield about $1\ \mu\text{g}$ of uranium, the current detection limit is 10^{-9} for the $^{236}\text{U}/^{238}\text{U}$ ratio⁴² and in the range of 10^{-10} to 10^{-11} by measuring milligram-sized samples.⁴³ This corresponds to a detection limit of around 1 femtogram for ^{236}U , which allows for a reliable estimation of the irradiated uranium content in the environment. This level of sensitivity has also been shown for Pu isotopes and ^{237}Np .⁴⁴ Thus the principal virtue of the AMS technique as compared with conventional mass spectrometry is extremely low background, leading to a capability to measure very low abundance isotopes, albeit in bulk samples.

PARTICLE ANALYSIS

Particle analysis is used to determine the elemental composition of individual particles in a sample. The analysis of individual particles has several advantages compared to “bulk” analysis. Particles are more representative of the range of elemental or isotopic information present at the inspected location. The study of particles containing Pu from inside hot cells can yield important information about the activities which have been carried out there. In particular, the handling of irradiated reactor fuel should produce particles in which the U/Pu ratio is high (a U/Pu of about 100–1000 depending on the irradiation history). Particles which contain more Pu than expected could indicate that chemical separation activities were carried out. In addition, the amount of Am in a particle in comparison to Pu can give an indication of the “age” of the material. The Pu impurity in a primarily U particle can be quantified down to approximately 0.2%, whereas the Am or U impurity in a primarily Pu particle can be measured at about half the concentration.

Scanning Electron Microscopy and Secondary Ion Mass Spectrometry

At present, two methods are used to analyze particles. The first method is Scanning Electron Microscopy (SEM) combined with X-ray Fluorescence Spectrometry (SEM/XRF). This method is used to locate particles containing elements of interest—primarily U and Pu—so as to study their physical characteristics and elemental composition. The second analytical technique is Secondary Ion Mass Spectrometry (SIMS), which permits the measurement of U and Pu isotope ratios in particles. Special operating software allows large areas of a sample planchet to be searched and automatic measurements of up to several thousand particles to be performed in a single analysis.

Scanning Electron Microscopy

The SEM method uses a microfocused electron beam that scans over the surface of the specimen in vacuum.⁴⁵ There are two operation modes used. A secondary electron mode is used for obtaining a magnified image of the sample surface. Elastic scattering of electrons at large angles (backscattered electrons) gives an image which is sensitive to heavy elements. An X-ray fluorescence mode detects X-ray emission from atoms in the sample to obtain an element map of the surface, or the composition of a single point on the surface. The detection of X-rays are made by using a solid-state detector which measures X-rays simultaneously in a wide energy range (EDX mode) or by using a spectrometer which disperses X-rays according to their wavelength and can only measure one wavelength at a time (WDX mode).

In safeguard applications, the search is directed at finding U and Pu containing particles over several square millimeters of the planchet surface using the backscattered electron signal to locate “heavy” particles first, then the EDX system to measure the XRF spectrum of each particle found.⁴⁶ An automatic measurement session typically takes four to six hours and covers several square millimeters of the sample surface. The result is a data file containing up to several thousand particles. The use of sophisticated software allows the analyst to detect and record data from many thousands of particles in a measurement session and these particles can be reliably relocated for more detailed examination.⁴⁶ The particle data can be sorted to find those with the highest U content, or various other user-selected parameters (e.g., U associated with F). After examining this information, one may choose to revisit selected particles for the more time-consuming WDX measurement which is the most precise for measuring elemental composition (the oxygen to uranium ratios in particles) as well as element ratios, such as uranium/plutonium or americium/plutonium, in each particle. WDX analysis of elemental ratios is especially useful in measuring the “age” of Pu materials collected on special swipe samples from inside hot cells. A particle containing mostly Pu may also contain measurable amounts of U from the original fuel as well as Am coming from the decay of the ²⁴¹Pu isotope. The growth of ²⁴¹Am is a measure of the time since the plutonium was last chemically purified. The measurement of U/Pu ratios in hot cell swipes may indicate whether spent fuel has been chemically treated to recover the Pu is capable of measuring the U and Am content of a Pu particle at concentrations of 0.1 wt.%. Scanning electron microscopy combined with X-ray fluorescence spectrometry can measure the elemental content of particles smaller than 1 micrometer in diameter. The amount of plutonium in a one micrometer-diameter particle is only a few picograms (roughly 10¹⁰ atoms). From this one can conclude that the SEM/XRF spectrometer in the WDX mode can detect minor components such as americium which are in the low-femtogram range.⁴⁷

Sample Preparation for SEM

Typical samples for SEM analysis are 100 cm² cotton swipes and cellulose hot cell swipes. There are two basic sample preparation methods. The simplest method is to use a self-adhesive carbon disc which is 1 cm in diameter attached to an aluminum SEM stub. The surface of this disc is coated with an adhesive which is used to pick up particles directly from the surface of the swipe. This method is primarily used for hot cell swipes because of the radiation hazard associated with more time-consuming methods. The fraction of material from the swipe which ends up on the disc is usually quite small (1–10%), but it is expected to be reasonably representative of the sample. For cotton swipes having a much larger surface area, a more representative sampling of the particles can be accomplished by cutting up the swipe into pieces of about 1 cm² and placing them into an organic solvent such as heptane in a small glass vial. The vial is then placed into an ultrasonic bath to release the particles from the swipe and suspend them in the solvent. The suspension can be centrifuged to concentrate the particles which are then pipetted onto a SEM stub and dried.

Secondary Ion Mass Spectrometry

In the Secondary Ion Mass Spectrometry (SIMS) technique, the surface of a sample is bombarded by high energy ions.^{3,48–50} The most commonly employed ions used for bombarding are O₂⁺ and O, but other ions (e.g., Cs⁺, Ar⁺, and Ga⁺) are preferred for some applications. This leads to sputtering of both neutral and charge species from the surface. The ejected species may include atoms, clusters of atoms, and molecular fragments. The secondary ions are accelerated and separated according to their mass in a magnetic field and finally detected with one of several devices. The most common type of the mass analyzer is a double-focusing Nier-Johnson instrument. The quadrupole and time-of-flight types of instrument are much less common. The SIMS instruments produce an image of the sample using secondary ions of a chosen mass. A sample containing uranium particles will produce an image using ²³⁸U⁺ ions (using the “ion microscope” mode of operation). By storing an image using ²³⁸U⁺ and ²³⁵U⁺ ions, it is possible to measure the “enrichment” of particles in a sample. Automatic scanning software (PSEARCH) allows one to scan significant areas of the planchet surface to find and measure many thousand particles in a measurement session lasting 4–6 h.

A second mode of SIMS data acquisition involves focusing the primary ion beam onto a single particle and measuring its mass spectrum (the “ion microprobe” mode of operation). This provides the best quality isotopic information for the major and minor isotopes (such as ²³⁴U and ²³⁶U). Analysis with the ion microprobe is a much more time-consuming operation: the measurement of a single particle may take 10–20 min, compared to about 1 min per field in the ion microscope mode. Depending on the relative sensitivity factor⁵¹ of the

analyte element, the detection limit of the SIMS instruments in the ng/g–pg/g range is achieved by optimizing different instrumental parameters.⁵²

In addition to ionization efficiencies, two other factors can limit sensitivity of the method. The first one is related to the output of an electron multiplier, which is called dark current. When the secondary ion signal is comparable with the variation in the dark current, then it is not detected. The second factor is related to background conditions. If the SIMS instrumentation contains portions of the analyte element, then the introduced level constitutes background limited sensitivity. Oxygen, present as residual gas in vacuum systems, is an example of an element with background limited sensitivity. Analyte atoms sputtered from walls of the mass spectrometer back onto the sample by secondary ions constitute another source of background. Mass interferences also cause background limited sensitivity. For instance the technique cannot be used for direct evaluation of the artificial uranium isotope ^{236}U since this mass is interfered by the formation of the uranium hydride species $^{235}\text{UH}^+$.

Sample Preparation for SIMS. The sample preparation method used for SEM measurements (i.e., ultrasoneration in heptane) is also used to prepare sample planchets for SIMS.

Recovery of Particles

One of the problems encountered in particle analysis is related to the recovery of particles from swipe samples. Procedures used in analytical laboratories for this purpose include ultrasonic baths to dislodge particles from the collection surface, a low temperature plasma asher, and a sticky carbon tape. However, application of these methods has negative consequences because remaining fibers and hydrocarbons affect the isotope ratio measurements due to the charging effects and interference by molecular ions. An alternative method, aspiration, minimizes this effect by removing particles via impaction collection with an air-sampler.³³ The method's advantages are that it is reagent free, provides for quick removal of particles from swipe samples, can collect particles directly onto carriers for subsequent analysis by TXRF and SIMS, and can be used to collect particles on the center part of the carrier. Most of the particles can be located in an area of 2 mm × 2 mm. Such a small area facilitates finding uranium particles in SIMS analysis. Size fractionated particle collection is also possible.

Total-Reflection X-Ray Fluorescence Spectrometry

Although the SIMS technique is very effective in analyzing trace level of elements on a sample, it is impractical if the sample contains too few particles for SIMS measurement. Total-reflection X-ray fluorescence spectrometry (TXRF) is suitable in this case.^{33,50} Prior to analysis, samples are decomposed using a wet chemical method and plasma ashing followed by acid dissolution. A few μL of the solution are deposited on the quartz/glassy carbon discs. An X-ray beam is directed to the highly-reflective sample carrier. The fluorescent

radiation from the sample are measured by a X-ray Si(Li) detector. The TXRF analyzer installed at SAL at IAEA is an example of such a system. It allows multielemental analysis for up to 70 elements in a sample.⁷ The main components of this system are 3 kW tungsten-molybdenum anode, 2.5 kW gold anode, long fine-focus tubes, a high voltage generator, and a Si(Li) high resolution detector. The uranium detection limit for the uranium nitrate solution is 5 picograms (10^{-12} g). For environmental swipe sample solution, the uranium detection limit is 15 picograms.

An External Quality Control of Analytical Techniques

A wide variety of measurement techniques are used by laboratories in the analysis of environmental samples. As such, one of the important issues in the measurements of isotopic composition of environmental samples with small amounts of fissile materials is the reliability of reported results. As part of a program on External Quality Control, a multilaboratory exercise was conducted to estimate the quality of techniques employed by laboratories participating in an environmental sampling program.⁵⁴ All laboratories received certified test samples which were to be analyzed using the laboratory's routine procedures. The obtained results on isotopic ratios $n(^{235}\text{U})/n(^{238}\text{U})$, $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ are presented, respectively, in Figures 1–3, taken from Wellum et al.⁵⁴ The efficiency of the different types of ICP-MS and TIMS techniques can be clearly seen in Figures 1 and 2. Radiometric technique showed a large bias in the measured ratio values. Finally, Figure 3 shows that all laboratories had a problem in measuring small ratio values.

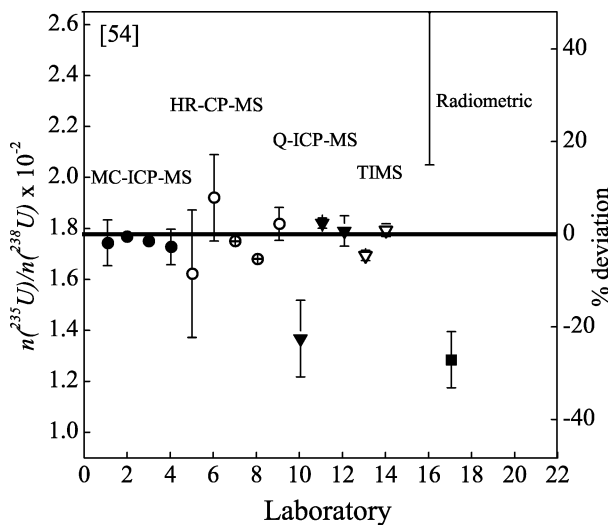


Figure 1: Measured values of $n(^{235}\text{U})/n(^{238}\text{U})$ by the MC-ICP-MS, HR-CP-MS, Q-ICP-MS, TIMS techniques, and Radiometric (alpha or gamma spectrometry).

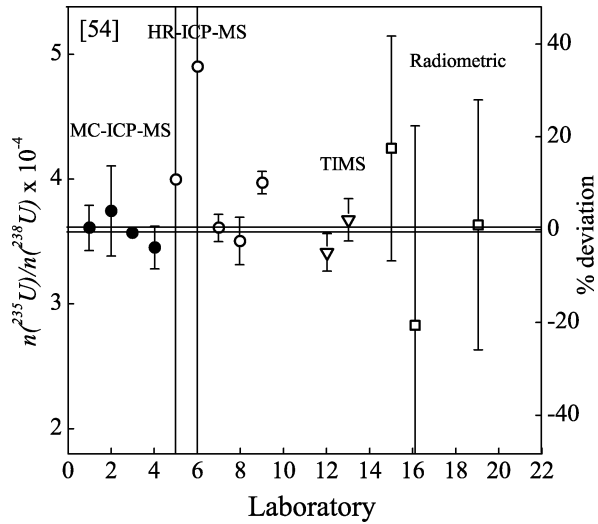


Figure 2: Measured values of $n(^{235}\text{U})/n(^{238}\text{U})$ by the MC-ICP-MS, HR-CP-MS Q-ICP-MS, TIMS techniques, and Radiometric (alpha or gamma spectrometry).

POTENTIALLY PROMISING METHODS

Noble Gas Mass Spectrometry

Until recently the main noble gas isotopes studied have been quasi stable isotope $^{85}\text{Kr}^{55}$ with half-life 10.76 years and xenon isotopes $^{131\text{m}}, ^{133}, ^{133\text{m}}, ^{135}\text{Xe}$,

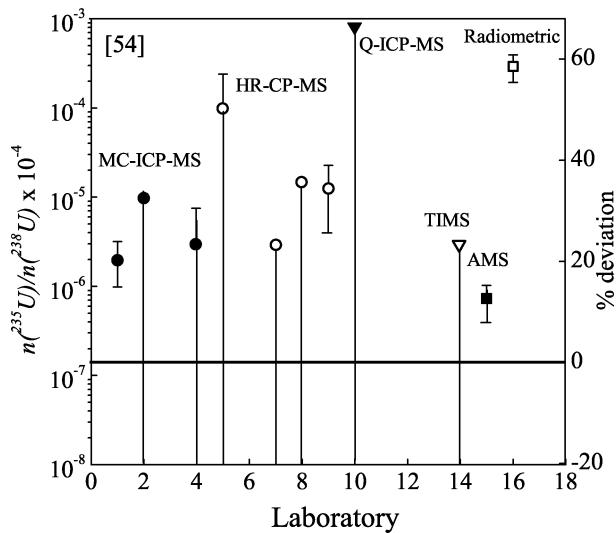


Figure 3: Measured values of $n(^{235}\text{U})/n(^{238}\text{U})$ by the MC-ICP-MS, HR-CP-MS Q-ICP-MS, TIMS, AMS techniques and Radiometric (alpha or gamma spectrometry).

which have half-lives in the range of nine h to twelve days.⁵⁶ These isotopes were chosen for their very low background.

One of the promising methods to be used in the environmental-sampling program is related to the measurement of stable atmospheric noble gas isotopes from a facility's stack effluents. Owing to chemical inertness, these isotopes are not disturbed by the chemistry of reprocessing and are released freely during the dissolution process.

Recently Nakhleh et al.⁵⁷ considered the possibility and utility of measuring the isotopic abundances signals from stable isotopes of Kr and Xe (other noble-gas isotopic abundances signals). Among all the possible fissionogenic Kr and Xe isotopes, the following stable, safeguard-usable isotopes were taken into account: $^{83,84,86}\text{Kr}$ and $^{131,132,134,136}\text{Xe}$. Other stable isotopes, ^{82}Kr and $^{129,130}\text{Xe}$ were not considered because they are shielded by the long-lived isotopes in appropriate fission product β -decay chains. The primary reason for choosing only stable isotopes is that the relative abundance of nonradioactive isotopes are not affected by a time delay between the removal of the fuel from reactor and the time of its dissolution during reprocessing. A second reason is that the composition of fissionogenic Kr and Xe differ considerably from the background composition of atmospheric Kr and Xe isotopes. The results of modeling calculations based on the attainable precisions of krypton and xenon abundance ratio measurements (a few parts in 10^5)⁵⁸ show that the proposed method should potentially be able to determine the correct reactor type, burn-up, and dilution factor for both high and low burn-ups of nuclear fuel.

Delayed Neutron Counting Method

The Institute of Physics and Power Engineering (Obninsk, Russia) developed methods for measuring trace-levels of fissionable nuclides based on the delayed neutron counting technique.⁵⁹ A proposed method for determining the isotopic content of a sample is based on the average half-life of delayed neutron precursors for different fissioning systems.⁶⁰ According to the systematics, the average half-life $\langle T \rangle$ of the delayed neutron precursors for the isotopes of thorium, uranium, plutonium, and americium elements is given by the following expression:

$$\ln\langle T \rangle = a_i + b_i \ln[-(A_c - 3Z_c) \cdot A_c / Z_c], \quad (1)$$

where coefficients a_i and b_i have the same values for isotopes of element under consideration (Th, U, etc), A_c and Z_c —the mass and atomic numbers of the fissioning nuclei respectively. The experimental data on the average half-life parameters for the 6-group model⁶¹ were obtained using the formula

$$\langle T \rangle = \sum_{k=1}^6 a_k \cdot T_k, \quad (2)$$

Table 1: Sensitivity of delayed neutron counting technique in the analysis of the content of fissionable elements in the environmental samples.

Nuclide	Minimal detectable amount, g		Detectable concentration, g/g	
	Fast neutron flux	Thermal neutron flux	Fast neutron flux	Thermal neutron flux
^{235}U	$6.3 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$1.3 \cdot 10^{-8}$	$3 \cdot 10^{-9}$
^{238}U	$1 \cdot 10^{-5}$	—	$2 \cdot 10^{-8}$	—
^{239}Pu	$1 \cdot 10^{-5}$	$2.6 \cdot 10^{-6}$	$1.9 \cdot 10^{-8}$	$5 \cdot 10^{-9}$
^{232}Th	$1.7 \cdot 10^{-5}$	—	$3.3 \cdot 10^{-8}$	—

where a_i and T_i are relative abundances and half-life of i -th group of delayed neutrons. The sample under investigation is cyclically irradiated by neutron flux from $^9\text{Be(d,n)}^{10}\text{B}$ reaction, after which a dependence of delayed neutron activity is measured as a function of time. The combination of thermal and fast neutron irradiation and the analysis of appropriate aggregate decay curves are used to determine the average half-life parameters and thus the isotopic abundances in the sample under investigation. The set-up was installed at the electrostatic accelerator CG-2.5 and has the following main parameters: ion (proton and deuteron) currents up to $500 \mu\text{A}$, pneumatic sample delivery system with 150 ms and 1 s for ‘fall down’ sample delivery system, acceleration energies up to 2 MV, a neutron detector comprised of 30 boron counters of SNM-11 type with very-low sensitivity to gamma-ray background embedded in the polyethylene moderator. The intensity of the neutron background during delayed neutron counting period is about 0.008 counts/s per $1 \mu\text{A}$ of deuteron current for (d,n) neutron-production reactions. Sensitivities for the delayed neutron counting techniques are presented in Table 1. They indicate that the delayed neutron counting technique coupled with the electrostatic accelerator based on a neutron source $^9\text{Be(d,n)}^{10}\text{B}$ is a useful instrument in performing the analysis of isotope ratio in bulk samples with trace level content of fissionable elements. The advantage of the method is that there is minimal sample preparation and no restriction on sample weight.

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Appendix Detection limit of specific techniques.

Method	Type of analysis	Detection limit for U, Pu and other	Target value	Time of analyses or time needed for report
Radiometry (HRGS)	Brief search of radioisotopes	Tens of μg for U, ⁷ tens of ng for Pu ⁷		Several h
Screening, hot cells samples (HRGS)	Brief search of radioisotopes	0.06 Bq ²⁴¹ Am 0.07 Bq ¹³⁷ Cs		2 h 2 h
Screening, environmental samples (HRGS)	Brief search of radioisotopes	0.03 Bq ²⁴¹ Am 0.04 Bq ¹³⁷ Cs		2 h 2 h
PGAA	Isotopic ratio, isotopic content	0.1 mg/g ⁹ (Th, U, Pu)		Several h
PIXE	Elemental composition	10^{-7} g/g ¹⁵		1 h
XRF/ED (20 mCi ¹⁰⁹ Cd source)	Elemental composition	4 $\mu\text{g}/\text{samp}$ ¹³		1 h
XRF/ED (50 mCi ¹⁰⁹ Cd)	Elemental composition	0.3 μg ⁷		
XRF/WD (3 kW X ray tube)	Elemental composition	100 ng/samp ⁷	A few ng U per swipe in 100 s	4 h
XRF/ED (TRIPOD system, 100 kW X ray tube)	Elemental composition	30 ng/samp ⁷		
XAFS	Elemental composition, molecular structure	ppm level ¹⁸		
TIMS (bulk)	Isotopic ratio, isotopic content	10^{-15} g/samp ^l for U and Pu ²¹	²³⁵ U/ ²³⁸ U $\pm 1\%$ ²³⁴ U/ ²³⁸ U $\pm 10\%$ ²³⁶ U/ ²³⁸ U $\pm 10\%$ ²⁴⁰ Pu/ ²³⁹ Pu $\pm 20\%$	20 min
TIMS (bulk)	Isotopic analyses (²³⁴ – ²³⁸ U, ²³⁸ – ²⁴¹ Pu)	100 pg with ²³³ U spike, a few fg with ²⁴⁴ Pu spike ⁷	The target value of detection limit is 10^{-15} g	60 d from receipt to report
FT-TIMS (particles)	Isotopic analyses (²³⁴ U, ²³⁵ U, ²³⁶ U, ²³⁸ U)	10^{-12} – 10^{-15} g/sample ³	1% RSD on ²³⁵ U/ ²³⁸ U	30 d from receipt to report
SEM/XRF (particles)	Elemental analyses	Detection limit in the femtogram (10^{-15} g) range ⁴⁷		

Appendix Detection limit of specific techniques.

Method	Type of analysis	Detection limit for U, Pu and other	Target value	Time of analyses or time needed for report
SIMS (particles)	Isotopic ratio, isotopic content	Detection limit in the ng/g-pg/g range ⁵³	$^{235}\text{U}/^{238}\text{U}$: $\pm 10\%$ (microscope mode) $^{235}\text{U}/^{238}\text{U}$: $\pm 5\%$ (microprobe mode) U/Pu: $\pm 20\%$ (microscope mode) $^{240}\text{Pu}/^{239}\text{Pu}$: $\pm 5\%$	1 min per field (microscope mode), 10–20 min per particle (microprobe mode).
TXRF	Multielemental analysis	5–15 pg for U, Pu ⁷	10 pg U, Pu per planchet	2 d from receipt to report
Q-ICP-MS	Isotopic content, isotopic ratio	From low ppt to ppb level ³¹	10^{-12} g/ml ³⁷	Several min
HR-ICP-MS	Isotopic content, isotopic ratio	Up to ppq level ³¹		
ICP-MS combined with Electrochemical Flow Cell	Isotopic content, isotopic ratio	0.12 ng/l ⁴⁰		10 min
AMS	Minor isotopes analysis ($^{236}\text{U}/^{238}\text{U}$)	$^{236}\text{U}/^{238}\text{U} < 10^{-9}$ (μg sample ⁴²), $^{236}\text{U}/^{238}\text{U} < 10^{-10}$ – 10^{-11} (mg sample ⁴³), (corresponds to 1 fg for ^{236}U)		Several h
AMS	Isotopic ratio, isotopic content	10^6 atoms of Pu ⁴¹ (corresponds to 1 fg for ^{239}Pu)		Several h
Delayed neutron counting	Isotopic content	5 \circ 10^{-9} g/g for ^{235}U and ^{239}Pu (thermal neutrons), 5 \circ 10^{-8} g/g for $^{235,238}\text{U}$, ^{239}Pu , ^{232}Th ⁵⁹ (fast neutrons)		1 h
Noble gas monitoring	Reactor type, burn-up and dilution factor for both high and low burn-ups of nuclear fuel			