



ANALYTICAL MEASUREMENTS FOR SAFEGUARDING LARGE REPROCESSING FACILITIES

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Abstract

Measuring samples taken at large reprocessing plants poses a particular challenge to an analytical laboratory. The size and complexity of these plants imply a high number of samples and a great variety of sample types. For meeting the safeguards goal of detecting the potential diversion of a significant quantity, strict accuracy requirements are imposed on these measurements. Consequently, criteria like accuracy, laboratory time, waste production, resource allocation and analysis costs determine the development and implementation of suitable analytical procedures. Analytical concepts have been developed at the Institute for Transuranium Elements for verification measurements at large reprocessing plants. These concepts take into account the specifics of the individual plant (feed materials, sample types and numbers) and the boundary conditions mentioned above.

Active and passive radiometric measurement techniques such as K-Edge densitometry (KEDG), X-ray fluorescence analysis (XRF), high resolution gamma spectrometry (HRGS) and neutron coincidence counting (NCC), either used individually or in combination, have become the primarily applied methods. Specifically, spent fuel solutions are measured by the Hybrid KEDG/XRF techniques, plutonium product solutions by KEDG, plutonium oxide and mixed oxide samples by NCC/HRGS, and uranium solutions by KEDG/HRGS. Intensive investigations have considerably contributed to improve the accuracy of these measurements. Additionally, development activities were carried out to further facilitate the use of the instrumentation and to increase the sample throughput by automation and unattended operation.

The application of methods based on chemical principles, due to their potential for superior accuracy, is shifting to specific fields like quality control i.e. to check the results obtained by physical methods and provide the reference basis for radiometric techniques. Accordingly, isotope dilution mass spectrometry and titration are used for the element and isotope assay in spent fuel solutions and products.

1. Introduction

Safeguards aims at the verification of the non diversion of fissile material from its intended and declared (peaceful) use. Therefore a reliable nuclear material accountancy has to be established by the plant operator. An at least evenly reliable system of verifications is the responsibility of the safeguards authority in charge.

Safeguarding nuclear material involves the quantitative verification of the accountancy of fissile material based on independent measurements. These measurements consist of a bulk measurement, hence a combination of mass and/or volume determination and the analysis samples taken from this bulk. The sampling procedure should guarantee that the sample is indeed representative of the bulk. It has furthermore to be ensured that the sample is not tampered with on its way from the sampling station to the measurement laboratory /11/.

A number of analysis strategies are currently being applied in parallel:

On-line analysis is limited to the monitoring of typically a single parameter by a non destructive measurement method. This technique is rather applicable for checking material flows.

In-field analysis requires the transport of mobile measurement equipment to the facility and the analysis of samples on the spot. This technique is only applicable to Uranium samples, as the transportation of Pu contaminated instrumentation poses practical problems. In another modification, in-field analysis uses equipment which is permanently installed at a certain facility, but it used and operated only by the inspectorate. This requires analysts to travel frequently.

Off-site analysis is the 'classical' way of performing verification measurements. Samples taken by an inspector are dispatched to an analytical laboratory which will then perform the measurements on request of the inspectorate. This enables the laboratory to operate under optimal conditions and with instrumentation permanently installed.

On-site laboratories represent a new concept which is based on the operation of a specialized laboratory working under the responsibility of the safeguards authority at the site of the facility to be inspected and analyzing material exclusively for safeguards purposes. Its independence and the confidentiality of the results produced have to be guaranteed by appropriate measures.

Depending on the plant size, material throughput and material type, an efficient measurement scheme has to be established, making use of one or more of the above mentioned possibilities.

The latter three analysis strategies do rely on the measurement of samples taken by an inspector. This paper focuses on the analysis of such samples as taken in large reprocessing plants and their treatment and measurement.

2. Sample Types

Depending on the nature of the plant, different types of samples are obtained. This includes different chemical compositions, different physical appearance and different handling techniques. The key elements of the nuclear fuel cycle immediately determine the types of samples to be expected. The sample spectrum in a reprocessing plant typically covers spent fuel solution, uranium products (uranyl nitrate solution, uranium oxide) and plutonium products (plutonium nitrate solution, plutonium oxide). Whenever a MOX fuel production plant is on the same site, MOX powders and pellets need to be analyzed as well.

2.1. *Reprocessing*

Irradiated nuclear fuel can be reprocessed after appropriate cooling time. Most of the reprocessing processes are based on a liquid-liquid extraction for the separation of the valuable materials uranium and plutonium. The most widely used technique is the so called PUREX process. Therefore, in a first step the fuel needs to be dissolved. The solution (**reprocessing input solution**) is stored in the input accountancy tank. Samples of the solution are taken from this tank. These samples are analyzed for uranium and plutonium content and for the respective isotopic compositions. Samples of input solutions contain apart from the fissile elements also the fission products and some activation products. Because of this and due to the intense radiation such samples are delicate to handle and difficult to analyze.

The separation of uranium, plutonium and the fission products results in concentrated, rather pure **solutions of U and Pu**. Samples from these 'product' solutions are subject to measurements of the concentration of the respective element.

The product solutions are used as base material for oxide powder production. UO_2 and PuO_2 samples are again subjected to measurements of the fissile isotope and element content.

2.2. *Fuel fabrication*

The civil fuel cycle knows two major categories of fuel: uranium oxide fuel and U/Pu mixed oxide fuel (MOX).

MOX fuel is manufactured from uranium and plutonium base materials. Depending on the production process U and Pu solutions or UO_2 and PuO_2 powders are used as starting materials. These however, are usually not measured (for safeguards purposes) in the fuel fabrication plant as this is already done at the reprocessing plant. In contrast to that the products, i.e. the MOX pellets are intensively verified. These samples have to be analyzed for uranium and plutonium element content as well as for their isotopic composition. The ^{241}Am content provides useful information on the last plutonium purification.

Metallic fuels or fuels of high initial ^{235}U enrichment are not commonly used in commercial reactors for electricity generation. These fuels therefore represent only a marginal fraction of the whole fuel production. Samples of these types of fuel are nevertheless of high relevance to Safeguards Authorities. They are analyzed in the laboratory with great care.

3. *Information Requested*

Depending on the sample characteristics and on the facility, the analytical requirements are set. As already indicated in the previous chapter, a variety of samples of different chemical and physical properties have to be analyzed. The information requested usually focuses on the one hand on the uranium isotopic composition, where the ^{235}U isotope abundance is the most relevant information for safeguards purposes. The uranium content in a sample also needs to be determined. The combination of the latter with the mass of the bulk and the ^{235}U abundance allows to calculate the total amount of fissile uranium. On the other hand, information on the plutonium element content is required, additionally the plutonium isotopic composition needs to be known. The combination of the sample analysis results with the information on the bulk results in the total amount of plutonium.

The knowledge of the ^{241}Am concentration, relative to the amount of Pu, allows to draw conclusions on the last plutonium separation.

Table 1 summarizes the plant types, material types and analysis types typically encountered in the fuel cycle. The third column specifies the sample sizes taken for verification measurement purposes. They are specified such that the uncertainties arising from sampling are kept to a minimum /1/. It has to be emphasized that the amount of material actually required for a measurement can be considerably lower (compare table 2).

TABLE 1. Simplified overview of plant categories, material types, desirable sample sizes and analyses

Plant Type	Material	Sample Size /1/	Analysis
Enrichment	UF ₆	4-8 g	U conc., U iso.
Fuel Fabrication	Solution: UO ₂ ²⁺	10 g	U conc., U iso.
	Pu	1-5 g	Pu conc., Pu iso.
	Powder: UO ₂	10 g	U conc., U iso.
	PuO ₂	2 x 0.5 g	Pu conc., Pu iso., Am
	Pellets: UO ₂	7-20 g	U conc., U iso.
	MOX	2 x (5-10) g	U conc., U iso. Pu conc., Pu iso., Am
Reprocessing	Solution: Spent Fuel	1-5 g	U conc., (U iso.) Pu conc., Pu iso.
	UO ₂ ²⁺ Nitrate Soln.	10 g	U conc., (U iso.)
	Pu Nitrate Soln.	1-5 g	Pu conc., Pu iso.

4. Sample Analysis Methodology

For any of the quantities to be determined as mentioned in table 1, a selection of analytical techniques is available, each of them could be applied to attain the desired goal. The choice of the measurement method to be applied for the determination of a certain parameter depends on a number of criteria, such as:

- sample composition
- available amount of material, which may be limited due to:
 - activity or dose rate restrictions
 - sample transport regulations
 - sampling procedures at the plant
- desired measurement uncertainty
- instrumentation and manpower available
- tolerable measurement delay
- creation of (secondary) waste

Whatever the method of choice might be, there are always advantages and disadvantages. Methods enabling a higher accuracy might require higher investment and/or running costs or might be more demanding in terms of operator skills and analysis time. This evaluation should in any case

be done in the light of the analytical needs, the available resources and the desired degree of "fitness for purpose". The list of methods presented below is neither exhaustive nor is it intended to describe a preference in any form. However, it covers the techniques currently being used or analyzing samples taken at large reprocessing plants.

4.1. Element Assay

The determination of the content of uranium and/or plutonium is of key importance for establishing the material balance in a plant, for accountancy purposes and for the verification of the latter. It is therefore essential to have a method at hand that allows to determine the respective element concentrations in samples taken at some place in the plant. Classical chemical methods compete with methods based on physico-chemical or purely physical principles. Whatever principle is applied, the analytical goal is the quantitative determination of the amount of uranium or plutonium in a sample. The different techniques may require different ways of sample conditioning (e.g. dissolution, dilution, special geometry).

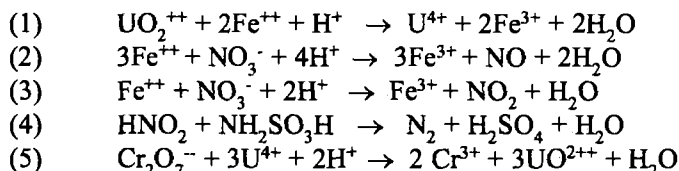
4.1.1. Titration

Titrimetric measurements are carried out by determining the volume (or mass) of a solution of accurately known concentration (the titrant) which reacts quantitatively with the solution of the substance to be determined (the titrand). The point at which the reaction is just complete is called the equivalent point or stoichiometric end-point.

This end-point can be indicated by

- the potential between an indicator electrode and a reference electrode, **potentiometric titration**
- the change in electrical conductivity, **conductometric titration**
- the current which passes through the titration cell between an indicator and a reference electrode, **amperometric titration**
- the change in absorbance of the solution, **spectrophotometric titration**

Uranium can be determined by potentiometric titration using the so-called "Davies and Gray" method /2/. It is based on the reduction of uranium(VI) to uranium(IV) in concentrated phosphoric acid solution, in the presence of sulfamic acid, by reaction with iron (II) sulfate. The excess of iron(II) is subsequently oxidized by nitric acid in the presence of molybdenum. The uranium(IV) is determined by mass titration with standardized potassium dichromate solution to a potentiometric end point.



Interferences are to be expected from bromide, iodide, chromium(III), silver(I), tin(II) and vanadium(IV) and (V).

Plutonium can also be determined by potentiometric titration, using the so called "silver oxide" method /3/. First the plutonium is quantitatively oxidized with silver(II) oxide. The excess of silver is destroyed by adding sulfamic solution. The plutonium(VI) is then reduced to plutonium(IV) with an excess of iron(II) sulfate. The excess is titrated with potassium dichromate solution.

Interferences are observed from V(V), Mn(II), Am and Np.

Titration techniques, also others than potentiometric titration, are widely applied for verification measurements in pure products, i.e. in U and Pu solutions and in the respective oxides.

4.1.2. Coulometry

Coulometry is considered to be a reliable method for the determination of uranium and/or plutonium. This method does not require a reference material for calibration, as it measures electrical charges and time. Coulometry is consequently a "primary method of measurement". It has furthermore the potential of being highly precise and accurate. However, reference materials are required to verify the proper working of the instrumentation.

The uranium determination by controlled potential Coulometry calls upon the reduction of uranium(VI) to uranium(IV) at a mercury electrode in sulfuric acid. A potential of -0.325V is applied for the reduction reaction. The amount of uranium is calculated from the number of electrical charges (Coulombs) required to complete the reaction. The end-point of the reaction is reached when the residual current (background) is as low as some μA . Corrections have to be applied for the blank current and the background. Interferences may arise from impurities such as copper, iron and manganese.

The determination of plutonium applies the oxidation/reduction of plutonium between its oxidation states +3 and +4 in sulfuric acid. Reduction is performed at a potential of +0.270 V, while the oxidation step requires +0.670 V. Interferences may arise from iron present in the sample solution.

Coulometry is only applied in a few laboratories for routine verification measurements on U and Pu product solutions or dissolved oxides.

4.1.3. Gravimetry

The gravimetric determination of uranium and plutonium is based on the assumption that calcination of a (rather pure, solid, oxidic) sample of either element will lead to a (stable) compound of defined stoichiometry. This compound is then easily weighable, from the difference in sample masses observed before and after calcination, the element content in the initial sample can be calculated. Corrections have to be applied for impurities contained in the sample, as they will cause systematic errors. Hence, gravimetry always requires an impurity determination. The latter may be achieved glow discharge mass spectrometry (GDMS), spark source mass spectrometry (SSMS) or inductively coupled plasma mass spectrometry (ICP-MS).

Gravimetry is also a "primary method of measurement" according to the BIPM definition. As it requires only weighing data and information on the sum of impurities, its potential for precision and accuracy is unsurpassed. Additionally, the amount of secondary waste produced is very small. This method is therefore of growing interest to safeguards laboratories.

Uranium is heated in air or oxygen at 950°C in order to obtain U_3O_8 . If prepared under these conditions, no deviations from stoichiometry are to be expected.

Similarly, Plutonium is heated in air or oxygen at 1250°C in order to obtain PuO_2 . If prepared under these conditions, the latter compound has been demonstrated to be stable and stoichiometric.

4.1.4. K-Edge Densitometry

Uranium or plutonium can be determined in a sample by K-Edge Densitometry (KED). The method /4/ uses a highly collimated X-ray beam passing through a solution sample of well defined path length. Its transmission is measured as a function of energy in critical energy regions. The underlying measurement technique is the K shell absorption edge spectrometry, colloqui-

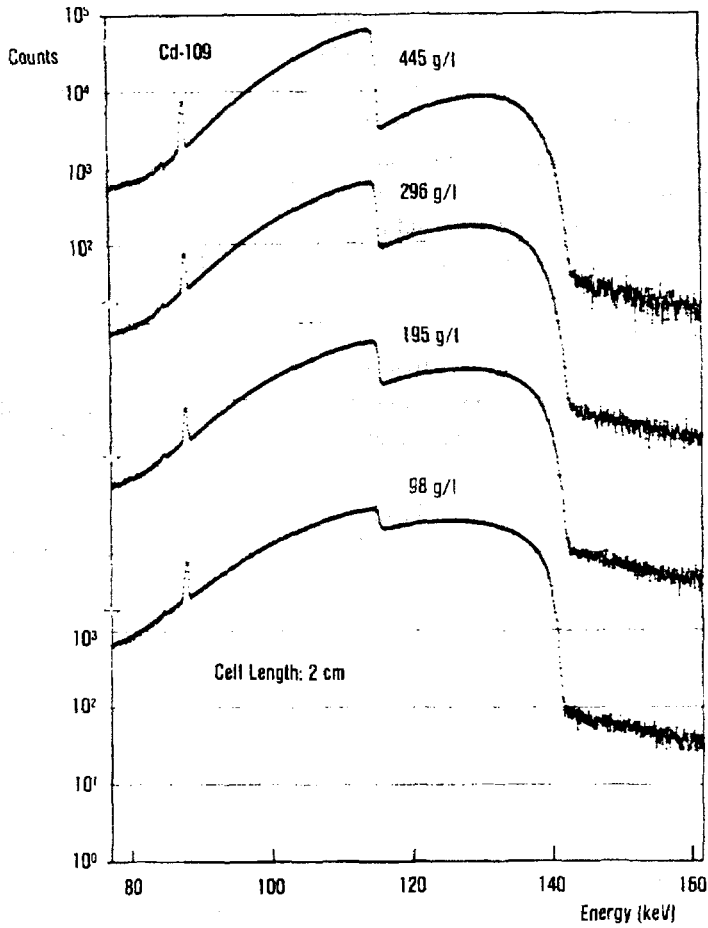


Fig. 1a K-Edge jump for different uranium concentrations

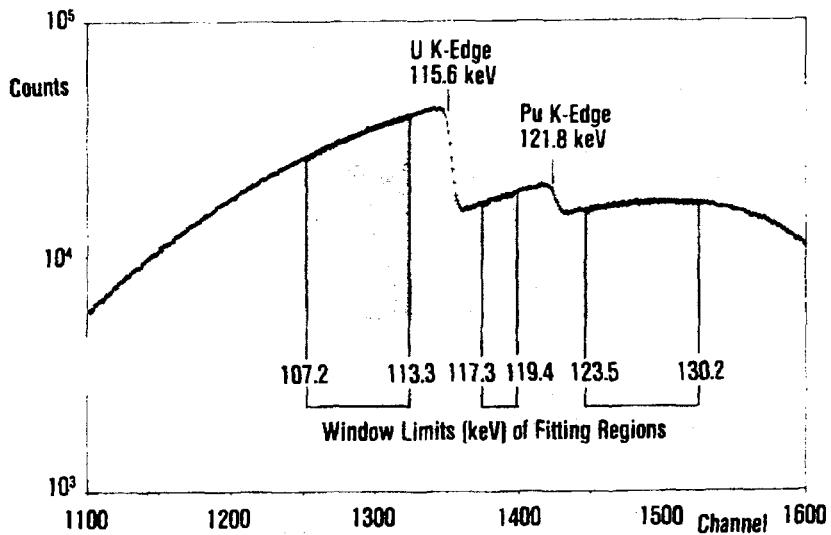


Fig. 1b X-ray transmission spectrum for a solutions with a U/Pu ratio of about 3

ally called K-edge Densitometry. The abrupt change of the transmitted X-ray intensity at the K absorption edge is a measure of the uranium or plutonium concentration in the sample as can be seen from fig. 1. The K-edge instrument requires a series of carefully characterized solutions of uranium and/or plutonium for establishing a calibration curve.

K-edge Densitometry can be applied to uranium or plutonium solutions from 25 g/L up to saturation (approx. 400 g/L). Interferences arise only from elements having their K absorption edge in the same energy region as the element under investigation. Consequently, the simultaneous presence of uranium and plutonium needs to be taken into account and an appropriate correction has to be applied.

K-Edge Densitometry delivers measurement results as volume concentration, i.e. in milligrams per milliliter or grams per liter. Most other techniques deliver results in mass concentration, i.e. in milligrams per gram. Consequently, one needs to determine the density of the solutions under investigation in order to be able to compare the measurement results obtained by the different techniques.

K-Edge is most advantageously applied to rather pure solutions of uranium and plutonium. If U and Pu are simultaneously present in a solution, the Hybrid K-Edge technique needs to be applied (see 4.3.2)

4.1.5. X-Ray Fluorescence

An X-ray beam of larger divergence stimulates the emission of characteristic X-rays from uranium and plutonium (X-ray fluorescence, XRF). The intensities of the induced X-rays may be used for the determination of the U/Pu ratio in a sample or, after appropriate calibration, for the absolute determination of the respective amounts of element. In the first case the U/Pu ratio is derived from the net peak areas of the $UK\alpha_1$ and the $PuK\alpha_1$ X-rays. The latter case calls upon the peak area measurement of the $K\beta_{1,3}$ line of uranium and plutonium.

Interferences are to be expected from any X-ray or soft γ lines of similar energy. Furthermore the self-absorption in the sample has to be taken into account. Measurement uncertainties of about 0.7% have been demonstrated.

4.1.6. Isotope Dilution Mass Spectrometry

Isotope dilution mass spectrometry (IDMS) is based on the addition of a known amount of enriched isotope (called the "spike") to a sample /5,6/. After equilibration of the spike with the sample, mass spectrometry is used to measure the altered isotopic ratio(s). The concentration of the element under investigation can be derived from the change(s) in isotope ratio(s). Consequently, only weighings (of sample and spike mass) and measurements of ratios (of ion beam intensities) have to be performed. The actual measurement is performed after equilibration of spike and sample and chemical separation of the element of interest. This assures the removal of isobaric interferences and a smooth ionization process.

Uranium samples are usually spiked with ^{233}U , an isotope which is not present in the sample. Therefore a single measurement allows to simultaneously determine the uranium concentration and the isotopic composition of the sample. Also enriched ^{235}U or ^{236}U may be used as spike isotopes, this however requires independent measurements of the ratios in the unspiked and the spiked sample.

Plutonium samples can be spiked with ^{244}Pu , an isotope which is usually not present in the sample. Due to its very limited availability, the use of this isotope has been restricted to exceptional cases. Mostly, plutonium is spiked with enriched ^{242}Pu . Furthermore, the application of ^{239}Pu or ^{240}Pu has been demonstrated successfully /12/.

IDMS is a highly selective method. It has the potential for high accuracy and precision. Also IDMS is a "primary method of measurement". Thermal Ionization Mass Spectrometry (see section 4.2.1) is mostly applied as isotope ratio measurement technique. However, also ICP-MS may be used, however allowing somewhat higher uncertainty. IDMS has found wide application in safeguards measurements and is applied in almost all analytical laboratories. Due to its high selectivity and its potential for high accuracy, IDMS is the method of choice for analyzing samples of spent fuel in reprocessing plants.

4.2. Isotope Assay

Besides the determination of the element concentration, the measurement of the isotopic composition of uranium and plutonium is of interest. This is due to the fact that not the elements uranium or plutonium are fissile, but their isotopes of uneven mass numbers. Despite this fact, plutonium is regarded as fissile material, irrespective of its isotopic composition. In contrast to that, safeguards authorities pay particular attention to the uranium isotopes ^{235}U and in special cases to ^{233}U .

However, the accurate determination of the isotopic composition of U or Pu is of prime importance for verification purposes. Different measurement techniques based on different measurement principles are available for this purpose. The choice of the method depends on the requested accuracy, the nature of the material and other factors as discussed already earlier.

4.2.1. Thermal Ionization Mass Spectrometry

Thermal Ionization Mass Spectrometry (TIMS) is widely applied for isotopic measurements. A sample preparation step prior to the actual measurement is required; this consists of the separation of the element of interest from other elements (e.g. matrix materials or impurities). The sample is then deposited onto a filament from which it is evaporated once being introduced in the mass spectrometer. These "vapors" are then atomized and at a hot surface ionized, from which the name "thermal ionization" is derived. The species U^+ are subjected to an acceleration by applying a high voltage and subsequent mass separation (e.g. $^{234}\text{U}^+$, $^{235}\text{U}^+$, $^{236}\text{U}^+$, $^{238}\text{U}^+$) by means of a magnetic field, an electrostatic field or a quadrupole.

An appropriate detection system allows the measurement of ratios of ion beam intensities. The isotope abundances are derived from these ratios. TIMS relies on chemically purified samples in order to avoid isobaric interferences. TIMS is therefore very selective and has proven to be highly precise and to have a potential for being very accurate. This method is widely applied in nuclear analytical laboratories and suitable for practically all types of material.

4.2.2. Gamma Ray Spectrometry

Also radiometric methods can be applied for isotope assay. These methods, however, are limited to non stable isotopes emitting either α -particles or gamma rays. The most prominent is certainly gamma ray spectrometry. It uses the characteristic gamma lines, or more precisely the energy of the gamma rays emitted from a particular isotope. Their intensity is a measure of the number of atoms present in the sample. It is applied in a variety of instrumental and software modifications. Detectors of different geometries (planar, coaxial, dwell) and prepared from different materials (NaI(Tl), Si(Li), Ge(Li), high purity silicon, high purity germanium, CdTe) are in use. Depending on the application, the desired spectral energy resolution, the efficiency and the useful energy range, the type of detector has to be selected. Furthermore, a number of computer codes have been developed for spectral deconvolution, for data reduction and evaluation.

One of the codes used is the so called MGA code, developed at Lawrence Livermore Laboratory /7/. The Multiple Group Analysis (MGA) allows to determine the isotopic composition of plutonium samples without external efficiency calibration. Its major drawback arises from the fact that ^{242}Pu does not show useful gamma rays. This isotope abundance has therefore to be estimated using isotope correlation techniques. However, it is a non destructive technique which has proven its capability in field application /8/ as well as under laboratory conditions.

The determination of the ^{235}U enrichment is typically done by measuring the intensity of the 186 keV line of this isotope. A particular geometry and calibration is required as the other isotopes can only insufficiently be determined. One of the major advantages is the possibility to use cheap NaI(Tl) detectors of relatively low resolution. A more sophisticated approach is the application of the MGAU code. Again, no external calibration is required.

Gamma spectrometric methods have considerably improved in performance over the last years. They are widely applied for accountancy and verification measurements.

4.2.3. Alpha Spectrometry

Alpha spectrometry uses the discrete energy of the α -particles emitted by certain radioactive isotopes for the identification and quantification of the respective nuclides. It requires the careful preparation of thin layers of analyte. The resulting α -spectrum allows to determine the activity ratio of the α -active isotopes present in the sample. The isotope abundance ratios can be derived from that. Its application in safeguards is limited to the determination of the $^{238}\text{Pu}/(^{239}\text{Pu}+^{240}\text{Pu})$ ratio. This information is complimentary to the mass spectrometrically obtained information on the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio which sometimes suffers from isobaric interference of ^{238}U .

4.3. Combined Methods

It is evident that the methods discussed so far can to some extent be combined for simultaneous use. Powerful measurement methods may result, often enabling increased sample throughput, reduced operator radiation doses and more efficient laboratory work. Combined methods usually rely on physical measurement principles which are applicable at the same time.

4.3.1. COMPUCEA

The combined product uranium concentration and enrichment assay (COMPUCEA) calls upon a combination of gamma ray spectrometry for measuring the ^{235}U abundance and K-edge Densitometry for the uranium element concentration measurement. The methods involved have been discussed in some detail in the sections above. Applications of the instrument are in verification measurements at enrichment plants, at fuel production plants and for the uranium product streams of reprocessing plants. Due to its compactness, the instrument is suitable for mobile use. The Euratom Safeguards Directorate has successfully been applying a COMPUCEA for in-field measurement campaigns at a large reprocessing plant and at Low Enriched Uranium fuel fabrication plants.

4.3.2. Hybrid K-Edge / K-XRF Densitometry

The combination of K-edge Densitometry with X-ray fluorescence resulted in the so called Hybrid K-Edge (HKED). This instrument is using a single X-ray source for both parts of analysis, the K-edge absorption and the fluorescence excitation. It has proven to be an extremely useful analytical tool in the verification of reprocessing input solutions. It is also applicable to mixtures of uranium and plutonium. The combination of the two techniques allows the simultaneous and quantitative determination of uranium and plutonium. This can even be done directly from samples of highly radioactive input solutions.

The number of such instruments in use and being installed is increasing, as the experience with existing instrumentation demonstrates the reliability of the results. At each of the two large European reprocessing plants, the Euratom Safeguards Directorate installed a hybrid K-Edge instruments. They have been operated by ITU staff for many years. Several hundred samples of spent fuel solution have been analyzed each year providing a solid experience in the operation of this type of instrument. The results are usually reported to the inspectors within a few days after sample arrival.

4.3.3. Neutron-Gamma Counting

Neutron coincidence counting relies on the spontaneous fission on ^{240}Pu and the neutrons produced with each fission process. The neutron count rate is a measure of the amount of ^{240}Pu present in the sample. However, accurate information on the isotopic composition of the sample is required in order to:

- correct for neutronic contributions from other Pu isotopes (^{238}Pu and ^{242}Pu)
- calculate the total amount of plutonium

If applied in combination with high resolution gamma spectrometry, a complete plutonium assay in solid samples (MOX or PuO_2 powder) is possible /9, 10/. The Euratom Safeguards Directorate has installed a neutron/gamma counter at a MOX production facility and gained positive experience in measuring small samples (individual pellets, powders). Such instruments will be used as primary tools for verification of Pu containing oxides in the on-site laboratories at the two large reprocessing plants.

5. Analysis of Samples for Verification Purposes

The analysis of samples for verification purposes needs to meet certain requirements, such as:

- accuracy of results
- laboratory delay
- efficient use of resources
- sample throughput

These requirements are intended to ensure an efficient and effective safeguarding of nuclear material. On the laboratory level measures have to be taken to make sure that these requirements can be met. These measures comprise organisational, infrastructural and scientific/technical arrangements. This can best be illustrated using a concrete example:

Inspectors take approximately a thousand samples per year in a large reprocessing plant. As mentioned earlier, these samples may be analysed in a specialized laboratory after having been transported. Seen the high number of samples and the delays going along with the transport arrangements, EURATOM decided to install On-Site Laboratories at the two large reprocessing plants in Europe. Already earlier, a hybrid K-edge instrument had been installed at each plant for verification measurements on spent fuel solution.

5.1. Analysis in the laboratory

The analysis of samples in the laboratory (be that off-site or on-site) represents certainly the ideal case from the measurement point of view. Optimal measurement conditions can be achieved, profiting from a well developed infrastructure and technical support. A selection of the measurement techniques described above can be applied.

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In the on site laboratories the following measurement techniques and instrumentation are routinely applied for verification sample analysis:

- thermal ionization mass spectrometry

Finnigan MAT sector field mass spectrometers are available

- isotope dilution mass spectrometry

sample preparation is performed in a glove-box by laboratory robots (Zymark)

- neutron coincidence counting combined with gamma spectrometry

a specially developed instrument is used

- K-Edge Densitometry

several instruments are available

- Hybrid K-Edge

several instruments (equipped with sample changers) are attached to the hot cells

- alpha spectrometry

several devices from Canberra and Ortec, some of them modified for use by the robot in a glove-box, are available

- COMPUCEA

an instrument is available in a dedicated glove-box (uranium only !)

5.1.1. Infrastructural Considerations

These instruments are operated by local computers (personal computers or work stations). The computers are connected via a local area network. A specifically developed software manages the analyses, collects the data, calculates the results, applies an integrated quality control and allows communication with the inspectorate.

Table 2 summarizes the amounts of material typically for a particular technique, required to carry out a measurement.

5.2. In-Field Measurements

In-field measurement campaigns using mobile equipment are carried out exclusively on uranium samples to avoid the transport of Pu contaminated equipment. In-field analysis comprises titration, COMPUCEA, thermal ionization mass spectrometry and gas source mass spectrometry. This spectrum of analytical techniques covers the needs arising in uranium handling facilities. It is perfectly suitable for verification measurements during physical inventory taking (PIT) by the inspectors. Hence, in-field measurements are an excellent tool for near real time verification measurements.

Another important area of in-field measurements covers the verification analyzes of reprocessing input solution samples. These measurements are carried out using equipment which is permanently installed (Hybrid K-Edge instrument) in the plant operator's laboratory, but exclusively used for safeguards measurements. More than six hundred input samples have been measured in 1997 by ITU staff members applying the HKED instrument at one of Europe's biggest reprocessing plants.

Table 2. Typical amounts of sample needed to perform a measurement

Method	Typical amount of element required for a single measurement (excluding sample preparation) ^a			Unit
	U	Th	Pu	
Titrimetry	20 - 100	50 - 100	5 - 50	mg
Coulometry	2 - 20	-	2 - 10	mg
Gravimetry	2 - 20	0.5 - 1	0.2 - 3	g
X-ray fluorescence	0.1 - 30	0.1 - 30	0.1 - 30	mg
Isotope dilution mass spectrometry	10 - 1000	10 - 1000	1 - 1000	µg
Spectrophotometry	20 - 500	5 - 250	b	µg
Fluorimetry	2 - 500	-	-	ng
Alpha counting	2 - 250	-	0.1 - 1	µg
K-edge	0.3 - 1	-	0.3 - 1	g
Gas mass spectrometry	20	-	-	mg
Thermal ionization mass spectrometry	1 - 1000	10 - 1000	1 - 1000	µg
Gamma spectrometry	0.1 - 1	-	-	
Alpha spectrometry	-	-	0.1 - 1	µg

a) The sample preparation is not considered except for the spiking and chemical treatment in isotope dilution analysis; b) Spectrophotometry direct measurement at 830 nm Pu(VI): 0.1-10 mg

6. Summary

Verification analysis of samples taken at large reprocessing plants can be performed off site after shipment of the samples to a specialized laboratory or, more advantageously in terms of cost and timeliness, on site. The latter may be achieved either by using permanently installed equipment which is operated by an inspector or in fully equipped on-site laboratory. Analytical techniques suitable for determining uranium and plutonium isotopic compositions as well as the respective element concentrations, are applied. Experience with a number of these techniques has shown that effective analytical support in safeguarding large reprocessing plants can be provided to the safeguards authorities.

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