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PERFORMANCE VALUES FOR NON DESTRUCTIVE ASSAY (NDA) TECHNIQUES APPLIED TO SAFEGUARDS:

THE 2002 EVALUATION BY THE ESARDA NDA WORKING GROUP

Edited by:
S. Guardini
EC-JRC-IPSC, Ispra (I)

R. Arlt,	IAEA, Vienna
M. Bickel,	EC-JRC-IRMM, Geel (B)
R. Carchon,	SCK/CEN, Mol (B) (*)
P. Chard,	UKAEA, Dounreay, (UK)
S. Iievlev,	SSTC, Kiev, (U)
A. Lebrun,	CEA, Cadarache, (F) (*)
F. Levai,	Technical University, Budapest (H)
T.K. Li,	Los Alamos National Laboratory (US)
M.S. Lu,	Brookhaven National Laboratory (US)
O. Mafra,	ABACC, Rio de Janeiro (Br)
P. McLelland,	UKAEA, Dunreay, (UK)
J. Morel,	CEA, Saclay (F)
H. Ottmar,	EC-JRC-ITU, Karlsruhe (G)
P. Peerani,	EC-JRC-IPSC, Ispra (I)
J. Rackam,	BNFL, Sellafield (UK)
W. Ruhter,	Lawrence Livermore Nat. Laboratory (US)
B. Thaurel,	IRSN, Fontenay-aux-Roses, (F)
A. Tiitta,	VTT, Helsinki (Fin)
P. Schwalbach,	EC-ESO, Luxembourg
M. Swinhoe	Los Alamos Nat. Laboratory (US)

Abstract

The first evaluation of NDA performance values undertaken by the ESARDA Working Group for Standards and Non Destructive Assay Techniques (WGNDA) was published in 1993. Almost 10 years later the Working Group decided to review those values, to report about improvements and to issue new performance values for techniques which were not applied in the early nineties, or were at that time only emerging.

Non-Destructive Assay techniques have become more and more important in recent years, and they are used to a large extent in nuclear material accountancy and control both by operators and control authorities. As a consequence, the performance evaluation for NDA techniques is of particular relevance to safeguards authorities in optimising Safeguards operations and reducing costs. Performance values are important also for NMAC regulators, to define detection levels, limits for anomalies, goal quantities and to negotiate basic audit rules.

This paper presents the latest evaluation of ESARDA Performance Values (EPVs) for the most common NDA techniques currently used for the assay of nuclear materials for Safeguards purposes.

The main topics covered by the document are:

- techniques for plutonium bearing materials: PuO_2 and MOX;
- techniques for U-bearing materials;
- techniques for U and Pu in liquid form;
- techniques for spent fuel assay.

This issue of the performance values is the result of specific international round robin exercises, field measurements and ad hoc experiments, evaluated and discussed in the ESARDA NDA Working Group.

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GLOSSARY

ABACC	Brasilian- Argentini~~a~~n Agency for Accounting and Control of Nuclear Materials
AGR	Advanced Gas Reactor
ANCC	Active Neutron Coincidence Counter
AWCC	Active Well Coincidence Counter
BWR	Boiling Water Reactor
BU	Burnup
COMPUCEA	COMbined Product Uranium Concentration and Enrichment Assay
CT	Cooling Time
CZT	CdZnTe
ENMC	Epithermal Neutron Multiplicity Counter
ESARDA	European SAfeguards Research & Development Association
FBR	Fast Breeder Reactor
GBAS	Glove Box Assay System
GXW	Gamma-X and Weighing
HEU	High Enriched Uranium
HKED	Hybrid K-Edge/K-XRF Densitometer
HLNCC	High Level Neutron Coincidence Counter
HPGe	High Purity Germanium
HRGS	High Resolution Gamma Spectrometry
INVS	INVentory Sample Coincidence Counter
KED	K-Edge Densitometer
LEU	Low Enriched Uranium
LWR	Light Water Reactor
MOX	Mixed Oxide
MTR	Material Test Reactor
NCC	Neutron Coincidence Collar
NDA	Non Destructive Assay
NMAC	Nuclear Material Accountancy & Control
PDGA	Passive Differential Gamma Absorptiometry
PHONID	PHOto-Neutron Interrogation Device
PNCC	Passive Neutron Coincidence Counter
PNMC	Passive Neutron Multiplicity Counter
PSMC	Plutonium Scrap Multiplicity Counter
PWR	Pressurised Water Reactor
PXRF	Passive X-Ray Fluorescence
RTGS	Room Temperature Gamma Spectrometry
SNM	Special Nuclear Material
TIMS	Thermal Ionisation Mass Spectrometry
UNCL	Uranium Neutron Coincidence Collar
UFBC	Universal Fast Breeder Counter
XRF	X-Ray Fluorescence

1. INTRODUCTION

The quantitative verification of the accountancy of fissile nuclear materials through independent measurements still represents one of the key elements of international nuclear materials Safeguards. The definition of internationally agreed performance values for the pertinent measurement techniques is an important prerequisite in this context, since international nuclear Safeguards are essentially based on the mutual understanding and agreement between the parties involved that the underlying system of measurements has well defined, documented and controllable performances, frequently referred to as: *"..latest international standards"* [1,2].

The assessment of the performances of non destructive assay (NDA) techniques represents one of the key areas where the Working Group for Standards and Non Destructive Assay Techniques (WGNDA) of the European Safeguards Research and Development Association (ESARDA) is permanently and intensively active. The wide international composition of the Working Group assures, a high degree of international consensus for the evaluated performance values. Indeed, besides the ESARDA partners several observers from US, ABACC, Ukraine, Hungary are regularly participating to the various activities of the WGNDA [3]. In addition, national, regional and international control authorities are also represented in the WG, together with plant operators and R&D laboratories.

Broadly speaking, two kinds of activities have been carried out by the WGNDA concerning the evaluation of performance values: First, the most important NDA techniques have been carefully reviewed with the aim of evaluating their "typical" uncertainty, when applied to different material types in different measurement conditions. This review was supported by international round robin exercises initiated by the WG with the aim to obtain a real picture of the performances and capabilities for selected methods and techniques [4,5]. This first kind of activity led to the compilation of ESARDA NDA Performance Values (EPVs) [6].

The second area of activities related to the assessment of performances concerns common projects specifically designed and launched by the WGNDA to determine the capabilities of specific tools pertinent to NDA measurements. The latest projects in this area involved:

- Monte Carlo round robin exercises which had the aim to assess and improve modelling capabilities [7, 8]
- the ^{242}Pu Project concerning the assessment and improvement of the ^{242}Pu abundance evaluation, which led to the establishment and use of a new correlation algorithm [9,10]
- a Project conducted together with the ESARDA Low Enriched Uranium (LEU) Working Group aiming at an assessment of the sampling error for NDA measurements [11].

The continuing research and development work for NDA techniques, together with technological advances, have improved the measurement situation and the performance in a number of NDA applications during the last decade. The WGNDA therefore felt it appropriate to review his former evaluation of ESARDA NDA performance values, published in 1993, in order to provide an updated account of the progress made in NDA measurement technology. The present report summarises the most important improvements and provides, if and where necessary, updated performance values.

1.1 Definition, Scope and Use of NDA Performance Values

NDA techniques have become an indispensable tool in Safeguards, and they are presently being used to a large extent in nuclear material accountancy and control both by operators and control authorities. They are of interest to several other potential users as outlined below, and they may find even wider application within the scope of future Safeguards, where non-destructive "confirmative"-type of measurements will play an important role.

The evaluation of measurement performances for NDA techniques is therefore of particular relevance to all Safeguards "actors": not having the best information about the performances of NDA measurement methods means losing the potential for optimising Safeguards operations and reducing costs.

The NDA Performance Values presented here are conceived to represent the "**knowledge of the overall uncertainty and sources of uncertainties associated with NDA measurement systems**", and they are intended to be used for the following purposes:

1. for the planning of inspections by Safeguards Authorities;
2. to provide guidance to users in judging the quality of their NDA measurements;
3. to decide if, under fixed settings, repeated measurements, repeated sampling or repeated inspections are an appropriate tool to reduce the overall uncertainty;
4. to analyse operator-inspector differences in Safeguards verification and accountancy;
5. to allow R&D laboratories to compare their achieved measurement performances with the latest internationally agreed PVs;
6. to define the required accuracy level of NDA standards;
7. to serve as input in accountancy error propagation models for MBAs or entire plants
8. to compare the updated performance values with earlier editions, in order to get an impression of improvements in measurement quality (change to lower values) or improvements in realistic perception (change to higher or lower values);
9. to provide orientation for national or international regulators for the definition of basic parameters (detection limits, goal quantities, anomaly definition).

The WGNDA has been fully aware of the general problems faced in the definition of NDA performance values in view of the diversity of measurement situations encountered in many NDA applications, ranging for the same determination from measurements performed with dedicated and specifically tailored equipment under controlled laboratory conditions, to measurements carried out with lower-grade portable equipment under adverse field conditions. Given this situation, it often appears difficult to quantify NDA performances just in terms of a single figure.

For this reason a range of performance values is quoted in many instances in order to take into account varying performances with measurement conditions and/or properties of the measurement items. The measurement conditions such as type of equipment, detector, counting times, etc. were also specified as far as possible in the tables providing the performance values. The values are normally rounded to one decimal digit.

It is important to note that the performance values published in this document represent measurement performances that are realistically achievable under fairly controlled measurement conditions. Where a technique is used under less favorable conditions, the actual uncertainty may be higher than published herein. On the other hand, under optimised conditions also somewhat better measurement performances than quoted in this paper might be realised in certain applications.

Furthermore, the given performance values should certainly not be used as replacement of a proper uncertainty statement for measurements performed: they should be rather considered as a kind of reference and guideline for the users in assessing the performance and quality of their own measurements.

NDA performance values for the following techniques and material types are presented and discussed in this paper:

- gamma-spectrometry, passive neutron techniques and calorimetry for the plutonium assay in unirradiated solid plutonium bearing materials;
- gamma-spectrometry and active neutron techniques for the fissile uranium assay in unirradiated solid uranium bearing materials;
- K-edge densitometry, X-ray fluorescence and gamma spectrometry for the uranium and plutonium assay in solutions;
- gamma-spectrometry and neutron techniques for spent fuels.

Salient features of the individual measurement techniques and important factors and parameters influencing their measurement performance are briefly outlined in each case. If existing, recent progress in measurement technologies and methodologies is also described. It is hoped that this additional background information will be helpful for the user in better understanding the measurement situations encountered in NDA applications and in assessing the quoted performance values.

NDA performance values for waste measurements, also included in the previous issue of the ESARDA NDA performance values, have been exempted from the present document. The Working Group felt it appropriate to address this special area of NDA applications, which has also a very large relevance for nuclear waste management, in a separate evaluation.

1.2 Origin and Structure of the Data

The ESARDA NDA performance values reported in this paper have been evaluated from data and information of different origin:

1. they come from tailored laboratory experiments;
2. they come from field inspection activities, re-elaborated and re-analysed with suitable statistical tools;
3. they are the results of ESARDA intercomparison exercises carried out with specially designed reference materials with the aim of assessing NDA performances [4,5,12,13].

Case by case the origin of the source information is quoted in the text or referred to in the literature.

As to the expression of uncertainty, the Working Group has decided, after intense discussions, to adhere to the previous categorisation in terms of random and systematic uncertainties. This decision takes into account the fact that the majority of statistical evaluations made on Safeguards measurement data (and the conclusions drawn from them) relies on this type of classification, and that specifically for the counting techniques used in NDA the random uncertainty due to pure counting statistics often represents the dominating uncertainty component.

The adherence to the "Guide to the Expression of Uncertainty in measurement" [14] is presently becoming a standard in scientific publications. The recommended categorisation of uncertainties therein (A/B) does, however, not exclude a further use of the random/systematic categorisation. The Guide explicitly states (E3.7): "*classifying the methods rather than the components does not preclude gathering the individual components ... into specific groups for a particular purpose in a given measurement, for example, when comparing the experimentally observed and theoretically predicted variability of a complex measurement system*". This is exactly one of the main purposes the present data will be used for.

The different ways of categorisation of uncertainties are therefore not at all contradictory, but rather "orthogonal" [H. Aigner, IAEA, Personal Communication], where, for the present purpose, the differentiation between random and systematic uncertainties appears to be more practical and better suited for the end users. In addition, in both systems the uncertainty propagation is performed in exactly the same way, hence, the same total uncertainty will result at the end.

The adopted definitions of the uncertainty components are also coherent with those given in: ISO, "International Vocabulary of Basic and General terms in Metrology, First Edition 1984" [15]. The categorisation of uncertainty components is also coherent with the ISO Guide 5725 [16] on Accuracy of Measurement Methods where the concept of "trueness" in statistical measurement data evaluation, has been further elaborated.

The random uncertainty component (r), which affects in an unpredictable manner the measurement result for a single item is for many NDA measurements determined to a large extent by the counting time (or of the number of repetitions). The figures given in this paper for "r" are relative to measurement times which are, generally speaking, "field" measurement times.

The systematic uncertainty component (s) contains uncertainties, which are shared by many samples, such as normalisation and calibration errors, uncertainty in nuclear constants, but also uncertainties connected with sampling and with differences in physical and chemical properties between measurement and calibration items , appearing as unknown biases.

Total (overall) uncertainty values are not given since they are generally assumed to correspond to the quadratic sum of "r" and "s" , assuming that the two types of uncertainty are independent.

All values given in the tables are relative uncertainties, given with an expansion factor k=1.

2. TECHNIQUES FOR PLUTONIUM-BEARING MATERIAL: PUO_2 AND MOX

This chapter discusses characteristic features and performances of NDA techniques utilised in Safeguards for the determination of the amount and of the isotopic composition of plutonium in unirradiated Pu-bearing solid materials. The most common NDA techniques applied for the determination of the total amount of plutonium in a measurement item are Passive Neutron Coincidence Counting (PNCC) and calorimetry. Both methods make use of isotope-specific nuclear properties and therefore do require the knowledge of the Pu isotopic composition for the interpretation of their responses in terms of the total amount of plutonium. The NDA choice for the complementary isotopic measurement is High Resolution Gamma Spectrometry (HRGS). However, very often also isotopic data from other sources such as mass spectrometry, if available, are used for the evaluation of the PNCC and calorimetry measurements.

2.1 High-Resolution Gamma Spectrometry (HRGS) for Pu isotopic composition

2.1.1 Fundamentals

HRGS represents since long time an important tool for Pu isotope abundance measurements in Safeguards. The technique, which bases on ratio measurements of isotope-specific gamma rays emitted in the natural decay of the Pu isotopes, offers the great practical advantage of not requiring a calibration with physical standards. The underlying intrinsic calibration approach relies on fundamental nuclear data such as isotope half-lives and gamma emission probabilities.

Plutonium isotope abundance measurements by HRGS can be made on virtually all kinds of plutonium samples containing unirradiated plutonium, with a wide range of plutonium masses (from mg to kg size samples). The method only requires that the sample containment offers sufficient transparency for the gamma rays to be detected for analysis. This requirement is fortunately met by a large number of sample containers for plutonium materials found in practice.

A major advancement for the measurement technique was achieved with the development of the Multi-Group Analysis (MGA) code, which successfully exploits the complex $XK\alpha$ region (94-104 keV) of a plutonium gamma spectrum for the isotope analysis [17,18]. Since this spectral region contains the most abundant plutonium gamma and X-rays detectable in a gamma spectrum from plutonium in the presence of some Am, fairly precise isotope abundance determinations became feasible with this analysis from gamma spectra accumulated in relatively short counting times (15-30 min).

During the last decade improved complementary analysis codes making use of the more energetic but less abundant gamma rays in the energy region between 125 and 660 keV have also become commercially available. A widely used code supporting the analysis of this energy range is the FRAM code [19]. The resort to the higher energy gamma rays for isotopic analysis provides some advantages in cases of stronger sample shielding [20]. The FRAM code has been recently upgraded to provide, like the MGA code, also analysis capabilities for the $XK\alpha$ region [21].

A drawback of the gamma-spectrometric technique is the lacking measurement capability for the isotope ^{242}Pu, which does not manifest itself with a detectable gamma-ray signature in a plutonium gamma spectrum because of its very low specific gamma activity. Therefore recourse has to be made to isotope correlation techniques for an estimate of the abundance of this isotope. A new type of isotope correlation relating the Pu isotope ratio 242/239 to the measurable ratios 238/239 and 240/239 has been proposed and validated from a large set of LWR isotopic data [9,10]. The new correlation provides a significant improvement for the ^{242}Pu estimate compared to previously used algorithms, especially for PWR plutonium. Nonetheless, the remaining uncertainties for the estimated ^{242}Pu abundance do still affect the overall accuracy of a complete gamma-spectrometric Pu isotopic analysis made on plutonium materials containing a notable fraction of this isotope.

2.1.2 Instrumentation

High-quality gamma spectra taken with good energy resolution are mandatory for a reliable and accurate gamma-spectrometric Pu isotopic analysis. High-resolution gamma spectrometers equipped with suitably sized HPGe detectors therefore still represent the prime choice. For the appropriate detector size, compromises have often to be made between desired optimum energy resolution and detector efficiency, but a variety of suitable HPGe are readily available.

The last decade has seen a remarkable degree of miniaturisation for the electronic part of the gamma spectrometer, resulting in light and compact portable equipment for in-field measurements. This also holds to some extent for the portable HPGe detectors, but the need for detector cooling to the temperature of liquid nitrogen during operation remains a practical obstacle for many in-field applications. Continuous efforts are therefore being undertaken with the aim to replace the cooling medium of liquid nitrogen by light and reliable electrical cooling generators.

Continuous research and development work is also going on for improved semiconductor detectors operating at room temperature or with Peltier cooling such as CdTe or CdZnTe detectors, and for the development of adequate spectrum analysis codes applicable to gamma spectra taken with such detectors. Although substantial progress and improvements have been reached in recent years, it appears unlikely that this type of detector, because of the inferior energy resolution and poorer energy response function, will become a full substitute for HPGe-based spectroscopy systems in the foreseeable future. Nonetheless, the feasibility of Pu isotopic analysis with a performance sufficient for the coarse categorisation of the isotopic grade of plutonium has been already demonstrated for measurements made with CdTe detectors [22].

2.1.3 Performance values

The evaluation of measurement performances for Pu isotope abundance measurements by HRGS has been a continuous working item for the WGNDA. To this end the WG has organised in the course of the years three inter-comparison exercises with international participation [23,24,5]. The evaluated performance values given in Table I are based on results from the last inter-comparison exercise [5], from dedicated performance studies [25,26,27,28], from information and experiences collected during a dedicated workshop [29], and from a larger number of routine laboratory measurements made for Safeguards.

The random uncertainties for the isotope abundances quoted in Table I are largely determined by counting statistics, which in turn depends on a number of measurement variables such as counting time, detector efficiency, amount of sample material, isotope ratio, type of sample shielding etc. The given performance data for the random uncertainty component refer to measurements made on samples with >1 g of plutonium in a non-strongly absorbing containment for a counting time of about 10-20 min, and for the evaluation of the isotope abundances from the XKα region. For applications involving smaller amounts of plutonium (<1 g) or strongly absorbing container materials, significantly longer counting times are usually needed in order to reach random uncertainties comparable to the systematic uncertainty components.

Systematic uncertainties are mainly associated with deficiencies in the algorithms used for the analysis of the complex gamma spectra for extraction of the required raw data like net peak areas and relative detection efficiency. The respective systematic uncertainties are difficult to quantify in general because they are dependent to some extent on the quality of the recorded gamma spectra in terms of energy resolution and quality of the peak shape. Another source of systematic uncertainty may be associated with uncertainties of the nuclear data required for the conversion of measured peak area ratios into atom ratios. The systematic uncertainties quoted in Table I represent the range of average differences between measured and declared isotope abundances as observed in a number of inter-comparisons. The data refer to HRGS measurements evaluated with declared ^{242}Pu abundances. The systematic uncertainties quoted for ^{238}Pu and ^{241}Am represent estimates, because real performance data are difficult to establish in view of the lack of accurate reference values for both isotopes.

Table I : Performance values for Pu isotope assay in PuO_2 and MOX.

Type of plutonium	**Isotope**	**r (%)** [a]	**s (%)** [b]
Low burnup	^{238}Pu	3	5
	^{239}Pu	0.2	0.1-0.2
	^{240}Pu	1	0.3-1
	^{241}Pu	1	0.2-0.6
	^{241}Am	1	0.5
High burnup	^{238}Pu	1	1
	^{239}Pu	0.5	0.2-0.4
	^{240}Pu	1	0.5-1
	^{241}Pu	1	0.5-1
	^{241}Am	1	1

[a] Counting time 10-20 min
[b] HRGS isotopic data evaluated with declared ^{242}Pu

Table II gives typical performance values for the ^{242}Pu estimate from the new type of correlation. The separation into random and systematic uncertainty components does not apply in this case. Instead, the performance is given in terms of the typical relative standard deviation (rsd) observed for the differences between estimated and declared ^{242}Pu abundances. Performance values are quoted for 4 different types of plutonium (Magnox, AGR, BWR, PWR), to which the correlation has been applied using specific sets of coefficients for the correlation. In many instances parametric plots of the measured ratios ^{238}Pu/^{239}Pu versus ^{240}Pu/^{239}Pu allow to identify unambiguously the respective type of plutonium [10]. If the given isotopic composition does not clearly point to a particular type of plutonium (e. g, in case of mixtures), larger uncertainties have to be expected and taken into account. The observed performance for the correlation proves that it is working best for PWR plutonium.

Table II : Performance of ^{242}Pu estimate from isotope correlation.

Type of plutonium	**rsd (%)**
PWR	3
BWR	6
AGR	4
Magnox	4

One of the main objectives of plutonium isotope abundance measurements made by gamma spectrometry is the determination of the quantities P_{eff} and $^{240}Pu_{eff}$ as defined in Sections 2.2 and 2.3, which are required for the interpretation of the plutonium assay by calorimetry and neutron coincidence counting, respectively. The performance values given in Tables I and II have been propagated as independent variables into the respective expressions for P_{eff} and $^{240}Pu_{eff}$ to calculate the expected random and systematic uncertainties for both quantities as listed in Table III. Two sets of HRGS performance data are listed in the Table, differentiating between the origin of the ^{242}Pu abundance: (i) declared ^{242}Pu from a TIMS measurement, and (ii) ^{242}Pu abundance estimated from the isotope correlation. The right-hand column of Table III lists, for comparison, random and systematic performance values for P_{eff} and $^{240}Pu_{eff}$ resulting from the propagation of uncertainties for Pu isotope measurements by Thermal Ionization Mass Spectrometry (TIMS)/Alpha Spectrometry according to recent International Target Values (ITV) [30].

Since the assumption of independence made for the uncertainty contributions of the individual isotopes is not strictly correct, the calculated HRGS performance values for P_{eff} and $^{240}Pu_{eff}$ may be overestimated to some extent according to practical experience. This holds particularly for the systematic uncertainty component, where the correlated uncertainties of the individual isotopes tend to partly cancel each other. For reactor-grade plutonium the performance values for P_{eff} are largely determined by the uncertainties for the ^{238}Pu abundance. This is also true for the TIMS/α data, where the current target values for ^{238}Pu abundance measurements in higher burnup plutonium (1.5 % random and 1 % systematic) would have to be tightened significantly in order to reduce their impact on the uncertainty of P_{eff}. The lack of accurate reference values for ^{238}Pu is currently also hampering the evaluation of the true performance of ^{238}Pu abundance measurements by HRGS, and hence also for P_{eff}.

Table III : Performance values for $^{240}Pu_{eff}$ and P_{eff}.

Quantity	**Type of plutonium**	**HRGS (^{242}Pu from TIMS)**		**HRGS (^{242}Pu from correl.)**		**TIMS/α (ITV for Pu isotopes)**	
		r (%)	s (%)	r (%)	s (%)	r (%)	s (%)
$^{240}Pu_{eff}$	Low burnup	1	0.3-1	1	0.3-1	0.15	0.1
	Magnox	0.9	0.5-0.9	0.9	0.5-1	0.1	0.06
	AGR	0.8	0.4-0.8	1	0.6-1	0.1	0.1
	BWR	0.8	0.4-0.8	1.3	1.1-1.3	0.15	0.2
	PWR	0.7	0.4-0.8	1	0.8-1	0.2	0.2
P_{eff}	Low burnup	0.25	0.25	0.25	0.15-0.3	0.25	0.25
	Magnox	0.5	0.3-0.5	0.5	0.3-0.5	0.4	0.3
	AGR	0.6	0.5	0.6	0.6	0.7	0.5
	BWR	0.6	0.6	0.6	0.7	0.9	0.6

	PWR	0.7	0.7	0.7	0.8	1.1	0.7

2.2 Calorimetry for Pu Mass Determination

2.2.1 Fundamentals

Calorimetry determines the amount of plutonium in an item through the measurement of the heat produced by the radioactive decay of the plutonium isotopes. Since the thermal power generated per unit amount of plutonium depends on the isotopic composition of plutonium, calorimetry requires knowledge of the relative plutonium isotope abundances for the conversion of the measured thermal power into the corresponding amount of plutonium. The calorimetric plutonium assay also needs information on the content of ^{241}Am in the measurement item, which also contributes to the measured thermal power and which as a decay product of ^{241}Pu is present in practically all plutonium samples.

The specific thermal power P_{eff} (W/g) of plutonium calculates from the expression

$$P_{eff} = \sum_i R_i \cdot P_i$$

where:

R_i = abundance of the i-th isotope (i = ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{241}Am)of the Pu expressed as a weight fraction, g isotope/g-Pu, and

P_i = a physical constant, the specific thermal power of the i-th isotope in W/g.

Table IV lists the thermal power values and their standard deviations for the plutonium isotopes, ^{241}Am and ^{3}H. The by largest specific heat is produced by ^{238}Pu. The uncertainties of the thermal power values are well below 0.1% for the main Pu isotopes. Table IV also indicates the main decay mode responsible for the heat production, which for all isotopes listed has a branching ratio of > 99.99%. The last column specifies the potential energy loss that might be lost from the calorimeter due to the escape of decay neutrons and photons. This energy loss is negligible for all isotopes except for ^{241}Am, where it could reach a maximum value of about 0.5% assuming the escape of all 59.54 keV decay photons.

Table IV: Specific thermal power values.

Isotope	Main Decay Mode	Specific Power (mW/g) [a]	Stand. Dev. (%)	Max. Energy Loss (%)[b]
^{238}Pu	α	567.57	0.05	3.1E-02
^{239}Pu	α	1.9288	0.02	1.3E-03
^{240}Pu	α	7.0824	0.03	5.5E-04
^{241}Pu	β	3.412	0.06	2.5E-02
^{242}Pu	α	0.1159	0.22	3.2E-02
^{241}Am	α	114.2	0.37	5.1E-01
^{3}H	β	324	0.14	-

[a] from Ref. [31]

[b] from Ref. [32]

The characteristic thermal power generated by different types of plutonium are listed in Table V (assuming Pu freshly separated from ^{241}Am). The Table also indicates the isotope contributing the largest fraction to the respective thermal power. For aged high-burnup PWR plutonium typically containing between about 1-3% weight % of ^{238}Pu and ^{241}Am, more than 90% of the thermal power will be generated by these two minor isotopes.

Table V: Thermal power of different types of plutonium.

Type of plutonium	**Thermal power (mW/g)**	**Main heat contributor**	**Contribution in %**
Weapons Grade	2-3	^{239}Pu	70-80
Magnox	4-5	^{240}Pu	35-40
AGR	5-8	^{238}Pu	40-50
BWR	6-10	^{238}Pu	50-60
PWR	10-20	^{238}Pu	60-90

The thermal power *W* measured from a plutonium item in a calorimeter is converted into the amount of plutonium as following:

$$m_{Pu} = \frac{W}{P_{eff}}$$

The thermal power measurement in the calorimeter is usually calibrated against electrical standards or certified plutonium reference materials (mostly ^{238}Pu heat standards). An important feature of practical relevance is the fact that the calibration samples must not be physical standards representative of the materials being assayed.

Calorimetry is a truly nondestructive method and can be applied to all kinds of plutonium bearing materials, because the heat measurement is completely independent of material and matrix type. Self attenuation does not occur. Interferences or measurement biases could be only introduced by undetected heat-generating radionuclides, or by chemical processes such as phase changes or endothermic or exothermic chemical reactions (normally not an issue for Safeguards samples). Packaging conditions of the measurement item cannot change the heat output of the sample but are usually the determining factor for measurement time. Typical assay times can range from 1-2 h up to 20 h or more. Statistical prediction algorithms are usually applied to predict thermal equilibrium and reduce measurement time.

Calorimetry is also routinely used for the assay of tritium in many physical forms of tritium compounds. For the tritium assay the measured thermal power can be directly converted into tritium mass using the specific power P_{eff} = 0.324 W/g of tritium.

2.2.2 Instrumentation

All calorimeters in use for plutonium assay are heat-flow type calorimeters, where the sample heat generated in a thermally insulated sample chamber flows past a temperature-sensing element, through a well-defined thermal resistance, to a constant-temperature heat sink. A variety of heat-flow calorimeters, differentiated by the temperature control techniques, the heat flow paths and the type of temperature heat sink, are in practical use for nuclear material measurements. The most common ones are known as isothermal „air bath“, water bath and rod calorimeter [31].

The majority of the existing calorimeters employ traditional Ni sense windings and Wheatstone bridge circuitry as temperature sensing element for measuring the heat flow. In recent years high-sensitivity thermopile sensors have become a viable alternative to the nickel thermocouple/Wheatstone bridge sensor for heat flow measurements. The intrinsically low noise and good baseline stability of the thermopile sensors make them particularly interesting for heat measurements in the milliwatt and sub-milliwatt range. Small sample calorimeters based on thermopile technology have been recently developed [33,34]. Another major advancement in terms of sensitivity and precision for low thermal power measurements has been achieved with a new generation of calorimeters, which are based on "inertial temperature control" using a metal block of high thermal inertia surrounded by heat flow sensing thermopile arrays. This variant offers an improvement of temperature control by up to three orders of magnitude, permitting the extension of calorimetric measurements down into the μW measurement range [35].

2.2.3 Performance values

The performance of a calorimetric plutonium assay depends on two basic variables: (i) the thermal power W as determined by the calorimeter, and (ii) the quantity P_{eff} as derived from an external isotope abundance measurement. The performance of the thermal power measurement is dependent on the sensitivity of the calorimeter, the baseline stability, and the item power.

Table VI lists typical performance data for the thermal power measurement obtained with taditional large sample calorimeters (air bath or water bath) equipped with Ni thermocouples and Wheatstone bridge circuitry, and with the new generation of small sample calorimeters (air bath or water bath) using thermopile sensors or combinations of thermopiles and Ni thermocouples (Hybrid calorimeters). The dominant contributions to the random and systematic uncertainties for the small sample calorimeters are due to heat distribution errors (spacial nonuniformity of the calorimeter response) and baseline fluctuations.

Table VI: Performance of thermal power measurement.

Calorimeter	**Thermal power level (W)**	**r (%)**	**s (%)**
Large sample	0.1	0.4-0.7	0.1-0.2
calorimeter	1	0.1-0.3	0.05-0.2
(Ni thermocouple)	10	0.05-0.07	0.05-0.2
	100	0.05-0.07	0.05-0.2
Small sample	0.001	0.8-1.0	0.2-0.5
calorimeter	0.01	0.1-0.3	0.1-0.2
(Thermopile)	0.1	< 0.1	0.1

The total random and systematic uncertainty of a calorimetric plutonium assay is obtained from a combination of the respective uncertainty components for the thermal power and P_{eff} determination. This yields the relative combined standard uncertainty for the Pu element assay from a combined calorimetry and isotopic measurement in accordance with the ISO definition for total uncertainty. For reactor-grade plutonium the uncertainties for P_{eff} as listed in

Table III of Section 2.1 outweigh by far the typical uncertainties from the thermal power measurement, irrespective of the method used for the isotope abundance measurement. The question of accuracy achievable for a calorimetric plutonium assay of reactor-grade plutonium simply reduces to the question of how accurate the ^{238}Pu (and ^{241}Am) abundance can be determined. For low burnup plutonium, however, where P_{eff} can be determined with much higher accuracy, calorimetry still represents the most accurate NDA technique for bulk plutonium samples.

2.3 Passive Neutron Coincidence and Multiplicity Counting Techniques for Pu Mass Determination

2.3.1 Fundamentals

The measurement of plutonium by passive neutron coincidence counting makes use of the fact that plutonium isotopes with even mass number (238, 240, 242) show a relatively high neutron emission rate from spontaneous fission. Table VII lists for the different plutonium isotopes the specific yields of fission neutrons, and the average number of neutrons, $<\nu>$, released per spontaneous fission. The actual number of prompt neutrons, ν, emitted from an individual fission event is described by the probability distribution $P(\nu)$ for the neutron multiplicity (Table VIII). This data show that in 70-80 % of the fission events two or more neutrons are released. These neutrons are emitted simultaneously and are therefore correlated in time. Delayed neutrons are neglected, since they do not contribute to the coincidence rate.

Table VII : Spontaneous fission neutron yields [41].

Isotope	**Spontaneous fission yield (neutrons /s-g)**	**Neutron multiplicity** $<\nu>$
^{238}Pu	2.59 10^3	2.21
^{239}Pu	2.18 10^{-2}	2.16
^{240}Pu	1.02 10^3	2.16
^{241}Pu	5. 10^{-2}	2.25
^{242}Pu	1.72 10^3	2.15

Table VIII : Neutron multiplicity distribution [41].

Probability	**^{238}Pu (spontaneous fission)**	**^{239}Pu (thermal induced fission)**	**^{240}Pu (spontaneous fission)**	**^{242}Pu (spontaneous fission)**
P(0)	0.054	0.011	0.066	0.068
P(1)	0.205	0.101	0.232	0.230
P(2)	0.380	0.275	0.329	0.334
P(3)	0.225	0.324	0.251	0.247
P(4)	0.108	0.199	0.102	0.099

P(5)	0.028	0.083	0.018	0.018
P(6)		0.008	0.002	0.003

The detection of bursts of time-correlated neutrons, which uniquely identify a spontaneous fission event among other neutron sources emitting neutrons randomly distributed in time such as (α,n) neutrons, allows to quantify the amount of plutonium in a sample. In reactor-grade plutonium the isotope ^{240}Pu usually dominates the overall emission of spontaneous fission neutrons. The primary quantity, that is commonly determined in passive neutron coincidence counting, is therefore an effective amount of ^{240}Pu, m_{240eff}, representing a weighted sum of the amount of the 3 even isotopes 238, 240 and 242:

$$m_{240eff} = \gamma_{238} \cdot m_{238} + m_{240} + \gamma_{242} \cdot m_{242}.$$

The coefficients γ_{238} and γ_{242} describe the contributions of ^{238}Pu and ^{242}Pu to the neutron coincidence response in terms of an equivalent amount of ^{240}Pu. For the conversion of m_{240eff} into the total amount of plutonium, m_{Pu}, the weight fractions R_{238}, R_{240} and R_{242} of the plutonium isotopes 238, 240 and 242 must be known to calculate the isotope-specific quantity

$$^{240}Pu_{eff} = \gamma_{238} \cdot R_{238} + R_{240} + \gamma_{242} \cdot R_{242}.$$

With this isotopic input data the total amount of Pu then calculates to:

$$m_{Pu} = \frac{m_{240eff}}{^{240}Pu_{eff}}$$

A major problem associated with many neutron coincidence measurements arises from the fact that the measured coincidence rate of spontaneous fission neutrons is not uniquely and invariably linked to the amount of the 3 even plutonium isotopes alone. Rather, in practice it is always altered (increased) by induced fission events. The magnitude of this perturbation (multiplication effects) generally depends on a multitude of sample and counter-specific properties. In real samples there exist normally two main sources of neutrons responsible for induced fission:

- The fission neutrons released from the spontaneous fission of the Pu isotopes to be measured. The probability that these fission neutrons, either as fast neutrons before leaving the sample or as re-entering moderated neutrons (albedo neutrons), cause induced fission increases with increasing sample mass. Furthermore it depends also on a number of additional parameters like geometrical form of the sample, its actinide element and isotopic composition as well as properties of the neutron counter surrounding the sample. The net leakage multiplication is denoted by M_L.
- (α,n) neutrons released from interactions of α particles with light elements in the sample (typically oxygen, boron, fluorine, aluminium or any element with a low atomic number). Again a number of sample properties like density, size, element and isotopic composition, ^{241}Am content etc. are factors determining the strength of this type of neutron source, and hence also the magnitude of neutron multiplication due to induced fission. Experience has shown that the presence of fluorine, for example, can lead to gross overestimates (sometimes by a factor of 2 or 3) of the actual amount of plutonium due to neutron multiplication. The ratio of (α,n) to spontaneous fission neutron emission, is denoted by the term α.

The plutonium assay from a neutron coincidence measurement will be also overestimated if other spontaneously fissioning isotopes such as ^{244}Cm are present in the sample. Traces of a few ppm of this isotope in plutonium would lead to (positive) measurement biases in the (few) percent range. Current neutron coincidence counters will not be able to discriminate against this interference at this level.

2.3.2 Instrumentation

The spontaneous fission neutrons emitted by a Pu-bearing sample have an average energy of about 2 MeV. They must be slowed down to thermal energies in order to allow them to be detected with ^{3}He tubes, which are the standard neutron detectors. In practice all passive neutron measurement systems are equipped with neutron moderating assemblies built from moderating materials such as polyethylene, in which the ^{3}He tubes are embedded. Important parameters characterising a neutron counter assembly are the average neutron life-time (die-away time τ) and the neutron detection efficiency (ε) in terms of their magnitude and uniformity. Generally, a larger number of ^{3}He tubes (sometimes more than 100) are incorporated in a neutron coincidence counter to achieve a high and uniform neutron detection efficiency (in best cases up to 70-80%). A high detection efficiency is important for coincidence counting because the probabilities for detecting dual and triple coincidences are proportional to ε^2 and ε^3 respectively. A short die-away time is important as it minimises the accidental coincidence count rate due to pile-up of random neutrons.

Most of the existing neutron coincidence counters in use for Safeguards applications are thermal neutron counters designed for detecting thermalised neutrons, with a typical die-away time $\tau \cong 50$ µs. Recently, less moderated counter assemblies detecting neutrons before thermalisation (epithermal counters) with a significantly reduced die-away time ($\tau = 22$ µs) have been designed and demonstrated.

Besides their categorisation into thermal and epithermal counters, the passive neutron counters are further differentiated according to the manner in which the neutron detector signals are processed and analysed. The two basic variants used in practice are:

(i) *Passive Neutron Coincidence Counters (PNCC)* providing the total neutron counting rate (denoted as 'Totals' or 'Singles'), and the rate of dual coincidences (denoted as 'Doubles' or 'Reals'), and

(ii) *Passive Neutron Multiplicity Counters (PNMC)* extracting in addition to the 'Singles' and 'Doubles' rates also higher-order coincidence events ('Triples',..).

(iii)

The most common hardware used so far in the PNCC systems for the extraction of the 'Singles' and 'Doubles' rate from the pulse train produced by the ^{3}He detectors is the 'Shift Register' [49b]. In the past this has been the most widely used type of coincidence analyser, and it still represents a good choice for the measurement of smaller amounts of well-characterised product materials like Pu metal or Pu-oxide exhibiting small and predictable neutron multiplication effects as well as low and predictable (α,n) production rates. For impure or inhomogeneous materials, such as scraps or waste, however, where corrections for multiplication, matrix and other effects become significant, the two experimental rates (Totals and Reals) are not sufficient for a reliable and accurate Pu assay.

To overcome these difficulties, the passive neutron multiplicity counting technique (PNMC) is being increasingly applied in recent years [50]. The enlarged experimental information provided by PNMC systems (3 measured quantities: Totals, Doubles and Triples) allows extracting quantitative information on existing neutron multiplication effects from the measurement data. In this way systematic measurement uncertainties can be greatly reduced, thus making the plutonium assay by PNMC much more reliable and accurate, particularly for poorly characterised and impure materials with a large induced fission component. For the assay of large containers, for example waste containers, the use of PNMC, already well advanced [50b], still can provide improvements. Interpretation of PNMC results for waste assay applications therefore requires considerable expertise and caution, although PNMC has shown to improve the overall accuracy under certain conditions.

2.3.3 Recent Improvements

The Research and development work for improved PNCC and PNMC techniques are still continuing. Some recent advances and improvements, which have resulted in notable improvements in measurement performance for certain applications, have been achieved in the areas of:

- interpretation and assessment of measurement results,
- detector technology,
- fundamental nuclear data.

Interpretation: The fact that a number of specific sample properties is affecting the measured coincidence rate of a neutron coincidence counter poses problems not only for the calibration of neutron coincidence counters, but also for the correct interpretation of the coincidence response in terms of a true value for m_{240eff}. In order to alleviate this situation, predictive modelling methods based on Monte Carlo calculations (mainly with the code MCNP at the present time) are being increasingly employed for the prediction of the neutron response for given samples under well-defined conditions. These calculations are now possible, at least on a relative scale, with very high precision and accuracy. In this manner the number of (expensive) physical standards for calibration can be greatly reduced, and systematic uncertainties could be lowered in favourable cases to $\leq 0.2\%$.

Closely linked to the issue of measurement interpretation is the increased use of multiplicity counting, which can offer significantly improved reliability for the correct interpretation of the measured neutron coincidence responses in terms of m_{240eff}.

Detector technology: A new generation of neutron assay counters for a wide range of plutonium items has been recently introduced with the Epithermal Neutron Multiplicity Counter (ENMC) [47]. The high efficiency of this counter, combined with the significantly reduced neutron die-away time ($\tau = 22\ \mu s$), offers substantial improvement in precision and accuracy especially for problem cases presented, for example, by impure materials with a large (α,n) contribution to the neutron emission.

Fundamental data: The quantity m_{240eff} as primarily measured by PNCC and PNMC counting is linked to the amount of the neutron emitting Pu-isotopes through the coefficients γ_{238} and γ_{242}. For high-accuracy analytical PNCC measurements, and for calibration procedures based, for example, on mono-isotopic ^{240}Pu reference samples, the uncertainty associated with these coefficients should be limited in order not to contribute a significant additional source of systematic uncertainty. The γ-coefficients are determined both by nuclear data-related components (specific neutron emission rates, second moment of the neutron multiplicity distribution for double coincidences and third moment for triple coincidences [47b]), and by a detector-specific component described by the relative difference in detector efficiency for the different average neutron energies of the spontaneous fission neutrons from ^{238}Pu, ^{240}Pu and ^{242}Pu. In a strict sense effective γ-coefficients are therefore counter-specific, but are expected in practice not to change significantly from counter to counter as long as the energy dependence of the counter efficiencies are similar. Effective γ-coefficients obtained for two different counters from recent experimental investigations [48,49], together with the general nuclear data related component obtained after factoring out the effect of detector efficiency, are summarised in Table IX. The new values, with significantly reduced uncertainty, have notably changed compared to previously adopted values.

Table IX: Experimental coefficients for the calculation of m_{240eff} from Doubles (D) and Triples (T) coincidences. Values in brackets are 1-sigma uncertainties in % [48, 49].

Counter $^{a)}$	γ_{238}**(D)**	γ_{242}**(D)**	γ_{238}**(T)**	γ_{242}**(T)**
	Counter-specific effective γ-coefficients			
OSL-INVS (ε = 40.3%)				
GW = 64 µs	2.707 (0.41%)	1.658 (0.30%)	-	-
GW = 128 µs	2.714 (0.41%)	1.667 (0.30%)	-	-
HENCC95 (ε = 44.3%) GW = 88 µs	2.7002 (0.88%)	1.6586 (0.28%)	2.6773 (1.88%)	1.6348 (0.95%)
Previously used effective values	2.52	1.68	-	-
	Nuclear data-related component of γ-coefficient			
New experimental values	2.784 (1.51%)	1.633 (1.24%)	2.803 (2.63%)	1.597 (2.05%)
Values derived from published nuclear data /18/	2.573 (4.37%)	1.708 (2.21%)	2.645 (13.8%)	1.744 (3.47%)

a) ε = detection efficiency for ^{240}Pu spontaneous fission neutrons
GW = width of coincidence inspection interval

2.3.4 Performance Values for Passive Neutron Measurements

PNCC is applicable to practically all kinds of Pu-bearing materials. The majority of the PNCC measurements for Safeguards are carried out on relatively pure and well-descript feed and product materials such as Pu-metal, Pu-oxides and MOX materials. The amount of plutonium contained in this type of measurement sample can typically range from the gram level up to several kilograms. A second type of items falling into the category of product materials includes finished physical products like individual MOX fuel pins up to complete MOX fuel assemblies. Accordingly, a large variety of different neutron coincidence counter assemblies have been designed and optimised for the respective applications, including, for example, counters known as Inventory Sample Counter (INVS) for relatively small samples, various types of High Level Neutron Coincidence Counters (HLNCC) with sample cavities accommodating items up to several kilograms of Pu, and counter assemblies for fuel assemblies like the Universal Fast Breeder Counter (UFBC) or the Neutron Coincidence Collar (NCC).

Another important category of materials covered by PNCC includes all kinds of poorly characterised Pu-bearing residues, scrap and waste materials to be assayed both for nuclear management and control, for accountability and for Safeguards verification. Neutron multiplicity counting is becoming the preferred neutron technique for this kind of materials.

During the past years PNCC has been also established as an analytical technique for Pu-element assay on small samples under well-controlled laboratory conditions. In those applications INVS-type counters incorporating also a HpGe detector for simultaneous Pu-isotopic measurements are operated as fixed installations at glove-boxes.

Updated performance values available today for the determination of m_{240eff} from passive measurements based on the shift register technique, thermal neutron multiplicity counting and epithermal neutron multiplicity counting are presented in Tables X, XI and XII. The data given for epithermal multiplicity counting should be considered as purely indicative, since they are based on measurements with a single prototype and therefore ENMC cannot be considered as a consolidated routine technique.

The performance data given in the tables are grouped for the various types of instruments and/or measurement items. The materials are further categorised according to their α-ratio ((α,n)/SF ratio), which represents an important parameter for PNCC measurements. Since counting statistics, and hence the counting time, in many cases is a leading factor determining the magnitude of the random uncertainty component, typical counting times are also given in the tables. This allows scaling the random uncertainty accordingly for different choices of counting times.

The error sources contributing to the given random and systematic uncertainties are manifold. For the PNCC technique the major uncertainty components are due to:

- Counting statistics (random)
- Calibration parameters and uncertainties in reference materials (systematic)
- Correction for multiplication effects, dead time, etc... (systematic)
- Nuclear data.

In PNMC we find the same components of uncertainty as in PNCC, but with certain additional effects and parameters becoming more important:

- Longer counting times are critical to obtain good counting statistics especially for the determination of the 'Triples' (random).
- The correction of dead time effects on the different counting rates (singles, doubles and triples) is difficult to quantify accurately (systematic) [43,44].
- The details of the interpretation model (superfission concept, point model, single exponential decay for neutron live time, etc.) used to solve the problem needs careful assessment, since the assumptions and approximations inherent in the model are critical to the accuracy of the result (systematic).
- Nuclear data have a high importance because of the involvement of the 3rd moment of the neutron emission distribution.

The total random and systematic uncertainties for the determination of the amount of plutonium from a PNCC or PNMC measurement is obtained from a combination of the respective uncertainty components for m240eff as listed in Tables X, XI and XII, and for the quantity $^{240}Pu_{eff}$ as given in Table III in Section 2.1. This yields the relative combined standard uncertainty for the Pu element assay from a combined PNCC and isotopic measurement in accordance with the ISO definition for total uncertainty.

Table X: Performance values for m_{240eff} measured in thermal passive neutron coincidence counters with shift registers.

Type of Counter	**Nuclear Material Category**	**Pu Mass (g)**	**Counting Time (s)**	**r (%)**	**s (%)**	**Notes**
HLNCC (ε = 17%)	Pu Metal	$10^2 \sim 10^3$	1000	0.5	1 – 2	
	PuO_2	$10^2 \sim 10^3$	1000	0.3	1 – 3	
	PuO_2	1	10 000	0.5	0.5	
	MOX Powders	$10^2 \sim 10^3$	1000	0.3	3 – 5	
UFBC (ε = 7%)	PuO_2 Powders	$10^2 \sim 10^3$	1000	0.5	1 – 2	
	MOX Fuel Pin Trays			< 1	2 – 3	
	FBR Fuel Elements			< 1	1 – 2	
INVS (ε = 40%)	PuO_2	1	10 000	0.2	0.2	a/b/
	LWR-MOX	1	10 000	0.2	0.2	a/b/
	FBR-MOX	1	10 000	0.2	0.2	a/b/
NCC-passive (ε = 13%)	LWR-MOX & FBR Fuel Elements		1000	1	1 – 3	

a/ Calibrated with certified monoisotopic ^{240}Pu reference sample

b/ Neutronic response of reference sample and measurement samples modelled by MCNP calculations

Table XI: Performance values for m_{240eff} measured in thermal neutron multiplicity counting mode [50].

Material Category	**SNM Mass (g)**	**(α,n) /SF rate**	**Counting Time (s)**	**r (%)**	**s (%)**
Pu-Metal	2000	0 to 0.2	1000	7.1	up to 10
	2000	0 to 0.2	3000	5.1	
	4000	0 to 0.2	1800	2.0	
	200-4000	0 to 1.3	3600	3.3	
Pu-Oxide	2000	1	5000	0.7	1 – 3
	1000	1	3000	0.8	
	1000	1	1800	2.2	
	4000	1-4	1800	3.0	
	1000	1-4	600	1 – 3	
Pu-Scrap	100	5	1000	12	1 – 5
	100-1200	1-6	3600	4.5	
Plutonium Residues	120	13-29	3000	20	2 – 10
	300	7-34	3600	18.9	
	20-100	8-30	3600	7	
	100	5-9	3600	8.7	
Plutonium Waste (estimated)	1	1	1000	2	1 – 2
	1	5	1000	10	2 – 5
	1	20	1000	50	5 – 10
Pu-Oxide in Excess Weapons Materials	1000	1-10	1500	6.0	1
	1000	1-8	1000	5.0	
	4000	1-6	1800	4.2	
	4000	1-6	1800	5.8	

MOX	300	1-2	1000	1 – 2	1 – 3

Table XII: Performance values for m_{240eff} measured with high-efficiency epithermal neutron multiplicity counters (ENMC) [47].

Configuration	**Pu Mass (g)**	**Counting Time (s)**	**r (%)**	**s (%)**
ENMC (ε = 65%)	< 10 g	1800	0.5 – 3	2 – 3
	10 – 1000 g	1800	0.2 – 1	0.5
ENMC/ INVS (ε = 80%)	1 g	3600	0.15 – 0.3	1

2.4 Gamma/X-Ray/Weighing (GXW) Method for Pu Isotopic Composition and Element Content

A new NDA technique known as Gamma/X-Ray/Weighing (GXW) method for the simultaneous determination of the plutonium element concentration and isotopic composition both in solid and liquid samples from a single HRGS measurement has been developed and tested during the last decade [51,52,53,54]. If combined with a sample weighing, the method determines the total Pu content in a sample.

2.4.1 Principles

The GXW method represents a generalisation of the standard plutonium isotopic measurements by HRGS in that it exploits the full spectroscopic information contained in a gamma spectrum from a plutonium sample to achieve also a determination of the plutonium mass fraction in the assay material. The method makes use of several gamma-spectrometric analysis techniques such as enrichment-meter-type measurements, passive differential gamma absorptiometry (PDGA) and passive X-ray fluorescence analysis (PXRF), either individually or in combination, for the determination of the plutonium element mass fraction from a single gamma spectrum.

The approach works in principle for any kind of plutonium-bearing materials, liquids and solids, provided the recommended measurement geometry is set up. A calibration or normalisation with at least one reference sample is normally required for the mass fraction measurement. The measured Pu mass fraction together with the knowledge of the net sample weight obtained from a weighing yields the total amount of plutonium.

2.4.2 Performance

A number of exercises involving measurements on liquid and solid plutonium materials have been carried out for demonstrating the capabilities and the performance of the method for Pu mass fraction measurements. Accurate measurements require a well-defined and controlled counting geometry, particularly for samples that are not "infinitely" thick.

Table XIII gives some indicative performance data for mass fraction measurements [54,55]. The performance values are given in terms of relative standard deviations for the differences between measured and declared mass fractions observed in demonstration exercises. Most of the measurements on Pu-bearing solid samples have been performed on MOX materials (powders, pellets). Results for those samples showed an agreement with reference values of the order of 1% or better for defined and uniform counting conditions. If the measurements were subject to some variability in the counting geometry, for example due to varying physical or geometrical properties of the measured samples, the accuracy degraded to about 2.5%, pointing to some degree of sensitivity of the method to experimental conditions. The method is still undergoing further optimisation for routine application.

For the isotopic composition measurement the GXW method makes use of the intrinsically calibrated analysis of the XKα region. Pertinent performance data are quoted in Section 2.1.

Table XIII: Performance of the GXW method for Pu mass fraction measurements.

Material type	**Range of mass fraction (wt. %)**		**Typical uncertainty rsd (%)**	
	w_U	w_{Pu}	w_U	w_{Pu}
PuO_2		85 – 88		1.5
MOX	20 – 80	2 – 65	2.5	1 - 2

3 TECHNIQUES FOR URANIUM-BEARING SOLID MATERIALS

This section discusses features and performances of the following NDA techniques for measurements on uranium-bearing solid materials:

- Gamma spectrometry for the determination of the ^{235}U enrichment in low-enriched uranium materials such as uranium oxide powders and pellets, fuel pins and assemblies, and UF6 in storage containers;
- Active neutron interrogation for the determination of the ^{235}U content in feed and product uranium materials;
- Gamma/X-ray/weighing method for the simultaneous determination of the ^{235}U enrichment and uranium element content.

3.1 Gamma Spectrometry for the Determination of the ^{235}U Enrichment in Low-Enriched Uranium Materials

The determination of the ^{235}U enrichment in uranium materials by means of gamma spectrometry represents one of the most widely used NDA applications since the beginning of Safeguards verification measurements. The method, which has early matured because of its simplicity, uses two different approaches for the measurement of the ^{235}U enrichment: (i) the "infinite thickness" approach, and (ii) the intrinsic calibration approach.

3.1.1 Infinite Thickness Approach

This approach is based on the so-called enrichment meter principle [56,57]. Here the most prominent gamma ray of 185.7 keV from the decay of ^{235}U is counted in a defined counting geometry from uranium samples satisfying the "infinite thickness" condition, i.e., which must be opaque for 186 keV photons. Under this condition the measured counting rate of 186 keV photons is proportional to the ^{235}U enrichment. The required infinite sample thickness ranges from about 0.25 cm for metal samples to about 7 cm for UF_6 with a density of 1 g cm^{-3}. Small corrections to the measured counting rates are needed to account for different chemical compositions of the uranium samples [57,58]. The method is best suited for bulk samples (e.g., uranium oxides and UF_6 in storage containers), which easily meet the infinite thickness requirement.

The enrichment measurement based on the enrichment meter principle requires physical standards containing a sufficiently large amount of uranium reference materials for calibration. The ESARDA NDAWG has early launched the production of a set of internationally certified calibration standards for this purpose [59,60], and a detailed user's manual for accurate ^{235}U enrichment measurements using these calibration standards has been issued [58].

3.1.2 Intrinsic Calibration Approach

Other methods based on the so-called intrinsic calibration approach have been developed to circumvent the need for calibration with physical standards. In these methods the $^{235}U/^{238}U$ isotope ratio is determined from the measured gamma spectrum using corresponding gamma and X rays from the decay of both isotopes. Since ^{238}U does not directly emit a useful gamma ray from its decay to ^{234}Th, gamma rays from the decay of its daughter nuclides ^{234}Th and ^{234}Pa must be used instead. This approach requires secular equilibrium between ^{238}U and its daughter nuclides, which is reached about 80 days after chemical separation. The method is therefore not suited for freshly separated uranium materials.

Since a few years the preferred method for intrinsically calibrated enrichment measurements bases on the analysis of the $XK\alpha$ region (89-99 keV), where fairly abundant but strongly overlapping gamma and X-ray signatures from the ^{235}U and ^{238}U daughter nuclides ^{231}Th and ^{234}Th occur [61,62]. This method allows rapid enrichment measurements on arbitrary uranium samples. The principal limitation of the method, besides requiring secular equilibrium for the $^{235,238}U$ daughter nuclides, arises from the fact that the gamma and X-ray signatures from ^{231}Th and ^{234}Th become strongly unbalanced in intensity at very low (< 1%) and very high (> 90 %) enrichments. This makes the measurements for those enrichment grades less precise and accurate [63].

An alternative but nowadays less frequently used intrinsic calibration approach makes use of the ^{235}U gamma rays ranging from 143 to 205 keV, and of the ^{234}Pa gamma rays occurring between 258 and 1001 keV [64,65]. The principal problem associated with this type of analysis is the difficulty to establish a reliable link between the relative detection efficiency for the radiation from both isotopes.

3.1.3 Detectors

The choice of the detector is an important criterion for the performance of a gamma-spectrometric enrichment measurement. For many years the enrichment measurements have been mainly made using either high-resolution HPGe detectors or low-resolution NaI(Tl) scintillation detectors. Both types of detectors can be principally applied for enrichment measurements based on the infinite thickness approach. As a matter of fact, the majority of the in-field measurements in the past used low-resolution scintillation detectors, with some degradation in performance (typically a factor of 2) compared to the results obtained with high-resolution HPGe detectors. For field measurements NaI(Tl) detectors remain a useful option, particularly when used in conjunction with improved software for spectrum analysis [66]. However, NaI(Tl) scintillation detectors cannot be used for enrichment measurements based on intrinsic calibration because of their inherently limited energy resolution.

In recent years semiconductor detectors such as CdZnTe (CZT) or CdTe operating either at room temperature or at slightly reduced temperature levels simply reached by Peltier cooling have become another viable detector alternative for enrichment measurements. Advanced technologies have permitted the fabrication of small volume detectors with good gain and efficiency stability when submitted to temperature variation, high intrinsic efficiency, and good energy resolution (FWHM at 186 keV up to 2.5 keV for room temperature CZT, and up to 1.7 keV for Peltier-cooled CdTe [67]). These detectors are in principle applicable to both the infinite thickness and intrinsic calibration type of enrichment measurement. However, enrichment measurements using CdTe or CZT detectors are still suffering from measurement precision due to the relatively small detector sizes available so far.

For the time being the CZT and CdTe detectors are mainly used for more qualitative attribute measurements. Typical Safeguards applications are commonly related to locating, monitoring or identifying nuclear materials. Recent improvements in the construction technology of larger volume CZT detectors and the use of new methods and algorithms for spectrum analysis have proven that those detectors, as an alternative to the systems based on HPGe and NaI(Tl) detectors, are also suited for routine ^{235}U enrichment measurements in drums, cylinders and other types of containers containing nuclear material. They have also become a useful tool for gamma-ray signature measurements to verify the ^{235}U enrichment in fuel pins [68], or even of inner rods within a fuel assembly, where the small detector size makes it possible to insert the detector between rows of rods.

3.1.4 Performance values

The performance values established for the above mentioned methods for gamma-spectrometric enrichment measurements, when applying different detectors and counting times, were mainly derived from an international exercise managed by the ESARDA NDA Working Group [5], and are further based on practical experiences of Working Group members as well as on literature data [63,65,69].

Table XIV lists the performance values for measurements on uranium oxide materials. The achievable measurement performance depends on the type of analysis (infinite thickness or intrinsic calibration), on the type of the detector and on the counting time. The random uncertainties are mostly due to counting statistics and apply for the given counting times. The systematic uncertainties are generally lower for well-calibrated infinite thickness measurements than for intrinsically calibrated measurements. Systematic uncertainties introduced by the unfolding of the complex XKα-region and also the poor knowledge of some of the nuclear data (gamma emission probabilities) involved in the analysis are the main factors responsible for the poorer performance of the intrinsic calibration approach. The data in the Table also underline the fact that measurements made with CZT detectors cannot yet compete in performance with measurements made with HPGe detectors offering higher efficiency and energy resolution.

Table XIV: Performance values for gamma-spectrometric enrichment measurements on low-enriched uranium oxide materials.

^{235}U Enr.	**Infinite thickness method**									**Intrinsic calibration method**					
	HRGS (Ge detectors)			LRGS (NaI detectors)			CZT			HRGS (Ge detectors)			CZT		
	CT (s)	r (%)	s (%)	CT (s)	r (%)	s (%)	CT (s)	r (%)	s (%)	CT (s)	r (%)	s (%)	CT (s)	r (%)	s (%)
0.3 to 0.7%	360	2	1	360	3	1	1200	10	1	360 3600	8 3	5 5	ns	ns	ns
2 to 4 %	360	0.7	0.5	360	1	0.5	1200	3	1	360 3600	2 1	1 1	10^4	10	5
5 to 10 %	360	0.5	0.5	360	0.5	0.5	1200	3	1	360 3600	2 1	1 1	10^4	10	5

ns = not suitable

Enrichment measurements made on UF_6 in standard storage containers represent a special case. The relatively thick container walls strongly attenuate the radiation in the XKα-region, which practically only leaves the counting of the 186 keV gammas in the infinite geometry for the enrichment measurements. Further, because of the relatively poor signal to background ratios obtained from the very large and well-shielded measurement items, reasonable measurements are only possible with high-resolution HPGe detectors.

Table XV lists performance values that can be obtained under carefully fixed experimental conditions [69]. The random uncertainty components mainly depend on the counting time and the geometrical set up, including a possible collimator. For LEU in 30" containers, the random uncertainty typically ranges between 1.5% (counting time of 3000 s) and 3% (1500 s). For natural or depleted UF_6 in 48" containers, the random uncertainty is about 7%.

Systematic uncertainty components for this type of enrichment measurements are determined by a number of factors like the poorly defined physical properties of the UF_6 (liquid, solid, spatial inhomogeneity), attenuation corrections to be made for the container walls, interfering radiation from deposits in the inner wall of the containers and from neighbouring storage containers, and the calibration procedure. They can vary from 2 to 10 % depending on the actual measurement conditions, on the evaluation and measurement procedures used, and on the calibration standards available for calibration.

One of the major problems for this kind of samples is due to the wide variability of the physical properties of UF_6 in storage conditions. Efforts to apply passive or active neutron measurement for uranium enrichment determination in UF_6 are presently ongoing.

Table XV: Performance values for enrichment measurements on UF_6 in storage containers.

Sample type	**r (%)**	**s (%)**
LEU	1.5 to 3	2 to 10
Natural or depleted U	7	2 to 10

3.2 Active Neutron Techniques for the Determination of the ^{235}U Content in Uranium Feed and Product Materials

3.2.1 Principles of Active Neutron Coincidence Counting

Due to the very low spontaneous fission yields of all the uranium isotopes, passive neutron coincidence techniques are generally not suitable for the assay of uranium bearing samples. However the fissile content in a sample can be readily measured by adding an external interrogation neutron source. The neutrons from the interrogation source will induce fission in the fissile nuclei of the sample. Neutron induced fission (like spontaneous fission) results in the simultaneous emission of several prompt neutrons ($<\nu>=2.41$ for fission induced by thermal neutrons in ^{235}U). The coincidence counting technique allows the distinction between events with the emission of single or multiple prompt fission neutrons. This makes it possible to discriminate between neutrons from the primary interrogating source and those from fission induced in the sample, provided that the primary source generates randomly non-correlated single neutrons. Coincidence counters with a random interrogation source are known as Active Neutron Coincidence Counters (ANCC).

Among the radioactive sources those based on (α,n) reactions are the best candidate for active neutron interrogation. A frequently used source is AmLi. The main advantage of the AmLi source with respect to other (α,n) reactions is the low energy of the emitted neutrons: the mean energy is 0.54 MeV, which minimises the probability of fast fission in ^{238}U.

For small samples the “Reals” coincidence rate is proportional to the quantity of fissile material in the sample. For large samples the self-shielding phenomena limit the “visibility” of fissile material to the interrogating neutrons, causing saturation effects in the response function and underestimation in the quantity of the fissile material (unless the calibration is designed to take the effect into account). This self-shielding effect is one of the major contributors to the systematic assay error of active neutron techniques.

3.2.2 Active Neutron Coincidence Counting Instruments

Apart from the presence of the interrogating source, the methods and procedures of shift-register based instruments for active neutron coincidence counting are very similar to those used in PNCC counting.

There are basically two major families of instruments in this category:

- the Neutron Coincidence Collar (NCC) in active mode;
- the Active Well Coincidence Counter (AWCC).

Neutron collars are typically composed of four slab detectors in a square arrangement, and are used for the assay of fresh fuel assemblies. Some models have a modular layout allowing the adjustment of collar dimensions to the fuel element size, others have fixed configurations for specific fuel type (PWR and BWR). Collars can be used both in passive and active mode. For passive only applications (MOX fuels) normally all the four sides are equipped with detectors, for active/passive applications (LEU fuels) only three detection slabs are used and the fourth wall hosts the source.

Active well coincidence counters are general-purpose devices for uranium bearing samples at practically any enrichment (HEU and LEU), chemical form (metal, oxide) and physical form (powders, pellets, plates, MTR elements). An AWCC is conceptually similar to a passive HLNCC except for the presence of two AmLi sources in the top and bottom polyethylene plugs. It can be operated either with or without a cadmium liner (fast or thermal mode).

3.2.3 Active Neutron Coincidence Counting in Multiplicity Mode

By extending the shift register electronics it is possible to operate ANCC systems in multiplicity mode. This is exactly analogous to the extension from PNCC to PNMC. Under certain conditions three unknown quantities can then be determined instead of just two. This allows, for example, a variable detection efficiency (perhaps due to variable moisture content) to be taken into account in the interpretation model. The use of multiplicity counting in ANCC systems is still undergoing development, and therefore no performance values are available to be quoted in this document.

3.2.4 Performance Values for Active Neutron Coincidence Counting

Performance values for the assay of the fissile uranium content obtained with two common instruments (NCC and AWCC) from different materials are given in Tables XVI and XVII, essentially based on field experiences [70,71]. Note that these values assume that a representative calibration exists, for each material type quoted. The systematic uncertainty for the fast mode assay is generally higher than for the thermal mode, due to the range of matrix effects, although the potential for gross assay underestimation is greatly reduced in fast mode.

It is worth noting that the AWCC technique is also used for other purposes, including waste characterisation. For these applications, where the physical composition of the waste package and fissile material can vary considerably, the assay uncertainties can be much greater than the figures quoted below.

Table XVI: Performance values for the determination of the ^{235}U mass loading in fresh LEU fuel elements (1000 s counting time).

Technique	Objects	Enrichm.	r(%)	s(%)
NCC (active mode)	UO_2 Fuel Elements for LWR	Up to 3%	1	1 – 2
	UO_2 Fuel Elements for LWR	3 – 5 %	1	2 – 4
	LWR fuels with burnable poisons	any	1	3 – 5

Table XVII: Performance values for the determination of the fissile content in U samples.

Technique	Objects	r(%)	s(%)
AWCC	HEU Metal	2	3
	HEU Powder (fast mode)	2	10
	HEU Powder (thermal mode)	2	5
	UF_4 Salt	5	2

	HEU/Th/C Pebbles	2	4
	HEU/Al MTR	1	3
	LEU Powder (fast mode)	2	5

3.2.5 Active Total Neutron Counting

Uranium bearing samples can be assayed through active neutron interrogation e.g. by PHONID (PHOto-Neutron Interrogation Device) [72] followed by total fission neutron counting.

The PHONID device contains two photo-neutron (^{124}Sb,Be) sources. The energy of these neutrons is relatively low (up to 400 keV), below the threshold of fast fission in ^{238}U, so thermal fission will be induced in ^{235}U only. Fission neutrons are then detected by an array of ^{4}He detectors for fast neutrons. Neutron counting is made in "Totals" mode.

In the PHONID system the discrimination between source and induced fission is not performed by the electronics like in the coincidence counters, but it relies on the sensitivity of ^{4}He detectors to the neutron energy which is much higher for fast neutrons than for thermal ones.

Performance values for the PHONID technique are shown in Table XVIII. The random components of the uncertainty are mostly determined by counting rates and counting times, background subtraction and normalisation. Systematic components are linked with neutron multiplication, calibration curve set up, accuracy of calibration standards, moisture and impurities. These values assume that a truely representative calibration exists, for each material type quoted.

Table XVIII: Performance values for total neutron counting active technique on U-bearing materials

Technique	**Objects**	**r (%)**	**s (%)**
PHONID	HEU-MTR Platelets	1	2
	HEU-Metal	1	1
	LEU-UO_2 Powder	1	1.5
	LEU-U_3O_8 Powders	1	2.5

Although PHONID proved to be a reliable and effective technique in measuring bulk samples of uranium bearing material, it did not encounter the favour of analysts since the procedure for its application is quite cumbersome. One of the main drawbacks of the technique is its high sensitivity to a lot of parameters affecting the measurement. For example, changes in the geometry of the sample, container and packaging material, matrix, and enrichment, all cause an alteration of the response function, requiring an extensive calibration effort. Practically any family of similar samples requires a separate calibration. Moreover the short half-life of the ^{124}Sb (60 days) requires frequent, and costly, replacements of the source.

For all these reasons, recently feasibility studies have been started to replace PHONID with passive techniques. In principle the amount of uranium can be measured by passive neutron coincidence counting in the same way as for plutonium, since its isotopes (principally ^{238}U) also decay by spontaneous fission. Therefore, through a combination of a neutron measurement with gamma spectrometry for enrichment, it becomes possible to verify uranium samples. A substantial problem comes from the low specific neutron yield of uranium due to the very long half-life. Counters with high efficiency are therefore required. Studies have shown that a statistical measurement uncertainty (below 0.5%) can be reached in a reasonably short counting time (1000 s) for large samples (uranium mass from 100 g to several kg) provided the counter has an efficiency of the order of 50% [73]. Design, construction and testing of a passive neutron device for large LEU samples are currently ongoing. Use of PNCC counting, in this way, is an established technique in NCC collars for ^{238}U assay of fresh fuel assemblies.

3.3 Gamma/X-Ray/Weighing (GXW) Method for the Determination of Enrichment and Uranium Mass Fraction

The GXW method described in Section 2.4 also provides measurement capabilities for the determination of the ^{235}U enrichment and the uranium mass fraction [54]. The underlying enrichment measurements are either based on the infinite thickness approach or on the intrinsic calibration approach as described in Section 3.1, and the performance values reported in Table XIV also apply here.

3.3.1 Principle of the Mass Fraction Determination

The method applied for the uranium mass fraction measurement depends on the type of detector used. For measurements made with HPGe detectors the uranium mass fraction is determined either by means of the Passive X-Ray Fluorescence (PXRF) technique, or by means of the Passive Differential Gamma Absorptiometry (PDGA) technique, or from a combination of both [54]. The PXRF method relates the measured intensity ratio of passively excited UKα X rays and 186 kev gamma rays from ^{235}U through a polynomial function to the uranium mass fraction. In the PDGA method the measured intensity ratio of isotopic gamma rays from ^{235}U (144/186 kev ratio) is related to the uranium mass fraction. Both methods require a calibration to establish the respective functional relationship between measured intensity ratio and uranium mass fraction.

In measurements made with NaI detectors the ^{235}U enrichment and the uranium mass fraction are determined in an iterative process from the measured intensity ratio of 186 keV (^{235}U) and 1001 keV (^{234}Pa) gamma rays.

3.3.2 Performance Values

Typical performance values for the uranium mass fraction determination in solid uranium samples by the GXW methods, expressed in terms of relative standard deviations for the differences between declared and measured values, are given in Table XIX. The data are based on recent performance assessments [54,55]. For measurements made with a HPGe detector an accuracy level of about 1% relative has been achieved. For measurements made with a NaI detector only few data are available, but an accuracy level of 1.5 % seems to be reachable.

Table XIX: Performance values for uranium mass fraction measurements in solid U-bearing samples by the GXW method.

Detector	**Range of U mass fraction (wt. %)**	**Typical uncertainty rsd (%)**
Ge	5 - 85	1.0
NaI	5 - 85	1.5

4, TECHNIQUES FOR U AND PU IN LIQUID FORM

The prime quantity usually determined by NDA techniques from nuclear samples in liquid form is the uranium and/or plutonium element concentration. The major technique currently applied for this purpose is K-Edge Densitometry (KED), which is ideally suited for concentration measurements at elevated concentration levels (≥ 50 g/l) in any type of solutions, containing both unirradiated and irradiated nuclear materials. For lower concentrations the technique of KED can be complemented by the technique of X-Ray-Fluorescence (XRF) analysis, which offers a larger dynamic range at the expense of slightly inferior overall measurement accuracy compared to KED.

Gamma spectrometry is also frequently used for uranium and plutonium concentration measurements. This technique also allows the simultaneous measurement the isotopic composition of plutonium and/or the ^{235}U enrichment of uranium. A direct gamma measurement, however, is only possible for unirradiated materials, while the analysis of irradiated materials requires a prior separation of fission products.

Radiometric techniques such as KED, XRF and HRGS are nowadays also frequently utilised in analytical measurements for the determination of element concentrations in solid samples such as powders and pellets. In those applications the solid samples need to be dissolved prior to the radiometric measurements. This is therefore no longer a purely non-destructive analysis. Nonetheless, we will also quote performance values for those applications, because the radiometric measurements applied to the dissolved samples are the same as those used for original liquid samples.

4.1 K-Edge Densitometry and XRF for Element Concentration

4.1.1 Principles

K-edge densitometry is a special form of photon absorptiometry [74,75]. In KED the photon transmission through the sample under assay is measured at two photon energies which should bracket as closely as possible the K-absorption edge energy of the element of interest. The logarithmic ratio of the photon transmission measured below and above the absorption edge is directly proportional to the volume concentration of the measured element in the liquid and to the thickness of the investigated solution layer. The latter parameter requires sample containers of well-defined path length holding the sample solution for the transmission measurements. KED provides an element-specific measurement because the K-absorption edge energy represents an element-specific signature.

KED is one of the most accurate NDA techniques because it reduces the determination of the quantity to be measured, i. e. the volume concentration of the element of interest, to a simple ratio measurement. This helps to significantly reduce or even eliminate a number of systematic uncertainty components present in other NDA measurements. The technique is even able to determine the concentration, at a reduced accuracy of about 2%, without any calibration, if the measurement evaluation is based on physical constants alone. For higher accuracy the KED measurements are usually calibrated against certified reference solutions. The lower concentration limit for accurate KED measurements is normally set at about 50 g/l.

The technique of XRF has to be applied if the element concentration to be determined falls below the useful range for KED measurements. The energy-dispersive analysis of fluoresced

K-X rays is applicable for quantitative concentration measurements down to concentration levels of about 0.5 g/l, with detection limits settled in the range of 0.02-0.05 g/l. The interpretation of the XRF measurements is not as straightforward as for KED, and it is also more sensitive to matrix effects. However, the XRF technique becomes very accurate for element ratio measurements to determine the concentration of a minor element relative to the concentration of a major element known from a KED measurement. The simultaneous determination of the U and Pu concentration in reprocessing input solutions, with a typical U/Pu-ratio of ≅ 100, represents an important example for such an application [76,77].

4.1.2 Instrumentation

The majority of the K-edge densitometers used for Safeguards are equipped with an X-ray generator as photon source for the transmission measurement [78]. This offers enough flexibility to tune the measurement conditions to the requirements of different applications. The high photon strength provided by an X-ray tube also makes measurements on highly radioactive samples possible. It can be also used as excitation source for simultaneous XRF measurements. The Hybrid K-Edge Densitometer (HKED) combining KED and XRF has become a standard technique and instrument for Safeguards verification measurements in reprocessing plants [79]. All K-edge densitometers equipped with an X-ray generator are stationary instruments attached to shielded or unshielded glove-boxes for sample handling.

Another type of K-edge densitometer applied to the analysis of uranium samples uses radioactive isotopes as photon source. A common densitometer of this type is the COMPUCEA instrument [80,81]. The currently adopted isotopic source for the K-edge measurements on uranium samples is a mixed ^{57}Co/^{153}Gd source. The COMPUCEA instrument is mostly used as a mobile instrument during physical inventories in fuel fabrication plants [82].

4.1.3 Performance Values

Performance values for the determination of the uranium and plutonium volume concentration in liquid samples by means of KED and XRF are listed in Table XX (see also [30]). The main component dominating the random uncertainty is counting statistics, whereas short and long-term instrument variability and the uncertainties associated with reference solutions used for calibration represent the major error sources contributing to the systematic uncertainty. The application of strict procedures for measurement control and assurance are vital to keep the systematic uncertainty at the quoted level.

Performance values for the determination of the percentage element content in solid samples, obtained from KED/XRF measurements after sample dissolution, are listed in Table XXI. The listed random and systematic uncertainty components include also error contributions from sample weighing, sample dissolution and from the additional solution density measurement needed for the conversion of the volume concentration measured from the dissolved sample into the wt. % concentration of the respective element in the original solid sample.

Table XX: Performance values for volume concentration in liquid samples from direct KED/XRF measurements.

Type of Sample	Technique	Measurand	Counting Time (s)	r (%)	s (%)	Remark
U-nitrate	KED	U-conc.	2000	0.2	0.15	> 100 g/l
U-nitrate	COMPUCEA	U-conc.	2000	0.2	0.15	> 100 g/l
U-nitrate	XRF	U-conc.	2000	0.5-0.2	1	1-50 g/l
Pu-nitrate	KED	Pu-conc.	2000	0.2	0.15	> 100 g/l
Pu-nitrate	XRF	Pu-conc.	2000	0.5-0.2	1	1-50 g/l
Reproc. input solution	HKED	U-conc.	2000	0.2	0.15	150–250 g/l
		Pu-conc.	3600	0.6	0.3	1-2 g/l

Table XXI: Performance values for element concentration in solid samples (powders, pellets) from KED/XRF measurements after sample dissolution (typical sample size ≅ 2 g).

Type of Sample	Technique	Measurand	Counting Time (s)	r (%)	s (%)	Remark
Pu-oxide	KED	wt. % Pu	2000	0.2	0.2	
Pu-oxide	XRF	wt. % Pu	2000	0.2	0.15	Internal U-spike
MOX	HKED	wt. % U	2000	0.2	0.2	
		wt. % Pu	2000	0.3	0.2	
U-oxide	COMPUCEA	wt. % U	2000	0.2	0.2	
	KED	wt. % U	2000	0.2	0.2	

4.2 Gamma Spectrometry for Element Concentration and Isotope Abundances

4.2.1 Principles

The uranium and plutonium element concentration in liquids can be determined from a purely passive HRGS measurement. The underlying measurements are based on intensity measurements of X-rays and isotope-specific gamma rays from uranium and/or plutonium isotopes in a well-defined counting geometry. Element mass fractions are determined via the PXRF and PDGA techniques, which are part of the general GXW method mentioned in Sections 2.4 and 3.3. For low concentration levels photon counting of isotope-specific gamma rays in a well-defined and calibrated counting configuration represents the preferred measurement approach.

The interpretation of the passive mass fraction measurements in terms of a total mass fraction of the analyte requires the knowledge of the isotopic composition of the uranium and/or plutonium material under assay, which can be derived from the same HRGS measurement as well. Plutonium isotope abundances are either determined through the intrinsic calibration approach as described for Pu solid material, or through calibrated photon counting of isotope-specific gamma rays. For the ^{235}U enrichment measurement from uranium solutions calibrated 186 keV photon counting is the preferred method. In the COMPUCEA instrument this counting is made in a HPGe well counter on a defined volume of uranium solution with known uranium concentration obtained from a parallel KED measurement [80,81].

4.2.2 Performance Values

Performance values for the mass fraction and isotope abundance measurements in solutions by means of HRGS are listed in Table XXII [30,54,55,82]. Performance values for Pu isotope abundance measurements are not quoted, because the most simple and reliable Pu isotopic measurement is made using the intrinsic calibration approach, yielding for liquid samples comparable performance as for solid Pu samples (Table I).

Table XXII: Performance values for the determination of element mass fractions and isotope abundances in solutions.

Solution	**Technique**	**Measurand**	**Range**	**r (%)**	**s (%)**
Pu	GXW	Pu mass fraction	0.2-13 wt%	1	1
U	GXW	U mass fraction	15-30 wt%	2.5	1
	GXW	^{235}U enrichment	0.7-90%	1.5	1.5
	COMPUCEA	^{235}U enrichment	2-4%	0.4	0.2

4.3 Other techniques

The techniques of calorimetry and PNCC, mostly applied for solid Pu-bearing samples, can be also used in principle for the determination of the amount of plutonium contained in a liquid sample, provided the amount of plutonium is large enough (≥ 1 g) to allow a precise assay by either technique. Performance values given in Sections 2.2 and 2.3 for solid samples will then also apply for liquid samples.

5 TECHNIQUES FOR SPENT FUEL ASSAY

5.1 Summary of the NDA techniques for spent fuel assay

NDA techniques on spent fuels are extensively used in safeguards both to verify items with regards to their attributes (level of irradiation, cooling time, fuel nature: MOX, LEU, HEU) and, with higher accuracy levels, to quantitatively determine the amounts of nuclear material contained: this second level of NDA would essentially contribute to the nuclear material accountancy in strategic MBAs. Quantitative assay requires the determination of the amount of nuclear materials (NM) through the evaluation of the spent fuel burnup, or a direct NM assay. The burnup determination is generally obtained with passive NDA techniques, also in case when direct nuclear material assessment in spent fuel requires active NDA techniques. At the moment passive techniques are under routine use. Active methods, that have been extensively studied, are less used due to their cost and complexity.

For the monitoring of irradiated spent fuel assemblies, four non-destructive methods can be applied:

- gamma spectrometry using HRGS or RTGS,
- total gamma counting with ionisation chambers,
- passive neutron counting using fission chambers,
- active neutron counting with isotopic neutron sources or neutron generators.

These methods allow the determination of the main physical parameters of an irradiated fuel assembly such as burn-up, cooling time and effective multiplying factor (k_{eff}). The evaluated performances as far as the above parameters are concerned are shown in Ref. [85].

The passive and active neutron signals from a spent fuel assembly can be used to evaluate the U-Pu residual mass:

- Passive neutron counting is well correlated with the Plutonium mass via the Curium passive neutron emission, which is actually assayed.
- Active neutron counting gives the fissile mass content (^{235}U + ^{239}Pu + ^{241}Pu) and, using passive neutron counting, leads to the ^{235}U mass content of the assembly [86,87].

In practice NDA on spent fuel for safeguards purposes, is often performed in reactor ponds and in wet or dry storage. As a consequence, devices used for spent fuel safeguards have to consider underwater operation in hazardous areas. In addition, instrumentation has to cope with very high radiation dose background, so requiring important shielding.

Performance values for the quantitative assay of Pu and U in spent fuel are mostly based on laboratory experiment (Table XXIII); safeguards verification activities are generally attribute verifications (eg burnup determination: Tables XXIV, XXV): the gap evidenced between the performances of the two areas reflects the difficulties encountered in transporting techniques from R&D to field, for the reasons outlined before: complexity of the field conditions, costs of the equipment, transportability of the equipment etc.

When safeguards measurement on spent fuels are attribute tests or semi-quantitative assay, it is more difficult to associate a performance value. However, information on routine in-field measurements is available for the same techniques applied for instance, in the frame of criticality safety [83]. It appears therefore appropriate to list here devices and related performances that are not actually used yet in the frame of safeguards, but could be applicable in future, together with performances of devices which are extensively used for safeguards and other purposes (the FORK device [89, 89b, 89c] is an example).

5.2 Performances of Uranium-Plutonium Mass evaluation in spent fuels

The random and systematic uncertainties related to the Plutonium mass determination are presented in Table XXIII. The figures for Pu mass estimation results from the use of an on-line depletion code, which calculates the Pu mass based on the declared irradiation history.

Another method is based on direct correlation between the neutron emission and the Pu mass [84]. This method does not use any on-line code and delivers consistent results on the total Pu balance for batches of several assemblies.

Table XXIII: Performance values related to the uranium-plutonium mass evaluation of a spent fuel assembly

Technique Used	**Calibration**	**Physical Parameter Determined**	**r(%) (*)**	**s (%)**
Passive neutron counting + on line depletion code	No (only detector yield)	Plutonium mass [83]	0.3 - 1.3	1. - 2.5
Passive neutron counting + correlation law (NE=f(Pu))	No (only detector yield)	Plutonium and Uranium mass [84]	0.3 - 1.3	(**) (PWR) 1. (BWR) 2.
Active neutron interrogation	Yes	Fissile mass $^{235}U+^{239}Pu+^{241}Pu$ [86]	0.15 - 2.5	< 4.

(*) These values depend on the kind of assembly, burn-up, initial enrichment and the irradiation history.

(**) These values are related to total balance of Pu for batches of several assemblies.

5.3 Determination of physical parameters of irradiated fuel assemblies

Knowledge of the physical parameters of irradiated nuclear fuel is required both for safeguards and operational safety purposes. Measurements on spent fuel encounter "logistic" difficulties as above mentioned, but also principle difficulties, as for instance the lack of primary physical standards, well calibrated and certified [83]. Instruments may be calibrated for gamma ray efficiency, efficiency to thermal neutrons etc., but these parameters may be used only for the quality assurance of the instrumentation and of the methods and not for calibrating for quantitative assay.

Calibration for NDA measurements on irradiated fuel is performed against some set of characterised assemblies (referred as Measured Calibration Curve mode in the Tables) and then used for later measurements [89]. Other methods use on line depletion codes [88, 90, 91] to establish the correlation link (Calculated Correlation Curve) between emissions and physical parameters: in this particular case the detector yields have to be determined by a reference measurement or calculation.

The importance of such measurements stimulated the development of a large variety of instruments and applications of known instruments to irradiated fuel. As for many other instruments used for safeguards purposes, a distinction should be made between mobile devices and fixed installations (in reprocessing plants, reactors...). Fixed devices are usually better calibrated and maintained, some have better characteristics as shown in Table XXVI.

National and international inspectors in field mostly use mobile devices. Fixed devices are usually used at reprocessing plants as a part of technological process or combined with Containment and Surveillance systems [93].

All instruments determine some irradiation signature for the assessment of unknown parameters by the method explained in Ref. [83].

Tables XXIV and XXV present performance values for mobile instruments based on neutron and combined neutron-gamma methods respectively. Some devices, presented as examples, are not intended for safeguards but used in the frame of criticality control. Nevertheless they are of potential interest for safeguards because they are transportable and could be used for in-field applications.

Systematic uncertainties on burnup, cooling time and Pu mass strongly depend on the number and the quality of input data used for signal interpretation. It is to be noticed that the active neutron methods are less data dependent, but unfortunately require heavy equipment [86].

Table XXVI presents actual information on instruments used at reprocessing facilities and reactors. One can easily see that estimated uncertainties are lower than the correspondent figures for mobile devices.

Table XXIV: Performances of neutron-only NDA for Spent Fuel: underwater mobile devices.

NDA Method	Physical parameter assessed	Example of devices	Assay Duration (min)	Calibration interpretation	r (%)	s (%)
Relative Passive Neutron	**LEU** Average BU MOX to LEU distinction	FORK Safeguards Safety - criticality [89]	10	Measured Correlation Curve$^{(1)}$	1	10
Absolute Passive Neutron	**LEU** Average BU LEU Extremity BU Pu amounts	PYTHON Safety - criticality	10	Calculated Correlation Curve$^{(2)}$	0.1	2 - 5
Active Neutron	**MOX** Average BU Pu amounts K_{eff}	PYTHON Safety-criticality	10	Calculated Correlation Curve : K_{eff}=f(Active Count Rate)	1	2
Passive neutron	**LEU** Average BU Pu amounts	SMOPY [95] Safeguards	10	Calculated Correlation Curve	1	5

(1) Measured Correlation Curve means that the correlation between the Count Rate and Burnup is measured using a set of homogeneous and representative Spent Fuels

(2) Calculated Correlation Curve means that the correlation between Neutron Emission and Burnup is calculated using an online depletion code. Only the detector efficiency is to be known by calculation or measurement of a single fuel assembly

Table XXV: Performances of gamma and (gamma + neutron) NDA for Spent Fuel: mobile devices.

NDA method	**Physical parameter assessed**	**Example of devices**	**Assay Duration (min)**	**Calibration interpretation**	**r (%)**	**s (%)**
Gross Gamma Assay	Cooling Time	FORK [90,91]	1	Correlation law	5	20
Gross Gamma Assay	Cooling Time	PYTHON [86]	10	Correlation law	1	20
RTGS (NaI or CZT)	Presence of irradiated material	SFAT Safeguards [96]	10	Fission Product	Attribute test	
RTGS (CZT)	Presence of radioactive material, Burnup	SFAT Safeguards [97]	5	Fission Product, ^{137}Cs correlat. law	6-17	23-36
HRGS (HPGe)	LEU Burnup	SFM Safety Criticality [88]	10	^{134}Cs/^{137}Cs or ^{137}Cs, ^{106}Ru.^{137}Cs/^{134}Cs Correlation law	1	4
RTGS (CZT) + Passive neutron	MOX to LEU distinction	SMOPY Safeguards [94]	15	Comparison of NE/(^{134}Cs/^{137}Cs) ratios	Attribute test	

Table XXVI: Performances of gamma and (gamma + neutron) NDA for Spent Fuel: fixed devices

NDA method	**Physical parameter assessed**	**Example of devices**	**Assay Duration (min)**	**Calibration interpretation**	**r (%)**	**s (%)**
HRGS	**LEU** BU, CT	BU PIT (Cogema La Hague) [86]	10	Isotopic Ratio ^{134}Cs/^{137}Cs	1 -3	2-10
HRGS	**LEU** BU,CT	BNFL Thorp [?]	10	^{134}Cs/^{137}Cs or ^{134}Cs/^{154}Eu, ^{106}Ru.^{137}Cs/^{134}Cs Correlation law	1	4
HRGS + passive neutron	**LEU** Average BU Extremity BU Pu mass	BU PIT (Cogema La Hague) [87]	10	Calculated Correlation Curve	0.1	2-5

Passive neutron	**RBMK LEU** BU	BUCK Safeguards [93]	10	Calculated Correlation Curve	1-10	3-5
Passive neutron	**LWR, FBR** Irradiation attribute test	CONSULHA [?]	<1	qualitative	Attribute test	

6 CONCLUSIONS

The first evaluation of ESARDA NDA performance values was published in 1993. Almost 10 years later the Working Group for Standards and Non Destructive Assay Techniques (WGNDA) decided to review those values, to report about improvements and to issue new performance values. By taking into account the latest developments in NDA measurement technology, the present compilation also provides performance values for techniques that were not considered in the previous (1993) edition. Examples are:

- Gamma spectrometry with CdZnTe detectors, which are gaining more and more importance in Safeguards verification activities;
- the Gamma/X/Weighing (GXW) method for the simultaneous determination of uranium and plutonium isotopic ratios and element content in U and Pu bearing materials, showing potentials for a significant advancement for Safeguards verification measurements;
- Neutron multiplicity counting techniques, which help to significantly improve the measurement situation for poorly defined materials such as scrap, waste, and "dirty" (high-alpha,n) materials.

For a number of techniques already considered in 1993 the performance values have been essentially confirmed, but also changes both towards lower and higher performances have been observed in some cases. For the major neutron techniques (active and passive) the updated performance values conform more or less to the previous values, with one important exception: for small sample measurements using the inventory sample counter (INVS), notable improvements have been achieved as a result of systematic studies and improved calibration procedures.

For isotope abundance measurements by gamma spectrometry, the latest international round robin exercises practically confirmed the performance values for the ^{235}U enrichment determination, but also showed somewhat lower performances for plutonium isotope ratio measurements, compared to the 1993 values, which had been mainly elaborated on the basis of dedicated laboratory measurements. These results do not actually reflect a downgrade in the performances of the technique, but derive from a different perception of uncertainties and the feedback of a wider amount of experience. The results also underline the importance of sound and wide round robin exercises in assessing realistic pictures of performances of methods and techniques.

For U and Pu assay in solutions, the assessment confirmed (with some improvement) the very high performances of K-edge densitometry and XRF.

NDA performance values for waste measurements, not covered by the present document, are under further consideration by the WGNDA. The Group will also continue monitoring the performances of NDA techniques in use for Safeguards purposes, as well as of new emerging methods.

7 MEMBERS AND OBSERVERS OF NDA WORKING GROUP

Massimo Aparo	Observer	IAEA
Rolf Arlt	Observer	IAEA
Michael Bickel	Member	European Commission, Joint Research Centre
Michel Bruggeman	Member	SCK, Belgium
Roland Carchon	Member	SCK, Belgium (now IAEA)
Patrick Chard	Member	UKAEA, UK
F. Domingo Moya	Member	ENUSA, Spain
Guy Granier	Member	CETAMA, France
Sergio Guardini	Convenor	European Commission, Joint Research Centre
Marko Hamalainen	Member	STUK, Finland
Serhii lievlev	Observer	SSTC, Ukraine
J. Lausch	Member	WAK-FZK, Germany
Alain Lebrun	Secretary	CEA, France (now IAEA)
Ferenc Levai	Observer	Technical University, Budapest, Hungary
Tien Keh Li	Observer	Los Alamos Nat. Lab., USA
Domenico Lisi	Member	ENEA, Italy
Ming Shih Lu	Observer	Brookhaven Nat. Lab, USA
Olga Mafra	Observer	ABACC, Brasil
Paul McLelland	Member	UKAEA, UK
Jean Morel	Member	CEA, France
Herbert Ottmar	Member	European Commission, Joint Research Centre
Paolo Peerani	Member	European Commission, Joint Research Centre
Jamie Rackam	Member	BNFL, UK
Wayne Ruhter	Observer	Lawrence Livermore National Lab, USA
Bernard Thaurel	Member	IRSN, France
Antero Tiitta	Member	VTT, Finland
Peter Schwalbach	Member	Euratom Safeguards Office
Martyn Swinhoe	Observer	Los Alamos Nat. Lab., USA
Colin Zimmerman	Member	BNFL, UK

Table XXVII: List of the ESARDA NDA Working Group members and observers

8 REFERENCES

[1] EURATOM Regulation Nr. 3227/76 (Oct. 1976); Part II, Art. 9.

[2] IAEA; "The Structure and the Content of Agreements between the Agency and States Required in Connection with the Treaty on the Non-proliferation of Nuclear Weapons"; INFCIRC/153 (corrected, para.55, (1972)

[3] S. Guardini; "ESARDA Working Group for Non Destructive Assay Nuclear Techniques: Role and Developments"; ESARDA Bullettin Nr 31, (April 2002).

[4] J. Morel, C. Hill, M. Bickel, A. Alonso-Munoz, S. Napier, B. Thaurel and ESARDA NDA-WG Members; "Results of the uranium enrichment measurement exercise", Note technique CEA-LPRI-98-23, CEA Saclay, France (1998) and Appl. Radiat Isot. 52 (2000), 509.

[5] J. Morel, M. Bickel, C. Hill, A. Verbruggen, "Results from the international evaluation Pu-2000 exercise for plutonium isotopic composition measurements", Note Technique DIMRI/LNHB/02-07, CEA-Saclay, France, (April 2002).

[6] S. Guardini, G. Bignan, R.J.S. Harry, E. Leitner, H. Ottmar; "Performance Values of Non Destructive Assay Techniques: The 1993 Evaluation by the ESARDA NDA Working Group"; Proc. of 15th Annual ESARDA Symp. Rome (I), (May 1993).

[7] P. Baeten, M. Bruggeman, P. Chard, S. Croft, D. Parker, C. Zimmerman, M. Looman, S. Guardini; "Results of the ESARDA "Reals" Prediction Benchmark Exercise"; ESARDA Bullettin Nr 31, (April 2002).

[8] P. Chard et al.; "Results of the ESARDA MonteCarlo 'Simple Case' Benchmark Exercise"; to be published, ESARDA Bulletin Nr 32.

[9] G. Bignan, H. Recroix, B. Mitterand, W. Ruther, "Recommendations for the ^{242}Pu content evaluation using a new algorithm", Proc. 5th Int. Conf. on Facility Operations-Safeguards Interface, Jackson Hole, USA, September 24-29, (1995) p. 225.

[10] G. Bignan, W. Ruther, H. Ottmar, A. Schubert and C. Zimmerman; "Plutonium isotopic determination by gamma spectrometry: Recommendations for the ^{242}Pu content evaluation using a new algorithm", Bulletin ESARDA Nr 28 (1998), 1.

[11] P. Boermans, M. Franklin, S. Guardini, S. Napier, P. Schillebeeckx, J. Verplancke "An Investigation of Sampling Error at LEU facilities"; 19th ESARDA Annual Symposium, Montpellier, (F), 13-15 May, (1977).

[12] C. Hill, W. Leidert, J. Mast, F. Hendrickx, M. Bickel, A. Alonso-Munoz, Preparation of Samples for the 1997 Uranium Enrichment measurement Exercise by NDA, IRMM Internal Report GE/R/ACH/08/97.

[13] C. Hill, A. Verbruggen, M. Bickel; "Pu-200: Description of the Samples Used for the Exercise", IRMM Internal Report GE/R/ACH/25/01.

[14] ISO: "Guide to the Expression of Uncertainty in Measurement", ISO Guide ISBN 92-67-10188-9 (1995).

[15] ISO: "International Vocabulary of Basic and General terms in Metrology", First Edition (1984).

[16] ISO : "Accuracy (Trueness and Precision) of measurement methods and results. Part 1: General principles and definitions", ISO Guide 5725, first edition (Dec. 1994).

[17] R. Gunnink, "A New One-Detector Analysis Method for Rapid High-Precision Plutonium Isotopic Measurements", Proc. 9th Ann. ESARDA Symp. on Safeguards and Nucl. Mat. Management, London, England, May 12-14 1987, ESARDA 21, (1987) 167.

[18] R. Gunnink, "MGA: A Gamma-Ray Spectrum Analysis Code for Determining Plutonium Isotopic Abundances, Vol. 1: Methods and Algorithms", UCRL-LR-103220, Vol. 1 (1990).

[19] T. E. Sampson, G. W. Nelson, T. A. Kelly, "FRAM: A Versatile Code for Analyzing the Isotopic Composition of Plutonium from Gamma-Ray Pulse Height Spectra", LA-11720-MS (1989).

[20] P. A. Hypes, "Plutonium Source Isotopic Analysis with up to 25 mm Pb Shielding Using the FRAM Isotopic Analysis Code", 41th Annual Meeting of the Institute of Nuclear Material Management, New Orleans, USA, July 16-20 2000, LA-UR-00-2511 (2000).

[21] T. E. Sampson, T. A. Kelley, D. T. Vo, "Improvements in the PC/FRAM Isotopic Analysis Software", Proc. 6th Int. Conf. On Facility Operations-Safeguards Interface, Jackson Hole, USA, September 20-24 1999, p. 206.

[22] D. T. Vo, P. A. Russo, "PC/FRAM Plutonium Isotopic Analysis of CdTe Gamma-Ray Spectra, LA-UR-01-876 (2001).

[23] H. Ottmar, H. Eberle, "Determination of Plutonium Isotopic Composition by Gamma Spectrometry: Results from Interlaboratory Comparison Measurements Organized by ESARDA", ESARDA 10 (1979), 366.

[24] J. Morel, B. Chauvenet and ESARDA NDA Working Group Members, "Intercomparison of plutonium isotopic composition measurements by X- and gamma-ray spectrometry - results from the PIDIE exercise, Final report", Rapport CEA -R-5582, CEA-Saclay, France (1992).

[25] D. d'Adamo, M. Franklin, S. Guardini; "Performance evaluation of gamma spectrometry codes for international safeguards", Proc. 32nd INMM Meeting, Los Angeles, USA (July 1990).

[26] S. Abousahl, A. Michiels, M. Bickel, R. Gunnink and J. Verplancke; "The MGA code for the determination of the isotopic composition of plutonium and MOX by gamma spectrometry - A performance study", Nucl. Instr. and Meth. A 368 (1996), 449.

[27] H. Ottmar, A. Schubert, O. Cromboom, H. Eberle, "Non-destructive Assay of Small PuO_2 Samples by Neutron-Gamma Counting – Expectations and Achievements", Proc. 5th Int. Conf. on Facility Operations-Safeguards Interface, Jackson Hole, USA, September 24-29 1995, p. 205.

[28] M. J. Koskelo, C. G. Wilkens, J. G. Fleissner, "Comparison of the Performance of Different Plutonium Isotopic Codes Using a Range of Detector Types", Proc. 23rd Annual ESARDA Symp. on Safeguards and Nucl. Mat. Management, Bruges, Belgium, May 8-10, (2001).

[29] M. Bickel, S. Abousahl and R. Gunnink; Proc. on International MGA Users Workshop at IRMM, 19-20 October 1994, Report EUR-16163 EN, IRMM-Geel, Belgium (1994).

[30] H. Aigner et al, "International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Materials", Intern. Atomic Energy Agency, STR-327, (April 2001).

[31] ASTM-Standard C 1458-00, "Standard Test Method for Nondestructive Assay of Plutonium, Tritium and ^{241}Am by Calorimetric Assay".

[32] D. S. Bracken, R. S. Biddle, L. A. Carillo, P. A. Hypes, C. R. Rudy, C. M. Schneider, M. K. Smith, "Application Guide to Safeguards Calorimetry", LA-13867-M (2002).

[33] D. S. Bracken, P. Hypes, "Solid-State Calorimeter", Proc. 41st Annual Meeting of the Institute of Nuclear Materials and Management, New Orleans, USA, July 16-20, 2000, LA-UR-00-3087 (2000).

[34] M. I. Thornton, "Performance Evaluation of a Small Sample Calorimeter", Technical Note No. I.01.07 (2001), European Commission, Joint Research Centre, Ispra, Italy.

[35] J. L. Hemmerich, L. Serio, P. Milverton, "High-resolution Tritium Calorimetry Based on Inertial Temperature Control", Rev. Sci. Instrum. 65 (1994) 1616.

[36] S. Guardini, W. Strohm, editors, Proc. Intern. Workshop on Calorimetry, Joint Research Centre Ispra, Italy, 23-27 March 1992, EUR 1407 EN.

[37] C. R. Rudy, "Overview of Calorimetric Assay of Plutonium in the United States", Proc. 23rd ESARDA Annual Symposium, Bruges (Belgium), May 8-10 2001.

[38] ESARDA NDA Working Group ,"Proc. of the ESARDA International Workshop on Passive Neutron Coincidence Counting"; Joint Research Centre, Ispra, Italy, 20-23 April, 1993; Rep. EUR 15102 EN.

[39] S. Guardini, G. Guzzi, F. Mousty; "Performance Evaluation of Non Destructive Assay Techniques and Characterisation of Standards for NDA in Safeguards, ESARDA Bulletin N° 17, December 1989.

[40] P.M.J. Chard, S. Croft, "A database of ^{240}Pu-effective and ^{235}U-effective coefficients for various fertile and fissile isotopes", Proc. 19th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Montpellier (F), 13-15 May, 1997, EUR 17665 EN (1997) 389.

[41] D. Reilly et al., "Passive Nondestructive Assay of Nuclear Materials", NUREG/CR-5550, LA-UR-90732 (1991).

[42] N. Ensslin et al., "Some target assay uncertainties for passive neutron coincidence counting", Proc. 31st Annual INMM Meeting, Los Angeles (CA), 1990.

[43] B. Pedersen, V. P. Maiorov, R. Jaime, "Numerical evaluation of dead-time correction methods in passive neutron assay", Proc. 19th ESARDA Annual Symp. on Safeguards and Nuclear Material Management, Montpellier (F), 13-15 May, 1997, EUR 17665 EN (1997) 543.

[44] A. Gavron et al., " Utilisation of BAETEN's dead-time correction formalism for multiplicity counting", Proc. 40th INMM annual meeting, Phoenix, USA, 1999 (CD-ROM).

[45] D. G. Langner et al., "The State-of-the-Art of Thermal Neutron Multiplicity Counting", Proc. 38th INMM annual meeting, Phoenix, USA, 1997.

[46] N. Ensslin et al., " Result from the first advanced neutron NDA workshop", Proc. 40th INMM annual meeting, Phoenix, USA, 1999 (CD-ROM).

[47] J. E. Stewart et al., "The Epithermal Neutron Multiplicity Counter Design and Performance Manual", LA-13474-M (2000).

[47b] Hage, Cifarelli, "Three parameters analysis.... "; Nuclear Instruments and Methods, A251, (1986), pp 550-563

[48] H. Ottmar, P. van Belle, S. Croft, P. M. J. Chard, L. C-A. Bourva, U. Blohm-Hieber, "An Empirical Measurement of the ^{240}Pu-Effective Mass of ^{238}Pu and ^{242}Pu", Proc. 21st Annual ESARDA Symposium, ESARDA 29, EUR 18963 EN (1999) 311.

[49] S. Croft, L. C-A. Bourva, D. R. Weaver, H. Ottmar, "^{240}Pu Effective Mass of ^{238}Pu and ^{242}Pu in Relation to Passive Neutron Coincidence and Multiplicity Counting", J. of Nuclear Materials Management Vol. XXX N° 1(Fall 2001) 10.

[49b] Bohnel, " Original SR paper ..."

[50b]. Hage, Bondar, Pedersen, "Waste ....", tbd

[50] N. Ensslin et al., "Application Guide to Neutron Multiplicity Counting", LA-13422-M (1998).

[51] T. Dragnev, F. Grinevich, V. Rukhlo, D. Rundquist, J. Safar, E. Szabo, "Gamma and X-Ray Measurement of Nuclear Material Concentration and Quantites", Proc. 13th ESARDA Symp. on Safeguards and Nucl. Mat. Management, Avignon, France, May 14-16 1991, p.739.

[52] D. A. Close, J. L. Parker, D. L. Haycock, T. Dragnev, "Isotopic Distributions, Element Ratios, and Element Mass Fractions from Enrichment-Meter-Type Gamma-Ray Measurements of MOX", Proc. 4th Int. Conf. on Facility Operations-Safeguards Interface, Albuquerque, USA, Sept 29-Oct. 4, 1991, LA-UR-91-3104.

[53] T. Dragnev, B. Barnes, S. Deron, J. Parus, W. Raab, V. Mojaev, V. Majorov, D.A. Close, J.L Parker, "Application Results of Gamma/X-Ray and Weighing (GXW) Measurements of Uranium and Plutonium", Proc. Symposium on International Safeguards, International Atomic Energy Agency, Vienna, Austria, 13-17 October 1997.

[54] M. Aparo, T. Dragnev, F.V. Frazzoli, G. Brunetti, S. Guardini, "Assessment of the Performances of a Gamma/X-Ray/Weighing Method for the Quantitative Assay of Nuclear Materials"; Proc. 42nd INMM Symposium, Palm Desert, (CA), July 2001.

[55] G. Brunetti, F. Bruno, F. V. Frazzoli, R. Rossi, "Testing of Gamma/X-Ray and Weighing Methods for Liquid and Solid Uranium and Plutonium Samples", (June 2001).

[56] T.D. Reilly, R.B. Walton and J.L. Parker, "A simple method for measuring isotopic enrichment", Report LA-4605-MS, Los Alamos National Laboratory, Los Alamos, U.S.A. (1970), 19.

[57] L.A. Kull, R.O. Ginaven and G.E. Glancy, "A simple gamma-spectrometric technique for measuring isotopic abundances in nuclear materials", Atomic Energy Review 144 (1976), 681.

[58] P. Matussek; "Accurate Determination of the ^{235}U Isotope Abundance by Gamma Spectrometry – A User's Manual for the Certified Reference Material EC-NRM-171/NBS-SRM-969", Report KfK 3752, Kernforschungszentrum Karlsruhe, Germany, (1985).

[59] P. DeBièvre, H. L. Eschbach, R. Lesser, H. Meyer, J. Van Audenhove, B. S. Carpenter, "^{235}U Isotope Abundance Certified Reference Material for Gamma Spectrometry", EC Nuclear Reference Material 171 Certification Report, EC communication 4135, 1985.

[60] R.J.S. Harry; "Enrichment standards for gamma spectrometry", Proc. 6th Annual ESARDA Symposium on Safeguards and Nuclear Material Management, Venice, Italy, (May 1984).

[61] R. Gunnink, W.D. Ruther, P. Miller, J. Goerten, M. Swinhoe, H. Wagner, J. Verplancke, M. Bickel and S. Abousahl; "MGAU: A New Analysis Code for Measuring U-235 Enrichments in Arbitrary Samples", UCRL-JC-114713, Lawrence Livermore National Laboratory, Livermore, USA, (1994).

[62] J. Morel, M. Etcheverry and G. Riazuelo; "Uranium enrichment measurement by X and γ-ray spectrometry with the "Urados" process", Appl. Radiat. Isot. 49 (1998), 1251.

[63] S. Abousahl, A. Michiels, M. Bickel, R. Gunnink and J. Verplancke; "Applicability and limits of the MGAU code for the determination of the enrichment of uranium samples", Nucl. Inst. and Meth. A368 (1996), 443.

[64] R.J.S. Harry, J.K. Aaldijk and J.P. Brook; "Gamma spectrometric determination of isotopic composition without use of standards", Proc. Int. Symp. on the Safeguarding of Nuclear Materials, IAEA, Vienna, 20-24 Oct. 1975, published by IAEA (1976) Vol. II, 235.

[65] T. Sampson, P. A. Hypes, D. T. Vo, "FRAM Isotopic Analysis of Uranium in Thick-Walled Containers Using High-Energy Gamma Rays and Planar HPGe Detectors", Report LA-13832-MS, Los Alamos National Laboratory, Los Alamos, USA, Sept. 2001.

[66] R. Gunnink, R. Arlt, R. Berndt, "New Ge and NaI Analysis Methods for measuring ^{235}U Enrichments", Proc. 19th Annual ESARDA Symp. on Safeguards and Nuclear Materials Management, Monpellier, France, 13-15 May 1997, EUR 17665EN (1997) 431.

[67] A. K. Khusainov, M. P. Zhukov, A. P. Krylov, V. V. Lysenko, V. F. Morozov, W. D. Ruther, D. Clark, T. Lavietes, R. Arlt, "High Resolution pinType CdTe Detectors for the Verification of Nuclear Materials", Proc. 19th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Montpellier, France, 13-15 May, EUR 17665EN (1997) 415.

[68] K. Abbas, J. Morel, M. Etcheverry, G. Nicolaou; "Use of a miniature CdZnTe X/γ detector in nuclear safeguards : characterisation of spent nuclear fuel and uranium enrichment determination", Nucl. Inst. and Meth. A 405 (1998), 153.

[69] J.L. Wieman, "Practical limits on accuracy and precision in gamma-ray enrichment measurements on low enriched uranium hexafluoride", ECN-84-185 (1984).

[70] G.P.D. Verrecchia, B.G.R. Smith, S. Guardini, "The calibration of four Euratom active well coincidence counters for a wide range of high enriched uranium material", Proc. of the 11th ESARDA Symposium on Safeguards and Nuclear Material Management, Luxembourg, 30 May -1 June 1989.

[71] M. Clapham et al., "Performance comparison of different Active Neutron Interrogation Techniques for Safeguards Applications", Proc. of the 19th ESARDA Symposium on Safeguards and Nuclear Material Management, Montpellier (F), 13-15 May 1997.

[72] R. Bardelli et al., "The measurement capabilities of PHONID 3b", Proc. of 13th ESARDA Symp., Avignon (F) 14-16 May 1991

[73] P. Peerani et al., " Verification of LEU samples: passive neutron assay versus conventional active neutron interrogation", Proc. of 23th ESARDA Symp., Bruges (B) 8-10 May 2001

[74] A. Hastings, Jr. Smith, P. A. Russo, in Passive Nondestructive Assay of Nuclear Materials, chapter 9, NUREG/CR-5550, LA-UR-90-732 (1991).

[75] H. Ottmar, H. Eberle, P. Matussek, I. Michel-Piper, "Energy-Dispersive X-Ray Techniques for Accurate Heavy Element Assay", Advances in X-Ray Analysis 30 (1987) 285.

[76] H. Ottmar, H. Eberle, L. Koch, R. DeMeester, E. Kuhn, "Field Demonstration of an X-Ray Densitometer for Uranium and Plutonium Input Verfication in Reprocessing", Nuclear Safeguards Technology 1986, Vol. I, IAEA (1987) 201.

[77] H. Ottmar, H. Eberle, H.G. Wagner, J. Görten, P. Louis, W. Pörsch, R. Schenkel, L. Koch, M. Ougier, R. Schott, P. Grison, J. Salaün, P. Courvoisier, "On-Site Analytical Measurements for Input Accountancy Verification in a Large Reprocessing Plant by Hybrid K-Edge", Proc. 4th Int. Conf. On Facility Operations-Safeguards Interface, Sept. 29-Oct. 04, 1991, Albuquerque, USA, publ. by American Nuclear Society, Inc., La Grange Park, Illinois 60525 USA (1992) 164.

[78] H. Ottmar, H. Eberle, P. Daures, W. Janssens, M. Ougier, P. Peerani, U. Blohm-Hieber, F. MacLean", Dedicated K-Edge/XRF Instrumentations for Euratom Safeguards – A Review of Present and Future Applications",Proc. 19th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Montpellier, France, 13-15 May, 1997, EUR 17665 EN (1997) 211.

[79] H. Ottmar, H. Eberle, "The Hybrid K-Edge/K-XRF Densitometer: Principles-Design-Performance", Report KfK 4590 (1991).

[80] P. Matussek, I. Michel-Piper, H. Ottmar, "A Compact K-Edge Densitometer for Uranium", Proc. 13th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Avignon, France, 14-16 May, 1991, EUR 13686 EN (1991) 329.

[81] P. Matussek, I. Michel-Piper, H. G. Wagner, B. Brandalise, O. Cromboom, "First In-Field Experiences with COMPUCEA, A Portable Assay System for the Combined Determination of Uranium Concentration and ^{235}U Abundance in Uranium Solutions by NDA Methods", Proc. 15th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Rome, Italy, 11-13 May, 1993, EUR 15214 EN (1993) 415.

[82] P. Matussek, Ph. Laurent, W. Janssens, F. MacLean, U. Blohm-Hieber, "Routine Use and Recent Developments of the COMPUCEA Instrument", Proc. 19th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Montpellier, France, 13-15 May, 1997, EUR 17665 EN (1997) 313.

[83] A. Lebrun, G. Bignan., "Nondestructive Assay of Nuclear Low-Enriched Uranium Spent Fuels for Burnup Credit Application", Nuclear Technology Vol. 135 n°3, September 2001.

[84] A. Lebrun et al., "On line spent fuels plutonium evaluation for safeguards at the head-end of a large scale reprocessing plan using NDA", Proc. of 39th INMM annual meeting, Naples (FL), (July 1998).

[85] S. Guardini, G. Bignan, R.J.S. Harry, H. Ottmar, B.G.R. Smith, G. Wells, "ESARDA Performance Values of Non Destructive Assay Techniques applied in Safeguards", Proc. of 4th International Conf. On Facility Operations, Safeguards Interface, Sept. 29-Oct. 4 1991, Albuquerque (NM).

[86] G. Bignan et al., "Active and Passive non-destructive measurements for fuel assemblies nuclear monitoring", 3rd Nuclear Fuel Reprocessing and Waste Management. RECOD 91 (SENDAI).

[87] G. Bignan, L. Martin-Deidier, "Evaluation of the U-Pu residual mass from spent fuel assemblies with passive and active neutronic methods", 13th ESARDA Symp. Avignon (F) 14-16 May 1991.

[88] A. S. Chesterman , "Modular stand alone spent fuel monitoring systems bring significant cost savings in storage, transport and disposal", 5th International Conference on Nuclear Engineering ICON5, Nice FRANCE, (May 1997).

[89] R. Carchon, et al., "Fork detector measurements on LWR spent fuel", ESARDA Bulletin n° 23 (March 1994).

[89b] G.E. Bosler, P.M. Rinard, "Burnup measurements with the Los Alamos FORK detector"; Proc of the 32nd INMM Annual Meeting, New Orleans, LA, July 28-31, 1991

[89c] R.Shenkel, G.Bosler, S. Klosterbauer, "Demonstration of spent fuel measurement equipment at KWO Obrigheim facility" Rep EUR 9877 EN (1985)

[90] R. Arlt, et al., "Room Temperature semiconductors for safeguards measurements", INMM 38th annual meeting, Phoenix, (1997).

[91] P.M. Rinard, et al., "Comparison of the Fork and Python Spent-fuel Detectors", Los Alamos report LA-11867-MS (1990).

[92] A. Lebrun et al. "Gamma spectrometric characterization of short cooling time nuclear spent fuels using hemispheric CdZnTe detectors", Nuclear Instrument and Method in Physics Research, Section A, July 2000, Volume 448 (page 598 603).

[93] H. Makil et al., "Burn Up Control Kit (BUCK), an original fuel monitoring system for the RBMK spent fuel assemblies", 21th ESARDA Symp., Sevilla (Spain), (1999).

[94] A. Lebrun et al., "Development of IAEA Safeguards for irradiated MOX assemblies using NDA", 21th ESARDA Symp., Sevilla (Spain), (1999).

[95] A. Lebrun et al., "SMOPY a new NDA tool for safeguards of LEU and MOX spent fuels". Symposium on International Safeguards", IAEA, Vienna (Austria), (2001).

[96] "SFAT attribute verification of LWR Spent Fuel", Standard Procedure SG-NDA-33, IAEA, Vienna (1991).

[97] A.M. Dvoyeglazov et al., "Optimisation of the measurement geometry of SFAT device for Ukrainian VVER-1000 facilities", 23rd ESARDA Symposium, Bruges (B), 8-10 May 2001.