JRC 85591

ISSN 1977-5296

ESARDA Bulletin

NUMBER 26
MARCH 1996

ISSN 0392-3029

Number 26
March 1996

ESARDA is an Association formed to advance and harmonize research and development for safeguards. The parties to the Association are:
European Commission
CEN/SCK, Belgium
ENEA, Italy
ECN, The Netherlands
UKAEA, United Kingdom
CEA, France
BNFL, United Kingdom
KFA, Germany
CIEMAT, Spain
WKK, Germany

Editor
C. Foggi
EC, Joint Research Centre
T.P. 450
I-21020 Ispra, Italy
Tel. +39-332-789372 - Fax +39-332-789509

Circulation & Deputy Editor
F. Genoni (Mrs)
EC, Joint Research Centre
T.P. 450
I-21020 Ispra, Italy
Tel. +39-332-789421 - Fax +39-332-789509

Editorial Committee
R. Carchon (Chairman) (CEN/SCK, Mol, Belgium)
M. Cuypers (EC, JRC, Ispra, Italy)
M. Dionisi (ANPA, Rome, Italy)
F. Garcìa González (CIEMAT, Madrid, Spain)
R.J.S. Harry (ECN, Petten, The Netherlands)
W.D. Lauppe (KFA, Jülich, Germany)
H. Lefèvre (CEA, Fontenay-aux-Roses, France)
H. Nackaerts (EC, ESD, Luxembourg)
M.D. Ward (UKAEA, Risley, UK)

Manuscripts are to be sent to the Editor

They should be typed double spaced.
The accepted manuscripts will be published free of charge.
Black and white photos or diagrams should be of a very high quality.
Authors wishing copies of their papers should request them before the publication of the Bulletin.

N.B. Articles and other material in ESARDA Bulletin do not necessarily present the views or policies of ESARDA.

ESARDA Bulletin, issued jointly by ESARDA and the Joint Research Centre, is irregularly published and distributed free of charge.

The publication is authorized by ESARDA

© Copyright is reserved, but part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, mechanical, photocopy, recording, or otherwise, provided that the source is properly acknowledged.

Designed by
J. Wells
EC, JRC, Ispra, Italy
Printed by
Arte Stampa Daverio (Va), Italy

ESARDA Bulletin

EUROPEAN SAFEGUARDS RESEARCH AND DEVELOPMENT ASSOCIATION

Contents

An International Collaboration Exercise on the Calibration of a Model Reprocessing Plant Accountancy (CALDEX) Tank using a Lutetium Tracer
H. Bokelund, S. Deron, H.H. Dratschmidt, C. Foggi, W.I. Hamilton, T.L. Jones, J. Kinney, M. Neuilly, W.J. Reed, G.E. Taylor, D.H. Smith, R. Weh 1

ESARDA Working Group on Reprocessing Input Verification (RIV) - Final Report
M. Dionisi 4

Report on the Joint Meeting of ESARDA Working Groups (LEU, MOX, C/S, NDA) on Unattended/Integrated Safeguards Systems
P. Boermans, S. Guardini, R. Ingels, B. Richter 7

VVER SFAT Reveals Presence of Irradiated Nuclear Fuel
M. Tarvainen, J. Kaartinen 9

SYCLOP (SYstem of Control of Locations and Objects by Parabola) Heat Flow Sensor Parabola Used for Surveillance in Safeguards
P. Guilmain, C. Korn, M. Cuypers, P. Thery 10

Determination of Uranium and Plutonium in Simulant Mixture Samples by ^{252}Cf Shuffler
Qiao Shengzhong, P.M. Rinard, E.L. Adams, R.H. Augustson 13

Thermal Ionisation Mass Spectrometry for Determination of Uranium and Plutonium: Ion Source Chemistry
S.K. Aggarwal, M.K. Saxena, P.M. Shah, Sanjai Kumar, H.C. Jain 17

A Simple, Rapid and Accurate Electrochemical Method for Uranium Determination in Dissolver Solution of Irradiated Fuel
P.R. Nair, M. Xavier, K.A. Mathew, P.M. Shah, S.K. Aggarwal, H.C. Jain 22

ESARDA News 24

Who's who in ESARDA

An International Collaboration Exercise on the Calibration of a Model Reprocessing Plant Accountancy (CALDEX) Tank Using a Lutetium Tracer

H. Bokelund
EC, JRC, Karlsruhe, Germany
S. Deron
IAEA, Seibersdorf, Austria
H.H. Dratschmidt
EC, Euratom Safeguards Directorate, Luxembourg
C. Foggi
EC, JRC, Ispra, Italy
W.I. Hamilton, T.L. Jones, J. Kinney
AEA-Technology, Dounreay, UK
M. Neuilly
COGEMA, Aix-en-Provence, France
W.J. Reed, G.E. Taylor
BNFL, Sellafield, UK
D.H. Smith
ORNL, Oak Ridge, TN, USA
R. Weh
GNS, Hannover, Germany

Abstract

An international collaboration exercise to test Calibration by tracers techniques, was carried out between DWK, WAK, GNS, the ESARDA Working Group for Reprocessing Input Verification and the IAEA.

Four laboratories participated in a measurement programme to determine whether Lutetium tracers may be effectively used to calibrate accountancy tanks with accuracy when the analysis is performed in different labs: BNFL, Sellafield, UK; Oak Ridge Na-tional Laboratory, Tennessee, USA; AEA-Technology (UKAEA), Dounreay, UK; Transuranium Institute of JRC, Karlsruhe, Germany. Results of the separate testing and analysis indicated that there was substantial agreement between laboratories, as confirmed by statistical analysis. Also, the experiment indicated that the technique is sufficiently developed to be used during the initial calibration of accountancy vessels.

Introduction

The potential usefulness of tracers for the calibration of accountancy tanks has long been recognised /1,2/. The successful use of a Lutetium tracer on a plant scale with analysis by isotope dilution mass spectrometry has been described /3/ and the work independently repeated /4/. In both cases the addition of the tracer and the analysis were performed by the same organisation over a comparatively short time period. The purpose of the present work was to explore whether it would be possible to obtain a similar precision when the analysis is carried out in several independent laboratories.

The experiments were carried out as part of the programme of work at the CALDEX test facility at KfK Karlsruhe. This test facility and the initial test programme have been described in more detail elsewhere /5/.

The following four laboratories participated in the measurement programme: BNFL, Sellafield, UK; Oak Ridge National Laboratory, Tennessee, USA; AEA-Technology (UKAEA), Dounreay, UK; Transuranium Institute of JRC, Karlsruhe, Germany. The WAK laboratories at KfK Karlsruhe, Germany, undertook the tracer solution preparation and the sample shipment.

The potential benefits for the safeguarding organisations of using tracers during calibrations include:

- greater participation in calibration activities at the reprocessing plants, leading to greater independence in the calibration of accountancy vessels and
- the ability to independently confirm the calibration of accountancy vessels throughout their operational life.

Tank Measurements

The trial of the conventional instrumentation installed on the 12,500 litre CALDEX tank was carried out by adding known volumes of water using a precision rotary piston pump. The rotary piston pump was calibrated by measuring the mass pumped, using a Sartorius balance with a working range of 61 kg and a precision of 1 g, using a known density for the calibration liquor and a measured temperature. The mass of liquor added to the tank was calculated by volumetric measurement, using an assumed density, and was determined with an accuracy of better than 0.1%, i.e., with an accuracy one order of magnitude better than any of the methods being used on the tank itself.

Each experimental run involved the steady addition of calibration fluid using the rotary piston pump, while simultaneously recording the response of the various instruments measuring the depth of liquor in the tank. To accommodate the tracer experiment, the liquor addition was stopped at about 4000 litres for the addition of 2.5 g of natural Lutetium tracer in solution. The tracer addition was followed by vigorous mixing, using the installed sparging system, and then by removal of a 1 litre sample of the tank solution. The volume of liquor in the tank at the time of sampling was recorded, after which the filling of the tank recommenced until a volume of approximately 6000 litres had been added. The tank was then sparged, and a further 1 litre sample of the liquor removed. This process was repeated twice more.

The first run was made using a 0.5 M sodium nitrate solution with methylene blue; runs 2 and 3 were made using 0.5 M nitric acid, up to a total of 15000 litres.

Sample Preparation Prior to Shipment

Samples provided for each run were:

- duplicate samples of the filling solution spiked with enriched ^{176}Lu; and
- one unspiked and duplicate spiked samples taken at each sampling level.

Also provided were one vial of enriched ^{176}Lu spike solution and three vials of the natural Lutetium tracer for determining a mass fractionation correction factor.

Samples taken from each of the 3 runs were sent to each of the participating laboratories in November 1989. The sample aliquots were weighed so that the receiving laboratory could confirm that there had been no sample loss or evaporation during transport.

Sample Analysis

Each laboratory was asked to determine the concentration of Lutetium per unit weight of the aliquot, to determine the tracer concentration relative to the known spike concentration, and thereby to calculate the weight of liquor in the tank when the sample was taken.

The four laboratories all followed broadly the same method, i.e., isotope

dilution mass spectrometry. The analyses took place in the various laboratories between January and November 1990.

The following comments were made concerning the method and results of analyses by the participating laboratories:

Laboratory No. 1

The samples, in liquid form, were known to contain Lu in the concentration range 0.5 - 0.7 µg/l. Aliquots were taken from the samples and separated by extraction into D_2EHPA , 0.75M in dodecane. The organic phase was isolated and washed with water to remove Na. The Lu was back-extracted into 8-9 N HNO_3 in multiple increments to achieve an overall extraction efficiency of > 75%.The acid solution was repeatedly evaporated and redissolved to destroy any residual organic matter. The samples were then dissolved in a small volume of HNO_3 for loading on the mass spectrometer filaments.

All measurements were done on a VG 354 thermal ionization mass spectrometer equipped with moveable multicollectors. Two off-axis collectors were used for the ^{175}Lu and ^{176}Lu ion beams. Natural Lu was also measured to arrive at a mass fractionation correction factor, based on the IUPAC recommended isotopic abundances of the two isotopes.

All data reported are fractionation corrected and represent the mean of at least 2 replicate measurements. Several samples failed to provide adequate ion current which was probably due to ionization interference from Na.

Laboratory No. 2

No problems with weight loss of samples were detected during the check weighing of the samples. Samples from run 1 were chemically separated to remove the sodium nitrate and methylene blue. The technique used was to load the sample onto a D_2EHPA/corvic column. After washing away the impurities, the Lutetium was eluted with strong nitric acid. The samples were then mounted on tungsten/rhenium beads (150 ng Lu) and analysed on two VG single collector machines using 0.5 V Faraday ion beam.

Laboratory No. 3

The aliquots were loaded on the mass spectrometer filaments without any chemical separation. The measurements were carried out using a Finnigan MAT 262 mass spectrometer equipped with a multicollector, and the total evaporation technique was used. In some cases the ion signals were low. Run 1 gave some problems with beam stability which may have been due to the salt content (sodium nitrate) on the filament and also suffered from a lower internal precision of the scans especially with the dilute samples. The measured blank values were negligible in all cases.

Laboratory No. 4

All the samples were run directly on a VG-Isotech mass spectrometer without any initial separation. The samples were mounted on the side filaments of triple filament rhenium beads; the centre filament was used to tune the instrument. The side filaments' current was slowly increased manually until a steady ion beam giving about 0.6 volts on the Faraday detector was obtained. Two runs of twenty cyclic scans were measured in the automatic mode. The results were evaluated using the spectrometer's computer system to obtain a LUTETIUM isotopic ratio from which the concentrations and equivalent volumes were calculated by hand.

Results

The estimates obtained for the weight of liquor in the tank from the four laboratories, compared with the weight of liquor added via the rotary piston pump, for the three experiments, are given in Table 1.

Statistical Analysis

There are three principal sources of error in the data given in Table 1:

(1) sampling errors, including addition of tracer, homogeneity, preparation, and dilution;
(2) errors in the measurement of the weight of liquor added to the tank by the rotary piston pump and
(3) errors in the mass spectrometric analysis.

For the purposes of this analysis it is assumed that:

(1) the systematic error and the standard deviation of the random errors associated with the measured weight of liquor are proportional to the true value and
(2) the variance of the random error in the mass spectrometric analysis is, as a first step, dependent on the place of analysis.

Taking:

i = index for lab, and
j = index for sample,

then, for the mass spectrometric analysis:

$$x_{ij} = \mu_j(1 + A_i + B_j + \epsilon_{ij})$$

where:

μ_j = true value,
A_i = systematic error for lab i,
B_j = random error in preparation of sample j,
ϵ_{ij} = random error of the analysis,
E = expected value, and

$E(B_j) = E(\epsilon_{ij}) = 0$, $Var(B_j) = \sigma_B^2$, and $Var(\epsilon_{ij}) = \sigma_i^2$.

For the measured weight of liquor:

$y_j = \mu_j(1 + \epsilon_{yj})$, $E(\epsilon_{yj}) = 0$, and $Var(\epsilon_{yj}) = \sigma_y^2$.

The relative deviation is:

$$e_{ij} = \frac{x_{ij} - y_j}{y_j} = \frac{A_i + \left(B_j - \in_{yj}\right)}{1 + \in_{yj}};$$

or:

$$e_{ij} \sim A_i + (B_j - \epsilon_{yj}) + \epsilon_{ij}$$

Experimental values for e_{ij}, in %, are given in Table 2.

The application of Dixon's Test showed that there were no outliers in the data.

Further statistical tests, based on the use of Grubb's Analysis for Two Measurement Methods, showed that the random error of the mass spectrometric analysis was independent of the labora-

Table 1

	Weight	Lab 1		Lab 2	Lab 3		Lab 4	
	Added	1	2		1	2	1	2
Run 1	4952	4949	4946	4935	4951	4966		
	7427	7458	7456	7445	7449	7468		
	9903	9915	9924	9887	9841	9933		
	12380	12386	12398	12351	12543	12312		
Run 2	4067	4083	4076	4071	4077	4073	4075	4073
	6102		6121	6106	6116	6113	6110	6115
	8136	8157	8163	8134	8162	8148	8144	8142
	10170	10182	10197	10162	10174	10185	10173	10174
Run 3	4068	4072	4070	4057	4062	4063		
	6103	6109	6111	6090	6110	6111		
	8132	8173	8158	8137	8155	8131		
	10170	(8882)[1]	10189	10171	10199	10183		

1 This sample results from Laboratory 1 is obviously a rogue result and been excluded from the statistical analysis

Table 2

		Lab 1	Lab 2	Lab 3	Lab 4
Run	**Sample**				
1	1	-0.0838	-0.3433	0.1313	
	2	0.4066	0.2424	0.4241	
	3	0.1671	-0.1616	-0.1616	
	4	0.0994	-0.2342	0.3837	
2	5	0.3049	0.0984	0.1967	0.1721
	6	0.3065	0.0656	0.2049	0.1721
	7	0.2938	-0.0246	0.2335	0.0860
	8	0.1883	-0.0787	0.0934	0.0344
3	9	0.0836	-0.2704	-0.1352	
	10	0.1147	-0.2130	0.1229	
	11	0.4076	0.0615	0.1353	
	12	0.1858	0.0098	0.2065	

tory. It was further concluded that the systematic error of the analysis was about 0.2% with a random error of 0.2% and that both the systematic and random errors associated with sample preparation were on the order of 0.1%.

It was not possible from this limited data set to draw any further conclusions.

Conclusions

This collaborative experiment has shown that the basic Lutetium tracer technique is extremely robust and capable. The agreement between the laboratories is good which the statistical treatment confirmed. The accuracy of the standards and fractionation do not affect the accuracy of the results as long as the tracer and the tank samples are analysed using the identical spike solution and under the same conditions.

The technique is sufficiently developed to be used during the initial calibration of accountancy vessels. The technique might be extended to the determination of the volume or mass of liquor in the head end accountancy tanks of reprocessing plants. The addition of Lutetium tracer to head end liquor would have no significant impact on the operation of the reprocessing plant, on the treatment of the liquid raffinates or on the purity of the Plutonium and Uranium products.

The experiment also suggests that international agencies can obtain a precision and accuracy comparable to that achieved by plant operators /4/ in the measurement of the volume of pure Plutonium solution in those cases where the quantitative addition of Lutetium to the product is practicable and acceptable.

A further extension of the technique to the direct determination of the Plutonium content by making a direct measurement of the Plutonium Lutetium ratio, hinted at in /4/, may be possible.

References

/1/ C.K. MATHEWS - Proc. Seminar on Accountability and Management of Fissile Materials, Trombay, April 1971, BARC/I-165 (1972) 17.

/2/ H. BOKELUND - ETR-266, Eurochemic, Belgium (1970).

/3/ D.H. SMITH, R.L. WALKER, J.A. CARTER - Anal. Chem. 55 (1983) 578.

/4/ W.J. REED, C.N. RAMSDEN, M.R. JAMES, G.E. TAYLOR - IAEA-SM-293/49.

/5/ H. DRATSCHMIDT, R. WEH - Proc. 11th Annual Symposium on Safeguards and Nuclear Materials Management, ESARDA 22, p. 65 (1989).

ESARDA WG on Reprocessing Input Verification (RIV) Final Report

M. Dionisi
ANPA, Rome, Italy
On behalf of the members of the ESARDA RIV Working Group

Introduction

The Reprocessing Input Verification Working Group was created in 1982 as an extension of the Isotopic Correlation Technique WG /1,2,3/. Its activity dealt with problems related to the determination of the input of nuclear materials into the reprocessing plant and to its verification in support to the Safeguards Authorities and also to Operators /4,5,6/.

Many organizations from inside ESARDA participated to the WG and also many outside observers actively contributed to the effective completion of its objectives.

The activities carried out included:

- exchange of information among participants (Operators, Safeguards Authorities, R&D people);
- experiments in laboratories and in reprocessing plants;
- determination of areas where further research and development were needed;
- performance evaluation of methods, techniques and procedures currently in use for the input determination in reprocessing plants;
- research and development of measurement procedures, measurement errors structures, mathematical models, computer programs, data bases.

Several projects have been promoted and successfully completed /7,8/, e.g.:

- ICE experiment at the WAK reprocessing plant;
- Integral Experiment at the WAK reprocessing plant;
- ICT Benchmark Exercise with data provided by the COGEMA reprocessing plant, the KWU and the KWO;
- RITCEX experiment at the former EUROCHEMIC plant;
- Seminar on the use of Tracers in Volume Measurements;
- CALDEX Exercise at the TEKO facility.

All these projects were carried out in close co-operation with the Operators. Both the Operators and the Safeguards Authorities took part in the definition of the scope and in the design of the experiments with a view to obtaining results which could be useful for their purposes.

The results obtained have opened the way to improvement of the Safeguards measurement systems (instruments, methods and procedures) and therefore to an overall improvement in the practice of the input measurement.

The Isotope Correlation Experiment (ICE) /9/

Objectives

To check the applicability of the Isotopic Correlation Technique (ICT) to the verification of the consistency of the analytical data obtained by the operator's laboratory and to the verification of the measured Pu/U ratio. To compare the performance of ICT with traditional verification techniques based on parallel measurements.

Description

The experiment took place in 1978-81, during the reprocessing of spent fuel from the Kernkraftwerk Obrigheim GmbH, KWO, at the Wiederaufarbeitungsanlage, WAK, Karlsruhe.

Ten consecutive input batches, corresponding to 5 fuel assemblies of the Obrigheim reactor, were routinely analysed for the concentration of uranium and plutonium isotopes by the plant operator, the IAEA, the Institute of Radiochemistry of KfK, and the JRC European Institute for Transuranium Elements on behalf of EURATOM. In addition, the latter institute analysed fission gases isotopic composition, long-living gamma-emitting fission products, transplutonium nuclides, americium, curium and determined the burn-up by Nd-148. Volume, density and dilution factor of the samples were measured at the plant. No measurements of the head-end losses could be made at the time. The uranium weight of the fuel at the time of fabrication was used for the isotope correlation technique.

In the evaluation of the experimental data, the following organisation and people were involved:

BNFL: J.C. Dalton
BNWL, Hanford: C.L. Timmerman
CEA, Cadarache: J. Bouchard
SCK/CEN, Mol: P. Bemelmans, F. Franssen
CNEN, Eurex-Saluggia: S. Ilardi, F. Pozzi
DWK, Karlsruhe/Hannover: R. Berg, R. Weh
ECN, Petten: W.L. Zijp
ESD Luxembourg: H.J. Arenz
JRC Ispra: C. Foggi
JRC Karlsruhe: L. Koch, C. Rijkeboer
IAEA: S. Deron, S. Sanatani, P. Siwy
KfK, Karlsruhe: E. Mainka, S. Schoof
KWO, Obrigheim: D. Sommer
KWU, Erlangen: G. Schlosser
UKAEA, Harwell: A.G. Wain

Results

The main objectives of the statistical data evaluation were the detection of outliers and the estimation of random and systematic errors of the measurements performed by four laboratories. Different methods for outlier detection, were applied: analysis of variances, Grubb's analysis with constant-bias model and Jaech's non-constant-bias model. Some of the results of the statistical analysis seemed inconsistent, which was due to the fact that no commonly agreed statistical evaluation procedure existed.

The results nevertheless proved that ICT was at that time as accurate as conventional techniques which have to rely on costly mass spectrometric isotope dilution analysis. The potential for outlier detection by ICT on the basis of the results from a single laboratory proved to be as good as outlier detection by costly interlaboratory comparison.

The application of fission product or Cm-244 correlations would be more timely than remeasurements at Safeguards laboratories.

Integral Experiment at the WAK reprocessing plant

Objectives

In order to determine the achievable accuracy of ICT, the RIV Working Group recognized that, in addition to input data, the head end losses should be considered as well. According to a request of the WG, DWK/WAK carried out an integral experiment at the WAK plant in summer 1983.

Description

Ten spent fuel assemblies from the KWO reactor, undergoing a reprocessing campaign at WAK, were investigated. All fuel assemblies which were part of the exercise had been non-destructively assayed some years before the reprocessing.

The practical part of the experiment included:

- Chemical/physical analysis of all input solution batches
- Determination of U, Pu and Cm in leached hulls
- Determination of U, Pu and Cm in feed clarification sludges

- Analysis of dissolver off-gas samples (Xenon).

The participating Organizations in this experiment were: DWK/WAK, KfK-IRCH; EURATOM Safeguards and IAEA were observers.

Results

A considerable amount of data was collected. Unfortunately, a sample pretreatment procedure never applied before, led to input measurement results which made the evaluation of the head end material balance impossible. Therefore, the goal of the experiment was not attained, although the safeguards samples were not affected.

The ICT Benchmark Exercise

Objectives

The existence of many different methods to use Isotopic Correlation (seven laboratories with their own sets of procedures), required to set up a benchmark exercise to test their application on a common data set, to compare their results. The ICT benchmark was initiated by the RIV-WG to clarify and to evaluate the possibilities, the limits, and the performances of the various approaches to the isotopic Correlation method /10,11, 12,13/.

The Benchmark Exercise had two main objectives: 1) to assess the precision and accuracy achieved by the various laboratories in determining the input inventory by means of their respective ICT method, and 2) to test the capability of each method to detect and possibly trace the origin of anomalies present in the analytical data.

Description

The CEA was in charge to organize the exercise. The dissolution data from La Hague reprocessing plant were released by COGEMA (53 batches for a total of 110 irradiated fuel elements from KWO, Obrigheim reactor).

Seven laboratories participated in the exercise (from Europe, US and Japan). The data were supplied in two sets: the first one, relevant to 24 dissolution batches, was used to test the capability of the various methods to assess the input balance; the second, relevant to 29 dissolution batches, contained anomalies introduced on purpose by the organizer, and was used to test the capability in discovering anomalies.

Results

For a reprocessing input balance using the "gravimetric" method, the verification of the operator data on plutonium was better than 1% (after correlated errors filtering).

All anomalies intentionally introduced in dissolution data, and relevant for Safeguards, have been detected and diagnosed.

In conclusion, the RIV WG recommended the use of ICT for detecting and resolving anomalies in reprocessing input data. The results have been presented in the ESARDA's Symposia held in Venice and in Avignon.

Workshop on Tracers

Objectives

A workshop was convened at Ispra on 8-9 November 1983 on the "Determination of the volume of reprocessing input solutions by tracers techniques", with the objectives of reviewing the state of the art and identifying the existing problems /14/.

Description

The Workshop convened experts from Safeguards Authorities (IAEA, EURATOM), Research Organizations (ENEA, CEA, ORNL, UKAEA, JRC) and Industrial Plant Operators (ITREC, EUREX, BNFL).

Past and ongoing experiment carried out world-wide were reviewed, as well as the status of the connected laboratories techniques.

Two possible applications of the tracers technique were evidenced:

- determination of the volume of the tank
- determination of the masses of the U and Pu in the solution

There was no common preference for the elements to be used as a tracer (Li, Mg, Sr, Gd, Lu, Nd, Er etc…), since the choice is also dependent on the final purpose of application, on the facility design, on the long term availability of the tracer and on economic considerations.

It was agreed that one of the most critical points in the whole technique is to obtain representative samples for mass spectrometry analysis.

The available procedures for chemical separation of the tracer from the hot solution seem satisfactory, although some standardization would be desirable.

At the end of the Workshop, some of the Plant Operators decided to test the method on their plant in order to assess the accuracy and precision of the tracer technique in operating condition.

The RITCEX Exercise

Objectives

Very little experience was available on volume calibrations of liquids in tanks. A variety of control instruments were available but they were never tested before or their performances compared. The statistical evaluation of calibration data was never explored in detail. Finally, a description of the ideal design and operation of an accountancy tank was missing.

After these considerations made by the RIV WG, the SCK/CEN decided to carry out an experiment at the EUROCHEMIC plant.

Several RIV WG members took part in this experiment, which analysed problems related to weighing, tank calibration, either with incremental weights or with continuous feeding, tank calibration with tracers, level measurement, statistical analysis of calibration data /15,16, 17,18,19/.

Description

The Reprocessing Input Tank Calibration Exercise (RITCEX) was organized in 1984 in the framework of the Belgian Support Programme to the IAEA Safeguards, and as a task within the RIV WG. The organization was done by the SCK/CEN of Mol (Belgium) and the exercise took place at the former European reprocessing plant EUROCHEMIC. Many countries and organizations did actively participate in the exercise.

Four calibration runs with incremental weights were performed during RITCEX. The performances of different level measurement instruments were investigated, namely the electromanometer (Ruska), the U-tube manometer, the acoustic system (SONAR) and the Time Domain Reflectometer (TDR). Special calibration runs with continuous feeding were carried out in order to evaluate the accuracy of continuous calibration.

Several organizations analysed, with their own procedures, the raw data in terms of: data standardization, precision and accuracy of each instrument, and derivation of a calibration curve.

Results

The comparison of the electronic scales with the mechanical ones proved that the performance of the weighing devices had very much improved since the production of electronic scales. The error due to weighing became negligible.

The use of electromanometer systems, compared to the use of conventional pressure measurements systems such as U-tubes or, even worse, the operator's panel recorder systems, improved the sensitivity and the accuracy of pressure measurements at least by a factor of ten. Reading and transcription errors are also eliminated by this system.

Other liquid level measurement systems were tested during the exercise such as the Time Domain Reflectometry (TDR) and an acoustic system, but both systems were in the phase of development and the results were not comparable to the conventional dip-tube system.

Transformation of raw data and statistical evaluation were extensively discussed and standardization was highly recommended.

The use of tracer techniques showed promising results especially if considered as a means of authentication or reverification of calibrations.

The continuous calibration of tanks was indicated as very promising, especially for the calibration of large tanks.

The sensitivity of the "new" pressure measurement systems (electromanometers) emphasized the problem of the run-to-run differences in tank calibrations. Standardization of calibration and measurement procedures was highly recommended.

The overall conclusion of RITCEX was that the exercise opened a large perspective of tank calibration issues never noticed before, which must be explored in more detail. It was considered to be the starting point in studying improvements of tank calibration and volume measurement.

The CALDEX Exercise

Objectives

In conjunction with the planned operation of the now abandoned Wackersdorf Reprocessing Plant, volumetric bulk determination for the purpose of input accountancy was investigated. To this end, a test rack was set up at the Karlsruhe nuclear research facility. Studies were made on the degree of accuracy achievable, making use of both domestic and international experience and equipment. In order to co-ordinate activities an international experiment and a workshop (CALibration DEmonstration EXercise, CALDEX) were carried out, /20,21,22,23/.

Description and results

The test rack provided the opportunity to take measurements with various instruments, such as pressure gauges, capacitive and acoustic probes. Two methods of calibration were tested, the incremental and the continuous feed, with the latter being considered to be preferable, because less time consuming. Also a test was carried out on the use of Lutetium as a tracer element for the purpose of verification.

The results of the experiment were evaluated at several organizations and laboratories in a model international co-operation, in which the ESARDA RIV Working Group played a crucial part. Although the evaluation of data collected during the experiments was never completed to its full potential, it provided a good indication of the principal benefits of input calibration in bulk handling facilities and gave hints as to future research and application.

The measurement results also showed some unexpectedly high differences, in particular as regarded the behaviour of various precision techniques and proved that the mechanical behaviour of the tank was not to be neglected. It could also be demonstrated that calibration can be automated. The continuous feed of calibration liquor and the application of Lutetium as a tracer could be of considerable practical importance.

In the course of evaluation, theoretical studies were made of the possible limiting factors of the CALDEX exercise due to the fact that the experiments were made in a scientific rather than an industrial environment.

Due to unforeseen circumstances, domestic interest in the experiment was cut short and, to save the equipment and the valuable knowledge gained, the test rack was transferred to JRC Ispra. Here the whole test set up was reconstructed in the TAME (Tank Measurements) Laboratory and the possibility was created to repeat and improve the original CALDEX exercise.

Another considerable success of the CALDEX exercise was to gather a large number of experts, companies and organizations from all over the world and co-ordinate constructive and fruitful co-operation.

Publications

/1/ R. ERNSTBERGER, L. KOCH, R. WELLUM - "Isotope Correlations used in fuel and waste management" ESARDA Symposium on Isotopic Correlation and its application to the Nuclear Fuel Cycle, Stresa 9-11 May 1978.

/2/ B. BRANDALISE, L. KOCH, C. RIJKABOER, D. ROHIKOWKI - "The application of Isotope Correlations in verifying automatic analysis of irradiated fuels" ESARDA Symposium on Isotopic Correlation and its application to the Nuclear Fuel Cycle, Stresa 9-11 May 1978.

/3/ S. SCHOOF, H. STEINERT, L. KOCH - "The influence of Plutonium recycling in Boiling Water Reactors on Isotope Correlations" ESARDA Symposium on Isotopic Correlation and its application to the Nuclear Fuel Cycle, Stresa 9-11 May 1978.

/4/ C. FOGGI - "The ESARDA Working Group on Isotopic Correlations and Reprocessing Input Accountancy" European Safeguards Bulletin No. 2, Spring 1978.

/5/ C. FOGGI - "Isotopic Correlation Techniques and Reprocessing Input Analysis" ESARDA Bulletin No. 1, October 1981.

/6/ C. FOGGI - ICT-RIA Changes to RIV ESARDA Bulletin 4, April 1983.

/7/ C. FOGGI - "Activities of the ESARDA Working Group for Reprocessing Input Verification" Proceedings of the 5th ESARDA Symposium, Versailles 19-21 April 1983.

/8/ C. FOGGI - "Description of the activities carried out by the RIV Working Group" Contribution to the 8th ESARDA Annual Meeting, Copenhagen 13-15 May 1986.

/9/ L. KOCH, S. SCHOOF - "The Isotope Correlation Experiment" EUR 7766 EN, 1983.

/10/ A. GIACOMETTI - "The ESARDA Exercise to Test the Performance of ICT Procedures" Proceedings of the 6th ESARDA Symposium, Venice 14-18 May 1984.

/11/ P.J. PERSIANI, R.G. BUCHER - "Implementation of Isotope Correlation Technique for Safeguards" Proceedings of the 11th ESARDA Symposium, Luxembourg 30 May-1st June 1989.

/12/ P.J. PERSIANI, R.G. BUCHER, R.B. POND, R.J. CORNELLA - "Fuel Reprocessing data validation using the Isotope Correlation Technique" Int. Conference on the Physics of Reactors, Marseille 23-27 April 1990.

/13/ A. GIACOMETTI - "Conclusion of the ICT Benchmark Exercise" Proceedings of the 13th ESARDA Symposium, Avignon 14-16 May 1991.

/14/ G. GUZZI, P. TRINCHERINI - "Report on the Workshop on Determination of the Volume of Reprocessing Input Solutions by Tracers Techniques" ESARDA Bulletin No. 6, 1984.

/15/ F. FRANSSEN - "Reprocessing Input Tank Calibration Exercise (RITCEX)" ESARDA Bulletin No. 6, 1984.

/16/ D. SELLINSCHEGG, G. NÄGELE, F. FRANSSEN - "Evaluation of Tank Calibration Data in RITCEX" Proceedings of the 6th ESARDA Symposium, Venice 14-18 May 1984.

/17/ P. DE REGGE, P. TRINCHERINI, J. VAN RAAPHORST, V. PAGLIAI, T. CANDELIERI - "RITCEX Exercise on Input Tank Volume - Results of the use of Tracer Technique" Proceedings of the 7th ESARDA Symposium, Liege 21-23 May 1985.

/18/ R. CARCHON, P. DE REGGE, F. FRANSSEN - "Reprocessing Input Tank Calibration Exercise (RITCEX) Final Report (Volume I) Statistical evaluations of the measured data (Volume II)" BLG 588, June 1986.

/19/ R. CARCHON, P. DE REGGE, F. FRANSSEN - "RITCEX, Aims and Conclusions" Nuclear Safeguards Technology, IAEA Symposium, Vienna 10-14 November 1986.

20. H. DRATSCHMIDT, R. WEH - "The Calibration of large reprocessing input accountancy tanks. The CALDEX Project" Proceedings of the 11th ESARDA Symposium, Luxembourg 30 May-1st June 1989.

/21/ S. SUDA, R. WEH - "Preliminary data analysis of the CALDEX Thermal Expansion Test" Proceedings of the 13th ESARDA Symposium, Avignon 14-16 May 1991.

/22/ R. WEH - "Reprocessing input tank calibration. An International Experiment under the auspices of ESARDA" Proceedings of the 32nd Annual INMM Meeting, New Orleans 28-31 July 1991.

/23/ H. BOKELUND, S. DERON, H. DRATSCHMIDT, C. FOGGI, W.I. HAMILTON, T.L. JONES, J. KINNEY, M. NEUILLY, W.J. REED, D.H. SMITH, G.E. TAYLOR, R. WEH - "An International collaboration exercise on the calibration of a model reprocessing plant accountancy tank (CALDEX) using a lutetium tracer" ESARDA Bulletin No. 26

Report on the Joint Meeting of ESARDA WGs (LEU, MOX, C/S, NDA) on Unattended/Integrated Safeguards Systems

P. Boermans
FBFC, Dessel, Belgium
Convenor, ESARDA LEU WG

S. Guardini
EC, JRC, Ispra, Italy
Convenor, ESARDA NDA WG

R. Ingels
Belgonucléaire, Dessel, Belgium
Convenor, ESARDA MOX WG

B. Richter
KFA, Jülich, Germany
Convenor, ESARDA C/S WG

1. Introduction

The evolution of the European Union nuclear fuel cycle is towards facilities with large throughput /1/, with nuclear material stored in difficult-to-access areas /2/, processed by automated equipments, sometimes permanently operated 24 hours per day. Therefore R&D laboratories are developing new instruments for safeguards inspectors based on new concepts like:

- combination of different sensors in the same system, collecting signals of very different nature all concurring to help the inspectors decision-making process. Examples are neutron and gamma signals together with camera images, infrared or microwave sensors etc.
- integration of the above signals, first at the level of data collection and transmission, then development of logical integrated approaches allowing to treat data formally with the same formalisms/algorithms /2/. An example could be the current approaches to treat both quantitative data and C/S data in the same equations
- development of unattended systems, combining surveillance and NDA devices to reduce the burden on inspectors and operators. This requires developing instrument automation, from one side, and implementing 'intelligent' automatic decision-making capabilities in the devices, on the other. In other words, the unattended systems should be capable of indicating a relevant alarm requiring an immediate intervention of the Headquartes or if the alarm is 'less important', that it is possible to wait for cumulative analysis on longer periods
- development of remote data transmission tools capable of managing large sets of data, from different sensors.

In May 1995 four ESARDA WGs, namely LEU, MOX, C/S and NDA, met together to discuss the above aspects of integrated unattended safeguards systems.

The discussions focused on the R&D needs in areas like data handling, evaluation and transmission, as well as the increased need of authentication tools to ensure the authenticity of safeguards data.

2. Presentations

Three lectures on integrated/unattended systems under development were given.

2.1 EURATOM Safeguards Directorate presented the Integrated Systems under development at JRC Ispra for Unattended Inspection of fresh LEU fuel assemblies

The EURATOM UMS (Unattended Monitoring System) /3/ most prominent characteristics are:

- the system is designed to assay 100% of the LEU assembly production without the intervention of the inspectors.
- the facility operator ensures the assemblies loading and unloading but does not have any involvement in the measurements or in safeguards data evaluation
- the system integrates NDA active neutron measurements (a new design active collar is employed) with a video system to read the ID assembly number
- the software is designed to perform automatic recognition of the ID
- the software allows to configure the automated measurement strategy, analyse results and generate inspection reports
- the system monitors its performances, protects itself from tampering and communicates with Headquarters via a modem.

The prototype system will undergo field tests in spring 1996.

2.2 FBFC presented a scheme for safeguarding a MOX Assembling facility by NDA and C/S techniques. FBFC International has constructed a new MOX assembling facility. Pins (received from outside MOX facilities) will be assembled in the workshop. After quality control checks the assemblies will be moved to the assembly store from where they will be sent afterwards to the loading area to be put in boxes. After sealing, the boxes will be loaded in transport containers for shipment.

A combined system of measurement devices, cameras and monitors will be installed, in close collaboration between operator and inspectors.

The pins will arrive in sealed boxes. An NDA device will be set up to give the safeguards authorities the opportunity to eventually remeasure the pins.

The finished assemblies will be assayed in the workshop by a passive neutron unattended measurement station (NCC) triggered by a neutron monitor at the moment they pass at the last working station. At the same moment the identification number of each assembly will be read by a camera.

The measured assemblies will be moved in the assembly store under camera surveillance. A neutron monitor will confirm this movement.

In the described verification scheme the presence of an inspector is only needed at the moment of the arrival of the pins and at the moment of the sealing of the transport container. All the safeguards relevant information, the neutron monitor data and the cameras pictures will be recorded and elaborated by safeguards authority only from the measurement stations.

2.3. SIEMENS A.G. presented in detail the integration between different techniques, in particular NDA and C/S, employed to safeguard the MOX fabrication plant.

- The flow diagram of the NMC & A employed in the facility has been presented.
- The different measurement and monitoring systems from the PuO_2 input through the stores, the process steps, the bundle assembling and store have been illustrated in details.
- Particular relevance was given to integrated systems like the neutron/ gamma assay system for input verification that combines improved high resolution gamma spectometry together with ad hoc designed passive neutron detector heads.
- In the area of pelletisation, the monitoring system combining electro-optical monitoring with neutron and gamma assay has been shown.

3. Conclusions

The Aachen meeting of four ESARDA WGs followed a number of other meetings /4/ in variable configurations where ESARDA WGs discussed the issues connected with automation/integration of safeguards instruments, remote monitoring and remote data transmission. These items are of utmost importance and interest today, in view of the evolution of the European fuel cycle towards large throughput nuclear plants as well as towards highly automated plants with sometimes inaccessible SNM process and storage areas.

The main conclusions of the meeting were

- the evolution of the safeguards assay and monitoring systems towards unattended/integrated devices is necessary and somehow unavoidable
- EURATOM Safeguards Directorate is already developing testing and implementing unattended/integrated measurement systems in plants where the benefit for inspectors of using such devices is higher
- For plant operators, also integrated/unattended system present advantages
  - for their material accountancy first, as shown by the presentations in the meeting
  - and, second, because automated/unattended inspector's devices provided with modern decision making tools and remote transmission systems will represent a reduction in the burden for the operator and a more effective safeguards system.
- For R&D laboratories, future developments represent a challenge and an opportunity to study and solve scientific/technical problems in areas like
  - automation and computerised decision making
  - integration of different techniques (e.g. C/S and NDA) first at the level of informatic data support then to a full logical compatibility
  - remote data transmission
  - authentication
  - remote assay and monitoring
- In view of the importance of these topics and the many developments that are taking place, further joint meetings amongst ESARDA Groups are necessary.

References

/1/ S. GUARDINI AND B. RICHTER - "Report on the Joint Meeting of the ESARDA Working Groups on Non Destructive Analysis (NDA) and Containment and Surveillance (C/S)" ESARDA Bulletin No. 24, October 1994

/2/ M.T. SWINHOE - "EURATOM Experience with Integrated Unattended Systems". ESARDA Bulletin No. 24, October 1994.

/3/ D. VAN DER EECKEN et al. - "An unattended measurement system for Safeguarding Fresh LEU Fuel Assemblies at the output of a Fabrication Plant". 17th Annual ESARDA Symposium, Aachen, Germany, May 1995.

/4/ Proceedings of the 14th Annual ESARDA Internal Meeting (Restricted Participation), Salamanca, Spain, May 1992.

SYCLOP[1] (SYstem of Control of Locations and Objects by Parabola) Heat Flow Sensor Parabola Used for Surveillance in Safeguards

P. Guilmain[2], C. Korn, M. Cuypers
EC, JRC, Ispra, Italy
P. Thery
University of Lille, France

Abstract

Today, many pyroelectric and semiconductor based sensors are used for the measurement of thermal radiations emitted by the human body in order to detect its presence by measuring its temperature. Movement detectors are also used for the same purpose.

Based on heat flow technology, a new parabola detector has been developed in the LaSCo laboratory at JRC Ispra for the surveillance of a simulated nuclear material area. This detector could also be used for individual surveillance of small Pu containers.

The technical innovation consists in detection based on thermal balance variations, instead of infrared analysis.

This new detector will be described and two applications will also be presented:

- one for the detection of human intrusion in protected areas
- the second for surveillance of individual Pu containers (i.e. protection against theft)

1. Introduction

To keep a continuous check on a previously defined quantity of material, different techniques are presently used: seal systems, optical surveillance, monitoring with cameras or classic sensors.

This article presents a scientifical innovation in the field of safeguards: the use of the heat flow technology for surveillance /1, 2/. It is a new low-cost approach which could complement or replace other monitoring techniques.

All traditional surveillance systems make use of semiconductor or pyroelectric sensors measuring the quantity of the incident infrared radition emitted by a source. In most detection applications these sensors are used to measure the radiation from heat sources in motion. Their principle is not particularly suitable for the surveillance of a defined zone (i.e. a corridor or a room) around which people are free to move and work, even in the unmonitored space.

The following table 1 shows the types and the characteristics of the infrared sensors presently available on the market /3/.

Passive surveillance systems are proposed here, which concentrate thermal radiation from the environment by means of a parabolic detector. Every modification of the thermal equilibrium in the monitored zone can be detected by means of a heat flow sensor. This device makes use neither of lenses nor of protective devices against convection. The spectral density of the radiation absorbed or emitted by the sensor is not disturbed.

2. Detection of Human Intrusion in Protected Zones

The aim of this system is the remote surveillance of locations or objects. Every object with a temperature over 0 °K emits infrared radiation, that is electromagnetic waves, the wavelength of which goes from 0.75 µm to 1000 µm, between visible light and microwaves.

Infrared radiation belongs to the physical field of thermodynamics. The heat flow sensor, usually measuring energy tranfer in steady conditions, is used here in transient conditions. Giving real information on the energy gap between a system and its environment, it can sense variations in the thermal charge (heat losses). As every variation in temperature is caused by gains or losses of energy, the EMF generated by a heat flow sensor makes it possible to determine the temperature variations in the system to which it is applied. The heat flow sensor allows to regulate the time constant according to the thermal process to be monitored, as it allows to sense the variations due to changes in the thermal charge of the process to be regulated.

The use of this detection system is a particularly important application of the heat flow sensor in transient condition.

The EMF generated by a heat flow sensor fixed to a wall represents the radiant and convective exchanges with the surrounding environment. The separation of these exchanges is interesting because the convective component depends on the radiant temperature of the wall to which the sensor is applied.

Table 1: Infrared sensors presently available on the market

Types of Detectors			Detectors	Spectral Response (μm)	Operating Temperature (T)	D* (cm.Hz½/W)
Thermal type	Thermocouple,Thermopile,Heat Flow			No wavelength dependence	300	$D^*(\lambda,10,1)=6*10^8$
	Bolometer				300	$D^*(\lambda,10,1)=1*10^8$
	Pneumatic cell		Golay cell, Capacitor microphone		300	$D^*(\lambda,10,1)=1*10^9$
	Pyroelectric detector		TGS, $LiTaO_3$		300	$D^*(\lambda,10,1)=2*10^8$
Quantum type	Intrinsic type	Photoconductive type	PbS	1 to 3.6	300	$D^*(500,600,1)=1\times10^9$
			PbS	1.5 to 5.8	300	$D^*(500,600,1)=1\times10^8$
			HgCdTe	2 to 16	77	$D^*(500,600,1)=2\times10^{10}$
		Photovoltaic type	Ge	0.8 to 1.8	300	$D^*(\lambda p,1000,1)=1\times10^{11}$
			InGaAs	0.7 to 1.7	300	$D^*(\lambda p)=5\times10^{12}$
			InAs	1 to 3.1	77	$D^*(500,1200,1)=1\times10^{10}$
			InSb	1 to 5.5	77	$D^*(500,1200,1)=2\times10^{10}$
			HgCdTe	2 to 16	77	$D^*(500,1000,1)=1\times10^{11}$
	Extrinsic type		Ge:Au	1 to 10	77	$D^*(500,900,1)=1\times10^{11}$
			Ge:Hg	2 to 14	4.2	$D^*(500,900,1)=8\times10^9$
			Ge:Cu	2 to 30	4.2	$D^*(500,900,1)=5\times10^9$
			Ge:Zn	2 to 40	4.2	$D^*(500,900,1)=5\times10^9$
			Si:Ga	1 to 17	4.2	$D^*(500,900,1)=5\times10^9$
			Si:As	1 to 23	4.2	$D^*(500,900,1)=5\times10^9$

[1] Patent No. LU-2488 "Dispositif de détection de rayonnement thermique et appareil de détection de présence à base d'un tel dispositif".
[2] Research fellow at the EC, JRC, Ispra, Italy

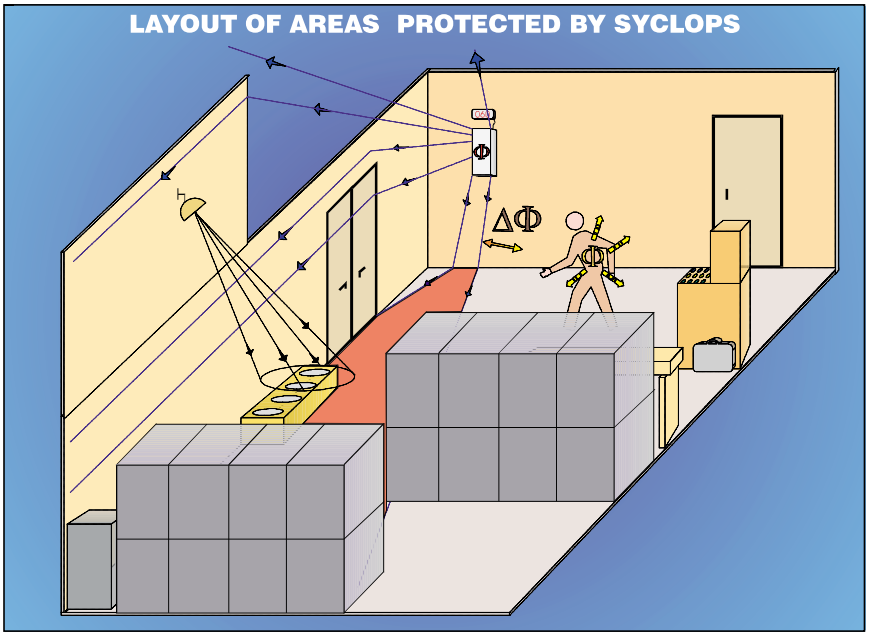

Figure 1: Layout of surveilled areas

The EMF is positive whenever the wall absorbs thermal radiation and negative when it emits. The great advantage consists in having a calibration coefficient which is independent of the sensor temperature. The detected EMF is zero only when the sensor temperature is the same as the radiant temperature of the wall.

Furthermore, in the case of human intrusion in the surveilled area radiative exchanges are so important that the sensor's structure has been modified to obtain an EMF proportional only to radiant exchanges.

The idea consists of detecting any modification of the thermal equilibrium in a well defined volume caused by human intrusion in a monitored zone, by means of a sensor and a thermal concentrator, and not only of detecting the infrared radiations emitted by a human body at a short range (lm).

The surveillance of some areas in LaSCo (Laboratory of Surveillance and Containment) with a system which can be adjusted according to the volume (i.e. according to the distance and the observation angle) is at the basis of the surveillance system proposed and used at the JRC Ispra.

3. Features of the Heat Flow Sensor

The heat flow sensor which was specifically built for this purpose is fundamental to the remote monitoring system. It is very thin (0.2 mm) and produces a tension showing only the radiant exchanges between itself and the environment. This EMF is proportional to the total (or radiant) energy absorbed or emitted by the active surface of the sensor whatever its temperature. Its use is very simple as the differential structure of the sensor does not require any compensation wires.

<u>The characteristics of this type of thermal sensor, which uses the heat produced by infrared radiation are:</u>

- response independent of the wavelength
- no need for a cooling system
- use at room temperature.

<u>Advantages of the association of a thermal sensor with a parabolic reflector:</u>

- flexibility in adapting to the field of view by means of a voltage regulator
- no optical lens needed to focus incident thermal radiation, therefore no optical filter effect, no transmission coefficient, no glass capacitive effect
- no packaging problems, type T0-5
- no cooling problems
- low fabrication costs (on a large scale)
- the sensitivity is practically the same as other sensors on the market
- very low thermal resistance (< 1000 Ω), hence low noise, possible amplification, long surveillance range

Advantages in comparison with other surveillance systems:

- SYCLOP has an additional interest if compared with other infrared or ultrasonic surveillance systems based uniquely on movement
- SYCLOP detects the movements of a source of thermal radiation in a monitored zone and also gives information on the evolution of the control signal during the time of modification of the thermal equilibrium in a well defined volume. The modifications are translated by the sensor, which generates a real tension variation directly proportional to the quantities of energy exchanged between the environment and the sensor itself. In this way, SYCLOP detects the intruder, his presence and his position according to the distance and the angle in the monitored zone
- The various simulated attempts to violate this surveillance system were not successful. The sensor generates an EMF proportional only to exchanges by irradiation: a thermal balance is established between the sensor's temperature and the one detected by the parabolic detector. The stability of this detected EMF is strictly bound to the stability of the exchanges.

Since it is almost impossible to know the temperature of every point of the surface entered by the intruder and since the intruder's temperature must be the same as the average temperature of the surface he enters for the thermal balance to be stable, it is very difficult to deceive this system.

4. Surveillance of Single Pu Containers

A second application of this 'parabolic reflector heat flow sensor' surveillance system is as a new way of monitoring Pu storage (individual containers).

Using the same technology as in the first application, we can remotely monitor a defined zone of a room with the possibility to move and work in other parts of it. In fact, this technology is very precise and can be used to monitor not only large but also small areas (i.e. corridors and entire rooms). For this reason the thermal concentrator is selected to monitor reduced areas where a single simulated Pu container is placed.

An experimental study has confirmed all forecasts from classical modelling of parabolic mirrors. In practice, a sensor's 30 mV/W sensitivity makes it possible to monitor a container at a distance of five meters without interferences from the environment (such a distance can be increased to 12 m or more with certain configurations) (figure 2).

To characterise the system's performance we need data to model a Pu container. A stainless steel container, regulated in temperature (from 40 °C to 60 °C) has been used to characterise the sensitivity and the reliability of the system.

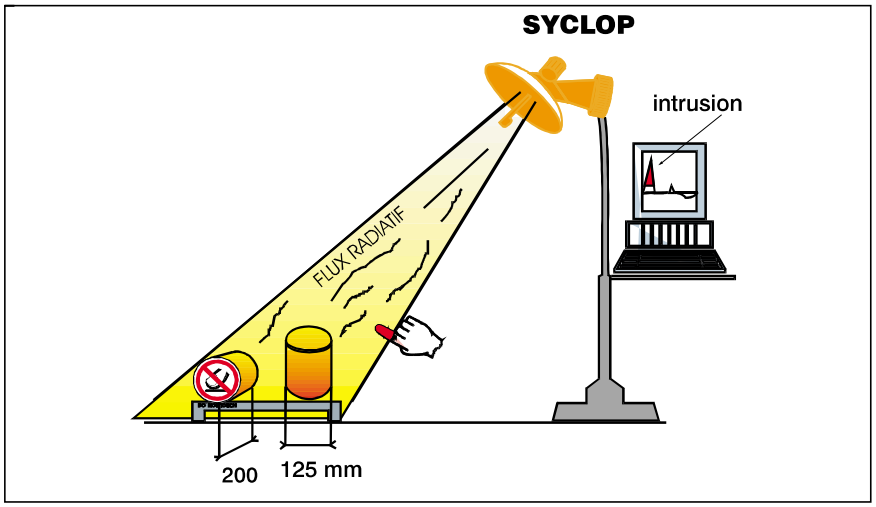

Figure 2: Containers surveillance with SYCLOP

5. Detection surveys

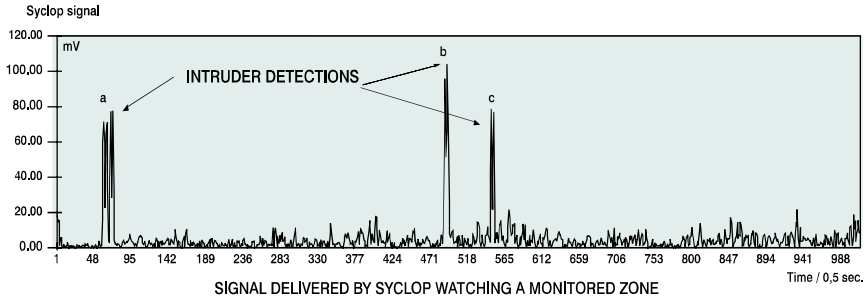

Figure 3: The trace at the left shows the stability of the signal emitted by SYCLOP watching a monitored zone. When an intruder enters the zone, the thermal balance changes causing a sudden signal variation (points a, b and c). This sets off an alarm when a threshold level is exceeded.

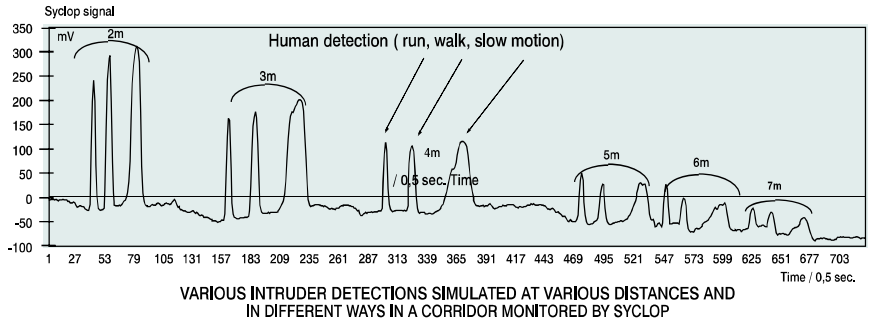

Figure 4: This graphic shows various intruder detections in a corridor monitored by SYCLOP. Intrusions were simulated at different distances and in different ways.

6. Conclusions

There is a technological breakthrough in a scientific or economic field when the consequences of a scientific innovation are unforseen and unexpected.

As the control of a relevant number of physical quantities can be related to a temperature measure, every innovation in the field of thermal sensors can bring up the analysis and control methods in several applications for discussion again.

This cannot be seen yet as a technological breakthrough since it is impossible to foresee whether and which application fields will be deeply modified by this scientific innovation.

The two systems proposed represent new applications in the field of surveillance. The association of a new thermal sensor to a parabolic reflector implies specific advantages for a passive surveillance system. It is important to underline that this system is not based on infrared analysis, but on the modification of the thermal equilibrium in the surveilled zone.

7. References

/1/ "Fluxmétrie Thermique: son application aux mesures de faibles puissances dégagées et au Confinement Surveillance du Plutonium" C. SANSON, J. MONIER (CEA, CEN Fontenay-aux-roses) P. BOURRELLY, H. PATIN, R. SCHOEPP (Laboratoire de Chimie Physique Générale, Faculté des Sciences et Techniques de Marseille Saint Jerome) ESARDA84.

/2/ "Contrôle non destructif quantitatif de Plutonium et de Tritium même en petites quantités par Fluxmétrie Thermique" ESARDA87 P. BOURELLY, M. PATIN, R. SCHOEPP (Faculté de Marseille-Saint Jerome), J. MONIER (CEA Fontenay-aux-Roses), C. SANSON (CEA-Cadarache).

/3/ Characteristics and Use of Infrared Detectors. Technical information Hamatsu SD-12/Jul. 93.

Determination of Uranium and Plutonium in Simulant Mixture Samples by ^{252}Cf Shuffler

Qiao Shengzhong
China Institute of Atomic Energy, Beijing, PRC
P.M. Rinard, E.L Adams and R.H. Augustson
Los Alamos National Laboratory, Los Alamos, NM, USA

Abstract

A method was developed for the determination of uranium and plutonium in simulant mixture samples by high density waste ^{252}Cf shuffler. The instrument calibration using ^{235}U, ^{239}Pu and ^{240}Pu by both the active and passive assay mode was described. The contents of the ^{235}U and ^{239}Pu in mixture samples were determined based on the calibration curve and then obtained based on the isotopic compositions of uranium and plutonium. Some other results of conditional experiments for the shuffler system were also given in the paper.

Introduction

It is very important to determine the uranium and plutonium content in nuclear fuel cycle for safeguards. The measurement field is quite wide, covering spent fuel elements, high level wastes, waste cladding hulls, sludges and so on. However, this kind of measurement is quite difficult by alpha ray spectrometry, gamma ray spectrometry or mass spectrometry because the samples contain a lot of fission products and salts and feature a very complex system. Many nondestructive assay (NDA) techniques use neutron interrogation methods because of the high penetrability of neutron irradiation and the selective sensitivity of nuclear material to neutron induced fission reactions. ^{252}Cf has proven to be one of the more useful sources because of its convenient half-life, high neutron yield, and low γ ray output per source neutron. The ^{252}Cf shuffler is able to solve some complex and difficult measurement problems. It can be used to measure the content of nuclear material in different kinds of fuels and different size of containers. Therefore, the shufflers are applied to some important measurements and specific cases. Usually, there are two kinds of shufflers: liquid sample shuffler /1-3/ and solid sample shuffler /4-8/.

The feature of the liquid sample shuffler leads to its enhanced sensitivity over other ^{252}Cf assay systems is that the neutron source is transferred to the center of the solution tank through a source insertion port. From centralized location, nearly every neutron emitted has a chance to induce a fission. The fission process is further enhanced because the hydrogenous nature of the solutions and polyethylene increases the thermal neutron component during irradiation. This instrument is used for measuring low levels of fission product contaminated fissile solutions. The detection limit of this technique is better than 1 mg/l of ^{235}U in 100s with a 4 standard-deviations confidence; irradiation doses as high as 50 R/h/l may accompany the uranium. This instrument has been built to monitor the uranium concentration in a liquid waste stream to avoid a criticality accident in a downstream holding tank.

The solid sample shuffler can be used to assay uranium in fresh fuel elements, uranium and plutonium in spent fuel, or uranium and plutonium in high level wastes. Using thermal neutron interrogation, the shuffler assay system (0.5mg ^{252}Cf) can measure an high temperature gas-cooled reactor fuel rod containing 0.2 g ^{252}Cf to 0.5% precision (1 sigma) in 1 minute. The system can assay samples with fissile contents from a few milligrams up to several kilograms using thermal-neutron interrogation for the low mass samples and fast-neutron interrogation for the high mass samples.

For the spent fuel, hulls and sludges, the neutron emission is mainly due to spontaneous fission neutrons from curium. Minor contributions are due to spontaneous fission neutrons from the even numbered plutonium isotopes and from (α, n) neutrons due to the plutonium α activity.

The passive measurement is not only used for correcting the results of the active measurement, but also used independently to determine the fractional fuel content, by correlating the measured neutron emission rate with that of the spent fuel prior to dissolution, and it can also be used to determine the fractional fuel content by correlating the measured neutron emission rate with that of the hulls and sludges after dissolution. The ratio Cm/Pu in the spent fuel, or in the hulls and sludges, can be determined previously by some other methods. The ratio Cm/Pu for the hulls is a factor of 2.7 lower than in the undissolved fuel. This factor is independent from burnup.

Experiments for the high density waste ^{252}Cf shuffler have been done in this work on the following aspects:

A efficiency;
B irradiation positions;
C matrix effect;
D calibration;
E determination of the uranium and plutonium mixture samples.

System Description

The high density waste ^{252}Cf assay system consists of the source shield tank, the decoupling CH_2 shield and the irradiation tank (including the assay chamber of irradiation samples), the transfer device of ^{252}Cf neutron source, a high efficiency neutron counter and electronic instruments. The neutron counter consists of a CH_2 matrix filled with 66 3He tubes (1 m of active length, 4 atm. pressure). The polyethylene slabs (10 cm thick) with holes, contain 12 ^{3}He tubes and cover the top and bottom of the measurement cavity. 6 banks (7 ^{3}He tubes per bank) cover the surrounding of the measurement cavity. The counter, which is surrounded by 30 cm thick polyethylene, can accept samples up to the size of a 55-gallon drum. The inner surface of the irradiation cavity is lined with 0.8 mm thick cadmium to absorb the low energy neutrons before they reach the sample.

The interrogating source shield is a 1.3 m cube of polyethylene on top of the counter assembly. The source storage position is at the center of this cube to reduce possible personnel exposure. The source is attached to a teleflex cable and is shuffled in or out of the measurement cavity by a compumotor stepping motor system. The computer, the compumotor controller and the counter electronics are located in an electronics rack next to the counter. The operator controls the system from a computer terminal.

The cycling period of the shuffler is the sum of the irradiation time, the count time and the two transfer intervals. The transfer time of the ^{252}Cf source, the irradiation time of the sample, the count time of the delayed neutron, and the shuffled times during each sample irra-

diation can be chosen according to the experiment conditions. In this work, the transfer time of the ^{252}Cf source from the storage position to the irradiation position is 1.85s, the reverse time from the irradiation position to the storage position is 1s; the sample was irradiated 38 cycles, the total irradiation time is 418s; the delayed neutrons were counted 38 cycles, 7s per cycle; the sample was shuffled 4 times. The sample was allowed to cool for five minutes between runs to reduce the buildup of delayed neutrons to an insignificant level.

The size of the interrogation neutron source is 466 µg ^{252}Cf (neutron strength is 1.56×10^9 n/s, March 15, 1991). The dose rate from the source is approximately 1240 mREM/h at one meter if the source is unshielded. When the source is inside the shield above the assay chamber, the exterior dose level is below 0.1 mREM/h.

Experiments and Results

A. Efficiency

The efficiency of the measuring equipment is very important. The variation of efficiency in the count chamber of the shuffler system is quite concerned. A standard ^{252}Cf source was used for testing the counting efficiency and the efficiency variation of the shuffler system. The original strength (S_0) of the ^{252}Cf source is 1.02×10^5 n/s (January 1, 1983). The decay constant (λ) is $7.166 \times 10^{-4} d^{-1}$. The time interval (t) is 2999d (January 1, 1983 to March 21, 1991), The strength (S) of the ^{252}Cf source in the process of measurement was obtained through $S=S_0e^{-\lambda t}$. The efficiency of the six positions in the count chamber of the shuffler system were measured (with rotation or no rotation at the side, R=10 inch). The data of the measurement and the results of the calculation are listed in Table 1.

Experimental results show that the average efficiency of the shuffler count system is 17.5%; the largest efficiency variation is 7.5%; the average efficiency variation is less than 5%. Comparison between experiment and calculation also shows that the efficiency in the count chamber is basically uniform, except that it is a little poorer at the top position of the count chamber.

B. Irradiation Positions

As mentioned above, the efficiency of the shuffler count chamber is basically uniform, but the irradiation probability is quite different for different positions in the irradiation tank (the count chamber). So, the fission delayed neutrons produced by the interrogation neutron source are different for different irradiation positions. The irradiations of the 855 gU oxide powder (^{235}U, 1.94%) assay sample at different irradiation positions were performed inside the count chamber used to count the fission delayed neutrons. The fission delayed neutrons of twelve irradiation positions without rotation and six irradiation positions with rotation were measured. The experimental results listed in Table 2 show that the irradiation probability by the ^{252}Cf source is biggest for the case without rotation, and smallest by the shuffler's door. The largest variation of the count rate is 4.7 times. The irradiation probability of the sample at any position for the rotation case is uniform because the variation 4% except on the top side of the count chamber. Thus, it can be seen that the fission delayed neutrons should be measured for the rotation case.

C. Matrix Effect

In fuel fabrication factories and reprocessing plants as well as nuclear power plants, nuclear fuel and nuclear wastes are always accompanied with some matrix, for instance iron, polyethylene, graphite and so on. The count rates of the shuffler measurement system are different for different kinds of matrices. In this work, the count rates of the active and passive assay for 1 gPu (^{239}Pu, 86%), 5 gU (^{235}U, 94%) oxide powder in the capsule blanks and 1 gPu+5 gU were measured at the six positions in the 55-gallon barrel with iron (158 Kg) and polyethylene (10 Kg), respectively. The measured results are listed in Table 3, which shows that the effect of the count rate is not big for both the active and passive assay. The effect of the count rate is quite big for the active assay, but it is not significant for the passive assay of the polyethylene; the count rate of the top position of the count chamber for passive assay is less than those of other positions. Thus, calibration is needed for each kind of matrices.

D. Calibration

Usually, each equipment requires its own calibration curve in actual application. The high density waste shuffler was calibrated using uranium and plutonium standard samples in this work. Experimental results of the response of the uranium and plutonium count rates in shuffler are listed in Table 4 and are shown in Figure 1, 2, 3 and 4, respec-

Table 1: Experimental Results of Detection Efficiency

Sample	Position (inch)		Rotation	Passive				Efficiency	Normalized
	R	Z		T(1/s)	Sigma	R(1/s)	Sigma	(%)	to R=0, Z=10
Cf-252	0	10	No	2109.21	1.44		1.62	17.48	1.0046
	10	10	No	2157.73	3.05	339.27	1.01	17.89	1.0282
	10	10	Yes	2139.72	1.62	331.98	1.12	17.73	1.0190
	0	20	No	2099.77	2.08	318.27	1.62	17.40	1.0000
	10	20	No	2173.96	1.13	343.96	1.33	18.02	1.0356
	10	20	Yes	2160.72	1.30	339.52	0.82	17.91	1.0293
	0	31	No	2004.12	1.83	291.95	1.07	16.59	0.9534
	10	31	No	2077.75	1.46	313.24	0.95	17.21	0.9891
	10	31	Yes	2068.65	1.88	310.41	1.22	17.14	0.9851
Background				30.63	0.21	2.83	0.14		

Table 2: Experimental Results of Effects of Irradiation and Efficiency*

Position (inch)			No Rotation		Rotation		Normalized to 0, 22.5	
	R	Z	T(1/s)	Sigma	T(1/s)	Sigma	No Rotation	Rotation
Center	0	12.5	111.20	0.90	106.50	0.88	0.9797	0.9707
	0	22.5	113.50	0.91	109.71	0.89	1.0000	1.0000
	0	33.5	115.04	0.91	116.00	0.90	1.0136	1.0573
Side	10	12.5 by Cf Source	253.54	1.20			2.2338	
	10	12.5 by Door	70.17	0.79	118.56	0.91	0.6182	1.0807
	10	12.5 by Right Side	99.40	0.87			0.8758	
	10	22.5 by Cf Source	249.71	1.19			2.2001	
	10	22.5 by Door	79.61	0.82	115.03	0.90	0.7014	1.0485
	10	22.5 by Right Side	106.31	0.89			0.9367	
	10	33.5 by Cf Source	307.53	1.30			2.7095	
	10	33.5 by Door	65.07	0.79	135.16	0.95	0.5733	1.2320
	10	33.5 by Right Side	93.68	0.86			0.8254	

* Irradiation sample is 855gU oxide powder in the metal can (U-235, 1.94%).

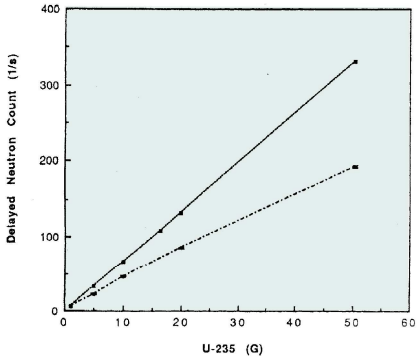

Figure 1: Delayed Neutron Counts vs U-235

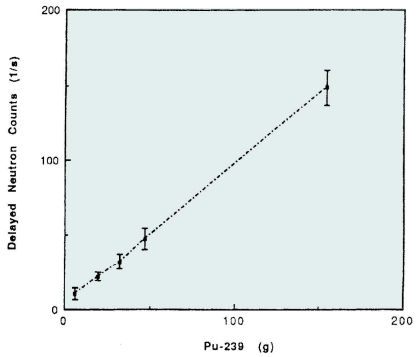

Figure 2: Delayed Neutron Counts vs Pu-239

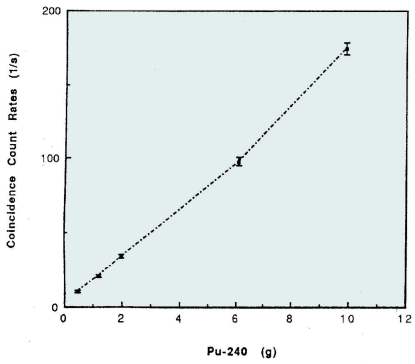

Figure 3: Coincidence Count Rates vs Pu-240

Table 3: Experimenlal Results of Effects of the Matrix

Sample*	Position(inch)		Iron**				Polyethylene**				No Matrix					
			Active***		Passive		Active***		Passive		Active***		Passive			
	R	Z	T(1/s)	Sigma	T(1/s)	Sigma	T(1/s)	Sigma	T(1/s)	Sigma	T(1/s)	Sigma	T(1/s)	Sigma	R(1/s)	Sigma
Pu	0	12.5	0.94	3.77	1366.04	2.48			1307.54	1.62	9.60	4.11	1628.67	1.09	9.50	0.68
	0	22.5	2.69	3.76	1361.71	1.87			1282.79	1.38	10.30	4.10	1625.70	1.30	9.98	0.78
	0	33.5	7.25	3.56	1221.31	1.43			1194.53	2.39	14.67	4.57	1553.70	1.53	9.19	0.79
	10	12.25	9.52	3.82	1405.45	1.81			1329.70	1.49	13.50	4.15	1666.70	1.23	8.95	0.36
	10	22.5	4.72	3.82	1401.26	1.53			1318.21	1.62	4.35	4.19	1685.40	0.78	9.64	0.80
	10	33.5	-6.11	3.63	1264.42	1.45	2.45	3.55	1214.13	1.25	10.65	4.05	1592.95	1.03	8.48	0.69
U	0	10	11.13	0.61	31.76	0.24	108.35	3.76			107.40	0.89	31.18	0.31	2.17	0.10
	0	20	10.07	0.61			91.76	3.71			113.26	0.89	30.18	0.18	2.21	0.10
	0	31	12.08	0.61			56.68	3.56			117.82	0.91	31.16	0.30	2.22	0.11
	10	10	10.23	0.61	30.10	0.36	48.89	3.77			118.26	0.92	30.96	0.23	2.01	0.13
	10	20	11.89	0.60			45.69	3.75			120.33	0.92	30.98	0.31	2.32	0.08
	10	31	10.16	0.61			27.78	3.57			146.21	0.98	30.63	0.21	2.38	0.14
Pu + U	0	12.5	9.46	3.78	1363.36	0.35	97.71	0.84	1311.00	1.48	125.30	4.18	1645.74	1.21	10.21	0.59
	0	22.5	13.10	3.76	1355.99	0.68	89.08	0.83	1286.85	0.90	123.24	4.17	1632.15	0.77	11.62	0.87
	0	33.5	19.57	3.57	1218.89	1.43	51.48	0.72	1195.81	2.16	127.31	4.06	1537.33	1.60	8.50	0.72
	10	12.5	12.68	3.83	1409.63	1.35	37.66	0.67	1349.41	2.20	130.02	4.22	1664.55	1.67	10.87	0.78
	10	22.5	14.61	3.85	1416.39	1.39	40.71	9.68	1329.98	1.49	124.15	4.25	1696.43	1.78	10.98	0.56
	10	33.5	10.78	3.63	1258.48	1.45	27.24	0.63	1210.50	1.36	152.21	4.14	1597.88	1.77	9.70	0.74

* 1 gPu, 5 gU capsule blank samples tor matrix of iron and polyethylene; 6.7 gPu oxide powder, 855 gU oxide powder samples in the metal cans for no matrix.

** Iron 158 Kg polyethylene 10 Kg.

*** Irradiation: 38 cycles; total irradiation time: 415s; total count time: 266s.

Table 4: Experimental Results of the Count Rate Response in the Shuffler's Count Chamber for Uranium and Plutonium

Material* U	Active**		Passive**				U-235 (g)	T/gU-235	Pu-239 (g)	T/gPu-239	Pu-240 (g)	R/gPu-240
	T(1/s)	Sigma	T(1/s)	Sigma	R(1/s)	Sigma						
Background	1.19	1.16	29.14	0.18	1.91	0.08						
100 g DU	9.10	1.17	29.69	0.62	1.66	0.17						
10 g Graphite U	6.79	1.14	28.48	0.22	1.75	0.06	1.006	6.7495				
50 g Graphite U	23.08	1.23	29.05	0.19	1.97	0.08	5.030	4.5885				
100 g Graphite U	46.78	1.25	29.19	0.21	2.39	0.07	10.060	4.6501				
200 g Graphite U	85.95	1.32	28.85	0.12	1.81	0.09	20.120	4.2719				
500 g Graphite U	192.63	1.50	29.52	0.19	1.91	0.07	50.300	3.8296				
841 g Powder U	103.46	0.85					16.315	6.3412				
855 g Powder U	113.26	0.89					16.587	6.8282				
990 g Powder U	281.64	1.25					116.523	2.4170				
6.7 g Powder Pu	10.30	4.10	1025.70	1.30	9.98	0.78			6.2173	1.6567	0.4555	17.7363
21 g Powder Pu	21.76	2.79	736.15	1.60	20.76	0.60			19.7539	1.1016	1.2153	15.5106
34 g Powder Pu	32.19	5.09	2476.75	2.34	34.40	1.15			31.8906	1.0094	2.0271	16.0278
53 g Powder Pu	48.12	7.11	4815.77	2.25	98.27	3.04			46.3755	1.0376	6.1189	15.7479
265 g Powder Pu	148.89	11.44	12442.28	7.56	174.23	4.05			248.4296	0.5993	15.9477	10.8053

* Graphite U samples in the plastic bottles, no matrix, R=0 inch, Z=20 inch.

** Irradiation: 38 cycles; total irradiation time: 415s; total count time: 266s.

Table 5: Measurement Results of the Mixture Samples for Uranium and Plutonium

	Sample	Position (inch)		Active		Passive			
		R	Z	T(1/s)	Sigma	T(1/s)	Sigma	R(1/s)	Sigma
Measurement results	1	0	20	123.24	4.17	1632.15	0.77	11.62	0.87
	2	0	20	138.30	4.96	2445.54	0.85	33.04	1.73
	Background			0.14	0.55	29.14	0.18	1.91	0.08

	Sample*	Pu-240 (g)	Total Pu (g)	Pu-239 (g)	Pu-239 Tact(1/s)	U-235 Tact(1/s)	U-235 (g)	Total U (g)
Calculation results	1	0.5480	8.06	7.48	12.39	110.85	16.8292	867.48
	2	1.9422	32.58	30.56	30.85	107.45	16.3130	840.88

	Sample	Uranium			Plutonium			
		Mesurement value	Standard value	Deviation (%)**	Measurement value	Standard value	Deviation (%)**	
Comparison with standard value	1	867.48	855	1.46	8.06	6.70	20.30	
	2	840.88	841	0.01	32.58	34.00	4.18	

* The U-235 enrichment is 1.94%; plutonium isotopic composition are 92.796% (Pu-239), 6.798% (Pu-240) for sample 1; 93.796% (Pu-239), 5.962% (Pu-240) for sample 2.

** Taking that the standard value is unity.

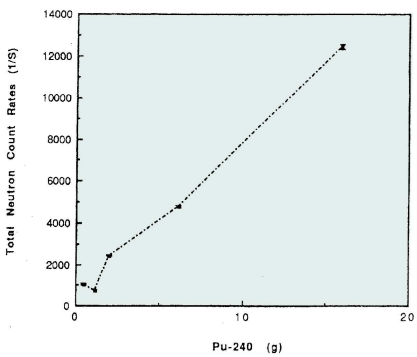

Figure 4: Total Neutron Count Rates vs Pu-240

tively. The uranium graphite samples in a plastic bottle and the plutonium oxide powder samples in a metal can were used for experiments. In order to obtain the curve of the uranium oxide powder samples, two uranium oxide powder samples in the metal can were measured. A normalized curve to these measurement points was obtained (Figure 1).

The delayed neutron count rates of the active assay were directly obtained from the content of the uranium and plutonium samples over a large of loading and sample sizes. When using thermal neutron interrogation, the system has a sensitivity limit of about 6 gram ^{235}U and 3 gram ^{239}Pu for production reactor mixture fuel, or 6 gram ^{235}U and 1 gram ^{239}Pu for nuclear power reactor mixture fuel. If plutonium of the same isotopic composition is used for calibration and measurement, the measuring sensitivity of the plutonium can increase very much, because the effects from (α, n) neutrons are negligible. The uncertainty is variation with different content of the measuring uranium and plutonium. The deviation with the standard values are 1.5% (Uranium) and 20.3% (Plutonium) for a mixture sample (including 855 gU and 6.7 gPu), under the condition of 38 cycles of irradiation 415s of total irradiation time and 266s of total count time.

Acknowledgments

The authors wish to thank Jo Ann Painter for providing operating program of the computer. We are also indebted to Willie Atencio and M.N. Hykel for some fuel samples.

References

/1/ T.W. CRANE - “Liquid Sample shuffler”, Los Alamos National Laboratory report LA10291-MS (January 1985).

/2/ T.W. CRANE - “Liquid Sample shuffler for Gamma Active Solutions,” Los Alamos National Laboratory report LA-10925-MS (February 1987).

/3/ P.M. RINARD, T.W. CRANE, T. VAN LYSSEL, K.E. KRONCKE, C.M. SCHNEIDER, S.C. BOURRET - “A Delayed Neutron Monitor for a Liquid Waste Stream with High Gamma Ray Intensity,” Los Alamos National Laboratory report LA-UR-89-2017 (November 1989).

/4/ T.W. CRANE - “Test and Evaluation Results of the ^{252}Cf shuffler at the Savannah River Plant,” Los Alamos Scientific Laboratory LA-8755-MS (March 1981).

/5/ J.K. SPRINKLE, JR., H.O. MENLOVE, N. ENSSLIN, T.W. CRANE - “Measurement of Uranium Using a Californium shuffler,” Los Alamos National Laboratory report LA-UR-89-3740 (November 1989).

/6/ H.O. MENLOVE, T.W. CRANE - “A ^{252}Cf based Nondestructive Assay System for Fissile Material,” Nuclear Instruments and Methods 152 (1978) 549.

/7/ T.W. CRANE - “Detectability Limits Precision for Shuffler,” Los Alamos National Laboratory report LA-10158-MS (August 1984).

/8/ E.L. ADAMS, T.W. CRANE, N. ENSSLIN - “In-Line shuffler Error Analysis,” Los Alamos National Laboratory report LA-10969-MS (March 1987).

Thermal Ionisation Mass Spectrometry for Determination of Uranium and Plutonium: Ion Source Chemistry

S.K. Aggarwal, M.K. Saxena, P.M. Shah, Sanjai Kumar and H.C. Jain
Fuel Chemistry Division, Bhabha Atomic Research Centre, Bombay, India

Abstract

Differences in the ion source chemistry of uranium (U) and plutonium (Pu) were investigated for their simultaneous analyses by thermal ionisation mass spectrometry (TIMS). Using synthetic mixture of U and Pu, the intensities of U^+, UO^+, UO_2^+, Pu^+, PuO^+ ions and the ratios Pu^+/U^+, UO^+/U^+ were monitored. The overall evaporation and ionisation efficiency for production of U^+ vs Pu^+ defined as $(U^+/Pu^+)/(U/Pu)$ was observed to be dependent upon U/Pu of the sample loaded on the filament. UO^+ was found to have enhanced stability when U and Pu are present together on the filament. Different methodologies were investigated for circumventing the isobaric interference of ^{238}Pu at ^{238}U during simultaneous thermal ionisation mass spectrometric analysis of U and Pu. The methodology of optimising the evaporation filament heating current for simultaneous mass spectrometric analysis of U and Pu and using the $^{240}Pu/^{239}Pu$ atom ratio obtained from first 2-3 blocks to arrive at $^{238}Pu/^{239}Pu$ atom ratio required in the on-line interfering element correction (IEC) approach was found to be applicable to all types of samples. The correction factors for fractionation i.e. K-factors (=certified ratio/observed ratio) for U and Pu were found to be lower during their simultaneous analyses compared with their separate analyses.

Introduction

There is a growing need to determine uranium (U) and plutonium (Pu) with the highest possible accuracy in different nuclear fuel materials, particularly in the dissolver solution of irradiated fuel. Thermal Ionisation Mass Spectrometry (TIMS) holds the potential to meet this requirement owing to its high sensitivity and the inherent advantages of isotope dilution technique /1-6/. The advent of fully automated magnetic sector TIMS instruments coupled with multicollector Faraday Cup Detector System has significantly enhanced the internal (within-run) precision (0.01% or better) on isotope ratio measurements. These automated mass spectrometers have also relieved the mass spectrometrists from the manual, time-consuming, laborious, error-prone and repetitive procedure of scanning the different peaks followed by the measurement of their peak heights for arriving at the isotope ratio data.

The introduction of multicollector Faraday Cup Detectors System in commercially available thermal ionization mass spectrometers (TIMS) has also made it possible to carry out oligo-element analysis from the same filament loading /7-9/. This is in particular attractive for actinide elements like U, Pu, Am and Cm in the nuclear technology as they lie in the close-by mass range and have similar evaporation and ionization characteristics. Conventionally, these elements are separated and purified from one another by suitable ion exchange or solvent extraction procedures prior to their independent mass spectrometric analyses on separate filament loadings. The sequential/simultaneous mass spectrometric analysis of two or more elements from the same filament loading is attractive due to the advantages of reduced analysis time and cost-effectiveness. This can also provide an opportunity to understand the differences in the ion source chemistry i.e. evaporation and ionization characteristics of a particular group of elements (e.g. actinides, lanthanides) under identical conditions of sample loading, degassing, heating and time of data-acquisition during mass spectrometric analysis. A number of other advantages provided by the multi-collector detector system include the possibility of obtaining analysis from small amounts of elements (ng size), acquiring data simultaneously on a number of isotopes of the same element or of different elements with the nearby mass range, reducing the data acquisition and processing time, improving within-run precision by eliminating time-dependent fluctuations in the ion current of different mass numbers, and performing total sample evaporation and ion integration. These features, along with the microprocessor controlled sample loading unit, computer controlled heating of the filaments, focusing of the ion beam etc., have made the TIMS technique a kind of "Black-Box" or "Magic-Box". Some of the mass spectrometrists may feel that with the present generation TIMS instruments capable of giving high internal precision, it is easy to derive accuracies approaching 0.03% (the accuracy of best available SRM's for U and Pu) on a routine basis. However, the inadequate knowledge of the ion source chemistry has been responsible for degrading the accuracy of data (0.1 to 1%) on isotopic composition and concentration.

The present study was undertaken with the main objective of evaluating differences in the ion source chemistry of U and Pu when the two elements are present together on the filament. The different parameters studied were: (i) differences in the ion yields of U^+ and Pu^+ under conditions of their simultaneous mass spectrometric analyses, (ii) comparison of the yields of UO^+ and PuO^+, (iii) optimising conditions for simultaneous mass spectrometric analysis of U and Pu, (iv) investigating different methodologies to determine $^{238}Pu/^{239}Pu$ atom ratio of Pu in the unknown sample with a view to making the interfering element correction (IEC) approach universally applicable to account for the isobaric interference of ^{238}Pu at ^{238}U, (v) differences, if any, in the K-factors of U and Pu during their simultaneous mass spectrometric analysis when compared to their independent analyses.

Experimental

Materials

Isotopic reference materials SRM-200-U (containing about 20 atom% ^{235}U) and SRM-947-Pu (about 75 atom% of ^{239}Pu) available from National Institute of Standards and Technology (NIST, USA) were used. Dowex 1X8 resin (200-400 mesh) was obtained from Dow Chemical Company, USA and was used for separation and purification of Pu from U and ^{241}Am.

Instrument

A Finnigan MAT-261 TIMS instrument updated with a multi-collector Faraday cup detector system was used. The instrument has an extended geometry with stigmatic focusing. 9 variable Faraday cup detectors, designated as FAR 2 to FAR 10, with each of them coupled to a 10^{11} ohms resistor, are provided for static multicollection mode. A secondary electron multiplier (SEM) is also available for ion detection and measurement. An ion acceleration voltage of 10 KV was used in the present

work. The mass resolution of the instrument (M/M) at 10% valley was about 500 and the abundance sensitivity measured at mass 237/238 was 1ppm. The mass spectrometer was initially coupled to an online HP-9000/300 series computer, which has recently been replaced with an IBM compatible PC-AT computer through the use of HT-basic software.

Procedure

SRM-947-Pu is a plutonium sulphate tetrahydrate which contains small traces of U and Am. This Pu solution was, therefore, purified from ^{241}Am and U by anion exchange procedure using Dowex 1X8 resin, 200-400 mesh, in the nitrate form. The concentrations of U and Pu in the master solutions of SRM-200-U and SRM-947-Pu (purified) were determined by ID-TIMS using ^{233}U and ^{242}Pu spikes, respectively. Synthetic mixtures of U/Pu were prepared by mixing accurately weighed amounts of the two solutions to obtain U/Pu ratio of about 3, 10, 30 and 300. Replicate mass spectrometric analyses were performed from the mixtures using a double rhenium filament assembly.

One µl of the solution containing Pu and U was used for mass spectrometric analysis. U and Pu were loaded as nitrate solutions (1M HNO_3) onto the evaporation filament of a double high purity rhenium filament assembly. After evaporating the solution to dryness, the filament was first heated in air at 2.2 A and then taken for a few seconds to red hot prior to fixing in the turrette. This procedure invariably leads to the formation of oxides of U and Pu on the filament and is conventionally used in our laboratory. During mass spectrometric analysis, the temperatures of the ionisation and evaporation filaments were optimised and reproduced in different mass spectrometric analyses by monitoring ^{187}Re$^+$ and ^{238}U$^+$/^{239}Pu$^+$ ions, respectively. During the analysis of the mixture with U/Pu as 10, the ionisation and evaporation filaments were heated manually to monitor the abundances of U$^+$, UO$^+$, UO$_2^+$, Pu$^+$ and PuO$^+$ ions at various evaporation filament currents. The heating currents of the ionisation and evaporation filaments during replicate analyses ranged from 5.8 to 6.2 A and 2.0 to 2.6 A, respectively. Data collection and reduction were performed using the COL. 5 and RED 1.5 programs available in the MAT-261 software. The data collection was performed using static mode of multi-collection. The background was measured at mass 230.5 for 32 sec. and the various peaks monitored with their cup numbers were ^{235}U$^+$ (FAR9), ^{238}U$^+$ (FAR7), ^{239}Pu$^+$ (FAR6), ^{240}Pu$^+$ (FAR5), ^{241}Pu (FAR4), ^{242}Pu$^+$ (FAR3) with integration time of 8 seconds.

Results and Discussion

Figure 1 shows a typical dependence of U$^+$, UO$^+$ and Pu$^+$ ion intensities, in a surrogate sample with U/Pu ratio of 10, monitored at m/z values of 238, 254 and 239, respectively, as a function of the evaporation filament current and maintaining a constant ionisation filament current (about 6 A).

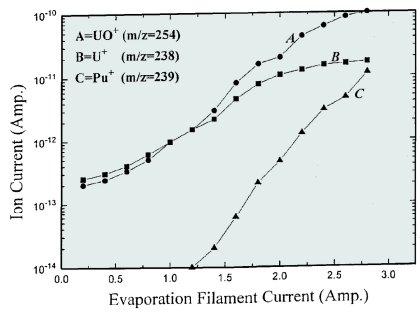

Figure 1: Variation in UO$^+$, U$^+$ and Pu$^+$ ion current as a function of evaporation filament heating current (ionisation filament heating current=6A, U/PU= 10)

As expected, the intensities of all the ions increase with increase in the evaporation filament current. There was no appreciable ion current of PuO$^+$ and UO$_2^+$ under the experimental conditions used and hence is not included in the Figure. It can be seen from figure that U$^+$ and UO$^+$ ions start appearing at lower temperature of the evaporation filament when compared to that for Pu$^+$ ions. At the ionisation filament current of 1.2 A, the intensities of U$^+$ and UO$^+$ are about two orders of magnitude more than that of Pu$^+$. This shows that under the conditions of simultaneous mass spectrometric analyses, U species have higher vapor pressure when compared to Pu species. It is difficult to make a definitive statement about the nature of the evaporating species present in the vapour phase because there may be interconversion of one form of species to the other. However, it can be conjectured that oxides of U are more stable compared to the oxides of Pu due to the absence of significant ion current of PuO$^+$. Further, it is noted that the intensity of UO$^+$ ion increases with increase in the evaporation filament current. This is in contrast to the general observation using a double filament assembly loaded with uranium solution alone that it is difficult to get a stable ion beam of UO$^+$ unless a special loading procedure (e.g. use of phosphoric acid) is employed or a constant supply of oxygen is available at the filament. Since the Pu oxides are known to be less stable in the vapor phase than the uranium oxides, the extra stability of UO$^+$ observed in the present work may be due to the oxygen provided by the dissociation of the Pu oxides coexisting on the evaporation filament. This indicates that UO$^+$ ion may be exploited for U determination by TIMS and this may also provide an approach for internal normalisation using ^{18}O/^{16}O ratio determined by monitoring UO$^+$ ions.

Table 1 gives the typical ratios of ^{235}U$^+$/^{239}Pu$^+$ and (^{238}U$^+$+^{238}Pu$^+$)/^{239}Pu$^+$ observed during replicate mass spectrometric analyses of mixture with U/Pu as 10. It is seen that there are significant differences in the values observed from one analysis to the next. This is expected in view of the exponential dependence of ion yield on the work function of the filament material, ionisation potential of the element and the temperature of the filament in the Saha-Langmuir Equation. Small physical and chemical differences from one filament loading to the next are responsible for these variations. Values ranging from 1 to 2 for (^{238}U$^+$+^{238}Pu$^+$)/ ^{239}Pu$^+$ compared to an inital U/Pu ratio of 10 in the sample loaded on the filament shows that under the conditions of simultaneous mass spectrometric analyses of U and Pu, Pu$^+$ yield is 5 to 10 times more compared to that of U$^+$. It may be mentioned that in view of the U/Pu ratio of 10 in the mixture used and the abundance of ^{238}Pu being only about 0.3 % of ^{239}Pu in SRM-947-Pu, it is clear that the contribution of ^{238}Pu$^+$ to the (^{238}U$^+$+ ^{238}Pu$^+$)/^{239}Pu$^+$ ratio is negligibly small compared to the variations observed during each mass spectrometric analysis (Table 1). Hence the ratio (^{238}U$^+$+ ^{238}Pu$^+$)/^{239}Pu$^+$ is referred to as ^{238}U$^+$/ ^{239}Pu$^+$ in the subsequent discussion for the sake of simplicity. This parameter would be useful to have an idea of U/Pu in the sample loaded on the filament for mass spectrometric analysis.

Table 1: Observed ^{235}U/^{239}Pu and (^{238}U+ ^{238}Pu)/^{239}Pu Atom Ratios From Replicate Mass Spectrometric Analyses of Synthetic Mixture

Sl. No.	MSA No.	^{239}U/^{239}Pu	(^{238}U/^{238}Pu)/^{239}Pu
1	6747	0.235 (19.9%)*	0.964 (19.9%)*
2	6782	0.288 (20.6%)	1.146 (20.5%)
3	6749	0.340 (5.8%)	1.353 (5.8%)
4	6746	0.354 (32.8%)	1.410 (32.7%)
5	6781	0.364 (12.6%)	1.449 (12.6%)
6	6780	0.379 (5.3%)	1.512 (5.3%)
7	6748	0.489 (18.7%)	1.945 (18.7%)

* Specifies the relative standard deviation (RSD) values obtained on the run summary from three blocks, each block consisting of twelve scans.

A graphical representation of ^{239}Pu$^+$/ ^{238}U$^+$ and UO$^+$/U$^+$ obtained as a function of evaporation filament current is shown in Figure 2 for the sample with U/Pu as 10. It is seen that ^{239}Pu$^+$/^{238}U$^+$ and UO$^+$/U$^+$ increase with increase in evaporation filament temperature.

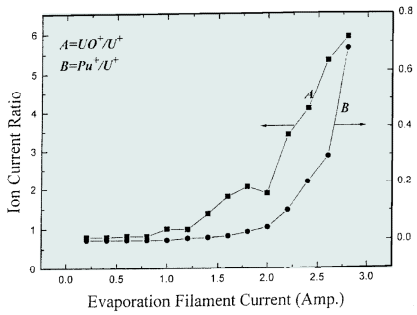

Figure 2: Dependence of UO^+/U^+ and Pu^+/U^+ ion current ratios as a function of evaporation filament heating current (U/Pu=10).

Figure 3 shows the $(U^+/Pu^+)/(U/Pu)$ ratios derived from a typical mass spectrometric analysis considering the atom% abundances of ^{238}U (80 atom%) and ^{239}Pu (75 atom%) and U/Pu ratio (10) present in the original solution taken for loading in the surrogate sample. It is clearly seen that at a constant evaporation filament current, the ratio $(U^+/Pu^+)/(U/Pu)$ is fairly constant. However, the $(U^+/Pu^+)/(U/Pu)$ ratio decreases by two orders of magnitude (from 2 to 0.02) when the evaporation filament current is increased from 1A to 2.8A.

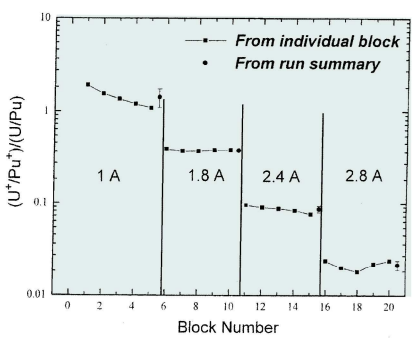

Figure 3: Variation in $(U^+/Pu^+)/(U/Pu)$ ratio as a function of time (i.e. block number) and evaporation filament heating current (ionisation filament heating current = 6.2 A); the duration of each block was 2 min and 30 sec.

It was of interest to observe experimentally the variation of $(U^+/Pu^+)/(U/Pu)$ ratio in the different surrogate samples with varying U/Pu ratios. Figure 4 presents the $(U^+/Pu^+)/(U/Pu)$ ratio as a function of the evaporation filament heating current in different samples. As expected, the $(U^+/Pu^+)/(U/Pu)$ ratio decreases with increasing evaporation filament current in each of the samples. Further, the change in the $(U^+/Pu^+)/(U/Pu)$ ratio appears to depend upon the U/Pu ratio of the sample loaded on the filament; $(U^+/Pu^+)/(U/Pu)$ ratio decreasing more rapidly in samples with low U/Pu ratio. However, considering the fact that the process of thermal ionization is governed by Saha-Langmuir equation consisting of exponential of various parameters (ionization potential, work function and heating temperature of the filament etc.), it may be stated that differences in the overall evaporation and ionization efficiency are not remarkable in different samples with varying U/Pu ratios. Further work would be needed to make any definitive conclusions on this aspect. Detailed investigations would also be very useful for developing a methodology for the mass spectrometric determination of ^{238}Pu in Pu samples containing traces of ubiquitous uranium.

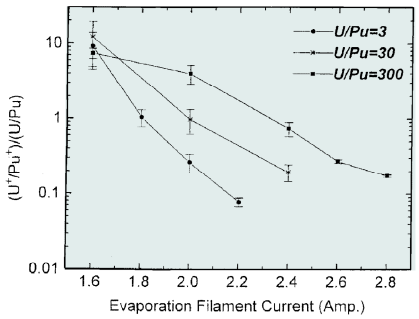

Figure 4: Variation of $(U^+/Pu^+)/(U/Pu)$ ratio as a function of evaporation filament heating current for three surrogate samples with U/Pu ratios as 3, 30, and 300.

To ascertain the accuracy of highly precise mass spectrometric data obtained during separate or simultaneous analysis, it is essential to correct suitably the observed atom ratios for the isotope fractionation effects in the ion source. These effects are known to depend upon a number of parameters and it is not easy to quantify separately the contribution of each of the parameters. An approach generally followed is to determine experimentally this isotope fractionation correction factor i.e. K-factor (=certified ratio/observed ratio) under the standardized conditions of mass spectrometric analysis.

Figures 5 and 6 depict the variations in the K-factors calculated from $^{235}U/^{238}U$ and $^{239}Pu/^{240}Pu$ ratios during a typical mass spectrometric analysis of a mixture with U/Pu as 10. The K-factors obtained from each individual block data as well as from the run summary of 3

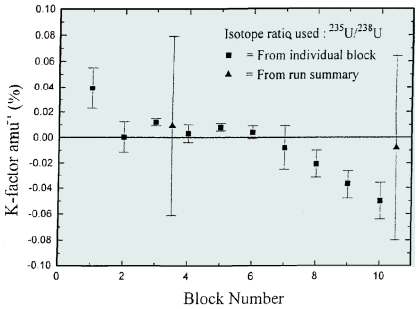

Figure 5: K-factor amu-1(%) from $^{235}U/^{238}U$ ratio in SRM-200-U calculated from different blocks data (the duration of each block was 2 min and 30 sec)

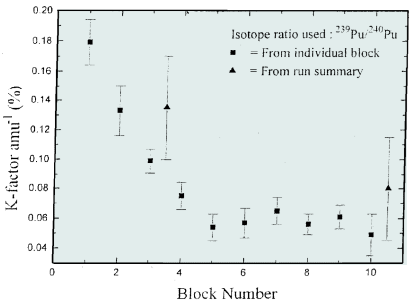

Figure 6: K-factor amu-1(%) from $^{239}Pu/^{240}Pu$ ratio in SRM-947-Pu calculated from different blocks data (the duration of each block was 2 min and 30 sec)

and 10 blocks data are shown in these figures. The duration of each block was 2 min and 30 sec. It appears that there is a mini-plateau region when K-factor remains almost constant for both U and Pu. Similar observations have also been reported recently by other investigators.

Table 2 summarises the K-factors per mass unit derived from $^{235}U/^{238}U$ and from $^{239}Pu/^{240}Pu$ and $^{239}Pu/^{242}Pu$ atom ratios. The K-factors were not calculated from $^{239}Pu/^{241}Pu$ ratios due to uncertainties which might be present due to the ingrowth of ^{241}Am and differences in the mass spectrometric behaviour of Am and Pu. The mean K-factors obtained per mass unit are -0.005% (i.e. close to zero) and 0.076% for U and Pu, respectively. The K-factor from $^{239}Pu/^{242}Pu$ ratio was calculated only to compare its value with that derived from $^{239}Pu/^{240}Pu$ ratio but is not accurate due to large error associated with the uncertified value of $^{239}Pu/^{242}Pu$ ratio in the SRM-947-Pu. The K-factors obtained in the present work are different (lower) from those reported previously /2/ from our laboratory (0.07% and 0.18% per mass unit for U and Pu respectively) when U and Pu were analysed separately. This is not surprising in view of the different ion source chemistry as discussed above e.g. different temperatures of the vaporisation filament needed in the present studies. The evaporation filament temperatures necessary to obtain sufficient ion currents of both U and Pu ions were found to be

Table 2: K-factors per atomic mass unit for Uranium and Plutonium During Simultaneous Mass Spectrometric Analyses of SRM-200-U and SRM-947-Pu

Sl. No.	MSA No.	K-factor amu^{-1} from ($^{235}U/^{238}Pu$)	K-factor amu^{-1} from ($^{239}Pu/^{240}Pu$)	K-factor amu^{-1} from ($^{239}Pu/^{242}Pu$)
1	6746	0.009%	0.130%	0.197%
2	6747	-0.032%	0.053%	0.152%
3	6748	0.028%	0.080%	0.107%
4	6749	-0.001%	0.063%	0.086%
5	6781	-0.024%	0.048%	0.079%
6	6782	-0.010%	0.080%	0.124%
Mean values		-0.005%	0.076%	0.124%

significantly higher compared to when these two elements are analysed individually from separate filament loadings. It is known that the K-factors due to isotope fractionation effects are lower at higher filament temperatures.

It was also of interest to determine experimentally the differences in the K-factors for $^{235}U/^{238}U$ ratio as a function of the evaporation filament heating current. Figure 7 displays the experimentally obtained K-factor for three mass units from $^{235}U/^{238}U$ atom ratio as a function of evaporation filament heating current. Each point in the figure represents the mean K-factor calculated from the K-factor obtained during independent analysis of these samples at the same evaporation filament heating current. The small error bars indicate reasonably good agreement in the K-factors obtained during independent analysis of different mixtures at nearly the same evaporation filament heating current. A large difference of 0.4% (i.e. increase from 0.9980 to 1.0020) in the K-factor is attributed to the combined effects of increase in the evaporation filament heating current and the time elapsed from the start of data acquisition. This demonstrates the importance of using the pre-determined K-factor from the standardized conditions of mass spectrometric analysis and stresses the need of reproducing as far as possible the identical conditions of sample loading and mass spectrometric analysis. From these data, the mean K-factor per mass unit for uranium turns out to be 1.0003 per mass unit for the evaporation filament heating current ranging from 2.0 to 2.6A and this is in agreement with the results given in the Table 2.

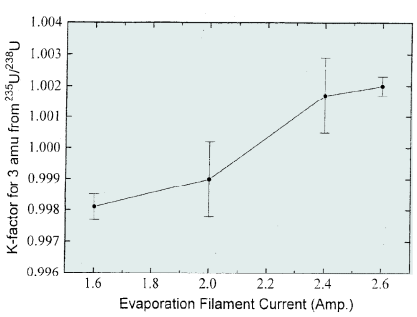

Figure 7: K-factor for 3 amu from $^{235}U/^{238}U$ ratio in SRM-200-U calculated from data obtained at different evaporation filament heating currents.

With an objective of accounting for the isobaric interference of ^{238}Pu at ^{238}U, it was considered interesting to follow a simple approach of first optimizing the evaporation and ionization filament heating currents with a view to obtaining sufficient ion currents of $^{238}U^+$, $^{239}Pu^+$ and other isotopes. The first 2 blocks of data were acquired by using the experimental procedure feeding a value of $^{238}Pu/^{239}Pu$ as zero in software of interfering element correction (IEC) approach. The value obtained during the first 2 blocks for $^{240}Pu/^{239}Pu$ was used to calculate $^{238}Pu/^{239}Pu$ atom ratio value which was subsequently given as input for isobaric interference correction in the IEC approach.

Table 3: Determination of $^{235}U/^{238}U$ Atom Ratio in the Samples with varying U/Pu ratio and with and without IEC approach

Sample	U/Pu	$^{235}U/^{238}U$ Atom Ratio	
		Without IEC	With IEC
SM-I	3	(a) 0.24750 (0.12%)	0.25077 (0.07%)
		(b) 0.24794 (0.19%)	0.25085 (0.04%)
SM-II	30	(a) 0.25078 (0.09%)	0.25052 (0.03%)
		(b) 0.25061 (0.07%)	0.25061 (0.06%)
SM-III	300	(a) 0.25220 (0.05%)	0.25205 (0.02%)
		(b) 0.25167 (0.05%)	0.25149 (0.04%)

1 (a) and (b) represent the data obtained from two independent mass spectrometric analyses of the same mixture.
2 The values given in the parentheses are the relative standard deviations from run summary of 3 or 5 blocks.
3 Without IEC means $^{238}Pu/^{239}Pu$ given as zero in the software used for the data reduction.

Table 3 gives the experimentally observed $^{235}U/^{238}U$ atom ratios in three different surrogate samples with U/Pu ratios as 3, 30 and 300. The results obtained without IEC (i.e. $^{238}Pu/^{239}Pu$=0) and using IEC are compared in the Table. It is seen that there is no significant difference in the $^{235}U/^{238}U$ atom ratios determined without IEC and with IEC from samples SM-II and SM-III with U/Pu ratios as 30 and 300. This is obviously due to the high value of U/Pu which leads to negligibly small isobaric interference from ^{238}Pu at ^{238}U in these two samples. As expected, there is significant difference in the $^{235}U/^{238}U$ atom ratios without IEC and with IEC for SM-I with U/Pu as 3. The values obtained for $^{235}U/^{238}U$ atom ratio with IEC approach are in good agreement with the certified value in the uranium reference material. Hence, interfering element correction approach using the methodology of knowing $^{240}Pu/^{239}Pu$ from first 2 blocks is ideal to account for the isobaric interference of ^{238}Pu at ^{238}U. This does not require any extra constraints on the part of the operator except for collecting data for two more blocks which takes only a few minutes (e.g. 5 minutes). Further, a comparison of $^{235}U/^{238}U$ atom ratios obtained without and with IEC approach would provide information about the extent of isobaric interference of ^{238}Pu at ^{238}U which indirectly can lead to a rough estimate of U/Pu ratio present on the filament.

Table 4 highlights the results obtained for $^{235}U/^{238}U$ ratios (corrected for isobaric interference from ^{238}Pu) and $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ isotope ratios in the synthetic mixture with U/Pu as 10 from replicate mass spectrometric analyses to evaluate the precision and accuracy under conditions of simultaneous mass spectrometric analyses. The ratios have not been corrected for any isotope fractionation or K-factor. The precision values obtained from the replicate mass spectrometric analyses are comparable to those generally obtained under routine conditions of their separate (individual) mass spectrometric analyses.

Conclusions

Experiments performed in the present work demonstrate the importance of understanding the ion source chemistry particularly when developing methods for accurate oligo-element analysis using

Table 4: $^{235}U/^{238}U$ (corrected), $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ Atom Ratios from Replicate Mass Spectrometric Analyses of Synthetic Mixture

Sample No.	MSA No.	$^{235}U/^{238}U$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$
Certified	Value	0.251259	0.241205	0.020251	0.015598
1	6746	0.251329 (0.068%)*	0.240874 (0.036%)*	0.020125 (0.115%)*	0.015506 (0.111%)*
2	6747	0.251014 (0.045%)	0.241076 (0.015%)	0.020216 (0.063%)	0.015524 (0.194%)
3	6748	0.251474 (0.032%)	0.241013 (0.024%)	0.020176 (0.162%)	0.015548 (0.165%)
4	6749	0.251254 (0.033%)	0.241054 (0.022%)	0.020174 (0.077%)	0.015558 (0.120%)
5	6781	0.251078 (0.061%)	0.241089 (0.018%)	0.020208 (0.061%)	0.015561 (0.101%)
6	6782	0.251181 (0.094%)	0.241011 (0.045%)	0.020176 (0.160%)	0.015540 (0.147%)
Mean value		0.251222	0.241020	0.020186	0.015540
Mean Internal Error		0.024 %	0.012%	0.047%	0.058%
External Error		0.067%	0.032%	0.177%	0.136%
Total Error		0.071%	0.034%	0.183%	0.148%

* Specifies RSD values from run summary of three blocks data.

TIMS. The results reported highlight the advantages of monitoring the intensities of various ions when developing a new method. It is also shown that the Interfering Element Correction (IEC) approach is universally applicable to different types of unknown U/Pu samples to account for the isobaric interference of ^{238}Pu at ^{238}U during simultaneous TIMS analysis of U and Pu. One need not perform an independent TIMS analysis of plutonium for apriori knowledge of ^{238}Pu/^{239}Pu atom ratio in the sample. The methodology suggested does not increase the work load for the operator and does not unduly increase the analysis time except for changing the parameter ^{238}Pu/^{235}Pu from zero to the actual value in the data reduction module of the software after first few blocks.

Acknowledgements

The authors express their sincere thanks to Dr D.D. Sood, Director of the Radiochemistry and Isotope Group at BARC for his keen interest in the mass spectrometric work. Thanks are due to the members of Electronics and Instrumentation Group of Radiochemistry Division for providing technical support for the maintenance of the instrument.

References

/1/ S.A. CHITAMBAR, V.D. KAVIMANDAN, B. SAHA, S.K. AGGARWAL, G. PERIASWAMI, K. BHAGYALAKSHMI, P.M. SHAH, P.A. RAMASUBRAMANIAN, A.I. ALMAULA, H.C. JAIN, C.K. MATHEWS - BARC Report, BARC-865 (1976).

/2/ S.K. AGGARWAL, A.L. ALMAULA, P.S. KHODADE, A.R. PARAB, R.K. DUGGAL, C.P. SINGH, A.S. RAWAT, G. CHOURASIYA, S.A. CHITAMBAR, H.C. JAIN - J. Radioanal. Nucl. Chem., Letters, 87 (1984) 169.

/3/ S.K. AGGARWAL, G. CHOURASIYA, C.P. SINGH, A.S. RAWAT, S.A. CHITAMBAR, H.C. JAIN - J. Radioanal. Nucl. Chem., Letters, 93 (1985)

/4/ S.K. AGGARWAL, R.K. DUGGAL, R. RAO, H.C. JAIN - Int. J. Mass Spectrom. Ion Proc. 71 (1986) 221.

/5/ S.K. AGGARWAL, G. CHOURASIYA, R.K. DUGGAL, R. RAO, H.C. JAIN - Int. J. Mass Spectrom. Ion Proc., 69 (1986) 137.

/6/ S.K. AGGARWAL, R.K. DUGGAL, P.M. SHAH, H.C. JAIN - Int. J. Mass Spectrom. Ion Proc., 85 (1988) 137.

/7/ K.L. RAMAKUMAR, R.M. RAO, L. GNANAYYAN, H.C. JAIN - Int. J. Mass Spectrom. Ion Processes, 134 (1994) 183.

/8/ S.K. AGGARWAL, M.K. SAXENA, P.M. SHAH, SANJAI KUMAR, USHA JAIRAMAN, H.C. JAIN - Int. J. Mass Spectrom. Ion Processes,139 (1994) 111.

/9/ K.L. RAMAKUMAR, S. JEYAKUMAR, R.M. RAO, L. GNANAYYAN, H.C. JAIN - J. Radioanal. Nucl. Chem., Articles, 190 (1995) 121.

A Simple, Rapid and Accurate Electrochemical Method for Uranium Determination in Dissolver Solution of Irradiated Fuel

P.R. Nair, M. Xavier, K.A. Mathew, P.M. Shah, S.K. Aggarwal, H.C. Jain
Fuel Chemistry Division, Bhabha Atomic Research Centre, Bombay, India

Abstract

A simple biamperometric method based on the reduction of U(VI) to U(IV) by Ti(III) and titration of U(IV) with standard $K_2Cr_2O_7$ solution was evaluated for the determination of U concentration in dissolver solutions of irradiated fuel with burn-up values in the range of 1,000 to 10,000 MWD/TU. The accuracy of the method compared with that of isotope dilution thermal ionisation mass spectrometry was excellent. Analysis of a primary standard NIST U_3O_8 in the 100 µg to 5 mg range confirmed the method to be bias free with precision values of 0.24% at 100 µg level to 0.01% at 5 mg level.

Introduction

Electrochemical methods based on redox titrations are conventionally used for the determination of uranium (U) in different unirradiated nuclear fuel materials. Biamperometry using two polarised platinum electrodes is a promising technique for the rapid and accurate determination of uranium and plutonium /1,2/. This approach has several attractive features which include (i) a simple, inexpensive instrumentation and (ii) a clear indication of the progress and completion of the reactions at different stages of the procedure. In this paper, the evaluation of a biamperometric method, based on the reduction of U(VI) to U(IV) using Ti(III), for determining the concentration of U in dissolver solution of irradiated fuel is presented.

Principle of the Method

The method is based on the reduction of U(VI) to U(IV) by Ti(III) in a mixture of HNO_3 and H_2SO_4, selective insitu destruction of the excess Ti(III) using HNO_3, addition of Fe(III) solution and titration of the generated Fe(II) with standard $K_2Cr_2O_7$ solutions added on weight basis. $K_2Cr_2O_7$ solutions of different concentrations, namely 0.05, 0.005, 0.001 and 0.0002 meq/g, were employed depending upon the amount of U in the aliquot.

Experimental

Materials

Standard uranium solutions were prepared from high purity sintered UO_2 pellets as well as from NIST U_3O_8 by dissolving in nitric acid. The mixture 0.5 M H_2SO_4 - 0.5 M HNO_3 was prepared by mixing 1 M solutions of the acids. 9 M H_2SO_4 was prepared by 1:1 dilution of concentrated H_2SO_4. $TiCl_3$ (about 0.5 M) was prepared by dissolving Ti sponge in 1:1 HCl. 0.5 M $Fe(NO_3)_3$ solution was prepared in 1 M H_2 SO_4. Standard $K_2Cr_2O_7$ solutions of 0.05, 0.005, 0.001 and 0.0002 meq/g were prepared using NIST reference material.

The amperometer used was fabricated indigenously. The electrodes consisted of two identical Pt wires (20 swg), about 12 cm long and fixed to a glass tube at 1 cm apart. Polyethylene weight burettes of 15 ml capacity were used for taking sample aliquots and $K_2Cr_2O_7$ solutions.

Procedure

Take an aliquot of the dissolver solution in a 30 ml cylindrical titration vessel. Add 2 ml of acid mixture (0.5M H_2SO_4-0.5M HNO_3). Stir and add 15% $TiCl_3$ solution dropwise from a dropper till the violet colour persists, followed by 5 ml of 9M H_2SO_4. Introduce the electrodes (in the solution) across which a potential of 200 mV is applied. Wait till the dark brown colour disappears with a sudden rise and fall in the current. Add about 1 ml of 1.5M NH_2SO_3H followed by 8 ml of distilled water. Now add sufficient amount of (~0.3 ml) 0.5M $Fe(NO_3)_3$ solution in 1M H_2SO_4 dropwise till the current reaches to about 200 µA. Add standard $K_2Cr_2O_7$ solution (0.05 meq/g) from a weight burette till the current decreases to about 10 µA. Continue titration with another 50 fold diluted $K_2Cr_2O_7$ solution (0.001 meq/g) till the current decreases to about 1 µA. Further titration is continued with the dichromate solution of 0.0002 meq/g concentration till there is no decrease in the current (~0.2 µA). The amount of U in the aliquot is calculated from the weights of the dichromate solutions consumed.

Results and Discussion

Determination of uranium in dissolver solutions of low burn-up

Table 1 shows typical results obtained on replicate aliquots from one of the dissolver solutions (burn-up about 1,500 MWD/TU). The amount of uranium in each of the aliquots was 4-6 mg. An RSD of 0.03 % was obtained which is comparable with that achievable by the internationally accepted method of isotope dilution-thermal ionisation mass spectrometry (ID-TIMS) for U determination in dissolver solution of irradiated fuel.

Table 1: U Determination in a Dissolver Solution (Burn-up ~1500 MWD/TU)

Aliquot No.	Aliquot wt. taken (g)	Amount of U obtained (mg)	U conc. (mg/g)
1	0.31700	4.5817	14.453
2	0.40180	4.8095	14.459
3	0.33770	4.8817	14.456
4	0.33420	4.8292	14.450
5	0.30010	4.3400	14.462
Mean U conc. (mg/g)			=14.456 ± 0.03%

Table 2 gives a summary of the data obtained from 5 different dissolver solutions with burn-up values about 1,500 MWD/TU. A mean precision of 0.08% was obtained. As can be seen, there is no significant difference in the RSD values in 1 to 6 mg range of U in the aliquot. It may be mentioned that for dissolver solution DS-5, an additional 5 fold diluted K_2Cr_2O solution (0.0002 meq/g) was also used near the end point, which may be responsible for a better precision of 0.06% at 1 to 2 mg level compared to RSD values of 0.10% and 0.14% in DS-3 and DS-4 at nearly the same level of uranium. The solutions DS-1 and DS-2 were 15 times diluted from the original solution while DS-3 to DS-5 solutions were about 50 times diluted, to reduce the radiation dose during titration.

Table 2: U Determination in Different Dissolver Solutions (5 aliquots from each dissolver solution were analysed)

Dissolver Solution No.	Dilution Factor	Amount of U per aliquot (mg)	Mean U conc. (mg/g)	RSD (%)
DS-1	15	4-6	14.456	0.03
DS-2	15	4-6	12.122	0.07
DS-3	50	1-2	3.629	0.10
DS-4	50	1-2	3.220	0.14
DS-5	50	1-2	3.296	0.06*
				Mean RSD = 0.08%

* Better precision (0.06%) for 1-2 mg U; very dilute $K_2Cr_2O_7$ solution (conc. 0.0002 meq/g) used near end point.

Determination of uranium in dissolver solutions of high burn-up

To apply this method for high burn-up fuels e.g. greater than or equal 10,000 MWD/TU, it would be necessary to increase the dilution factor to reduce the radiation dose and hence the aliquot will contaill less than one milligram of U.

With this objective aliquots of a working standard solution were analysed at 100-300 µg levels. The results indicated positive bias equivalent to 1 µg of uranium. This was also confirmed by blank titrations. The source of this blank was attributed to some oxidisable impurity present in the distilled water used for dilution before dichromate addition. Use of quartz distilled water eliminated the positive bias and the blank problem.

Subsequently, precision and accuracy of the method was evaluated using NIST U_3O_8 chemical assay reference material at 100 µg to 5 mg level. Table 3 presents the results obtained on U determination in the NIST reference material. As is seen, precision values of 0.01%, 0.03%, 0.14% and 0.24%, respectively were obtained using 5 mg, 1 mg, 300 µg and 100 µg of U in the aliquot, with no detectable bias. These results demonstrated that the present methodology may also be applied to U determination in the case of dissolver solutions of irradiated fuels with high burn-up.

Table 3: U Determination in NIST U_3O_8 Primary Standard taking Different Amounts of Uranium

Uranium amount	U conc. (mg/g)	RSD (%)	Difference (%)
5 mg	3.7898	0.01	0.01
1 mg	3.7906	0.03	0.03
300 µg	3.7921	0.14	0.07
100 µg	3.7894	0.24	0.00
	Expected U conc = 3.7894 mg U/g solution		

Table 4 presents the results obtained on three other dissolver solutions of (long cooled) irradiated fuel with burn-up values of about 10,000 MWD/TU. A mean RSD values of 0.10% with the individual RSD values ranging from 0.05 to 0.15% were obtained. The mean RSD is comparable with an RSD of 0.08% observed in the case of low burn-up dissolver solutions.

Table 4: U Determination in High Burn-up Dissolver Solutions (5 aliquots from each dissolver solution were analysed)

Dissolver Solution No.	Amount of U per aliquot (mg)	Mean U conc. (mg/g)	RSD (%)
DS-6	4-5	8.036	0.05
DS-7	1-2	3.562	0.15
DS-8	10-13	23.570	0.10
			Mean RSD = 0.10%

Comparison of Biamperometry with ID-TIMS

It was of interest to evaluate the present methodology with respect to the internationally recognised method of isotope dilution - thermal ionisation mass spectrometry (ID-TIMS). Table 5 shows a comparison of U concentration values determined using biamperometry and ID-TIMS. As can be seen the RSD values obtained using replicate aliquots by the two methods are comparable (about 0.1%). Further the mean value of 0.99974 ± (0.006%) for the ratio biamperometry/ID-TIMS shows the biamperometric methodology to be bias free.

Table 5: Comparison of Results of Uranium Determination in Dissolver Solution of Irradiated Fuel using Biamperometry and Mass Spectrometry

Dissolver Solution No.	Concentration of uranium in Dissolver Solution (mg/g)		
	Biamperometry (A)	ID-TIMS (B)	(A/B)
DS-1	14.456±(0.03%)*	14.435±(0.005%)	1.00145
DS-3	3.629±(0.10%)	3.638±(0.09%)	0.99753
DS-4	3.220±(0.14%)	3.223±(0.03%)	0.99907
DS-5	3.296±(0.06%)	3.293±(0.08%)	1.00091
	Mean A/B = 0.99974±(0.006 %)		

* RSD from replicate aliquots

Conclusions

The titrimetric method discussed in this paper, besides being simple, accurate and precise, does not require the use of strong complexing agents like H_3PO_4 and the volume of the waste generated is small. It is rapid, convenient and does not require any elaborate or expensive instrumentation. It may also be noted that the volume of the different reagents used are not critical and hence the method may be adopted easily by any laboratory.

The interference of Pu is eliminated by the suitable choice of experimental conditions. Nitrous acid generated during the destruction of Ti(III) by HNO_3 selectively oxidises the Pu(III) to Pu(IV). The method appears promising for uranium determination in dissolver solutions and should be tried on high burn-up fuel samples by different international laboratories.

Acknowledgements

Authors express their sincere thanks to Dr. D.D. Sood, Director, Radiochemistry and Isotope Group, BARC for his keen interest and constant encouragement.

References

/1/ P.R. NAIR, K.V. LOHITHAKSHAN, M. XAVIER, S.G. MARATHE, H.C. JAIN - J. Radioanal. Nucl. Chem., Articles, 122 (1988) 19.

/2/ M. XAVIER, K.V. LOHITHAKSHAN, P.R. NAIR, S.G. MARATHE, H.C. JAIN - Ibid, 148 (1991) 251.

ESARDA NEWS

A Workshop to advance R&D in the field of Safeguards

A Workshop on "Modern Science and Technology for Safeguards" will be jointly organized by ESARDA and INMM from 28 to 31 October 1996. The objective of the Workshop is to discuss how the latest improvements in technology and sciences could contribute to establishing new and co-operative research programmes for strengthening safeguards and improving its effectiveness and efficiency.

The meeting will convene safeguards experts and specialists of various disciplines including, amongst others: environmental and in-process sampling, satellites and satellite imagery, new sensors and new measurement technology, networks and neural networks, multimedia technology, expert systems, artificial intelligence, decision theory, game theory and conflict analysis.

The participants will discuss how the various disciplines could find application to "data generation, collection, organization, analysis and use for decision support" in the area of safeguards. Also the relations of safeguards with the political/social framework will be discussed.

Although participation in the Seminar is in principle reserved to invited people, observers can be admitted at no charge. The Seminar will be held near Ispra, in the Hotel Concorde of Arona (Italy). For more information please contact the ESARDA Secretariat (Mrs. F. Genoni, Tel. +39-332-789421, Fax +39-332-789509).

1997 ESARDA Symposium

In 1997 ESARDA will organize its 19th annual Symposium on "Safeguards and Nuclear Material Management". It will be held in south France, in May. The location and the date will be announced soon.

An ESARDA seminar in Russia

ESARDA is planning to organize a joint Seminar with the Russian Institute for Physics and Power Engineering (IPPE). The objectives are: i) to bring up-to-date information on the latest developments of safeguards techniques to the russian scientific public, ii) to review the existing co-operative collaborations between the European Community and the CIS Countries in this field and iii) to be informed on the ongoing safeguards R&D activities in Russia.

The Seminar will be held in Obninsk (Russia) in 1997.

Changes in ESARDA

Mr. G. Déan has left his assignment as Member of the ESARDA Steering Committee representating the French CEA; he had been a Member since 1991. Mr. D. Flory has been appointed as his successor.

Mr. J.A. Cookson, of the UKAEA, has left his assignment as ESARDA Co-ordinator for UK. Mr. M.D. Ward of the UKAEA has been appointed his successor.

Mr. F. Mousty, of the Joint Research Centre, has been appointed Convenor of the ESARDA Working Group for Low Enriched Uranium Conversion and Fuel Fabrication Plants (LEU). ESARDA wishes to express its gratitude to Mr. H. Boermans, past Convenor, for his competence and his selfless dedication to the activities of this Working Group.

As of 31-12-1994, the Reprocessing Input Verification (RIV) Working Group has been closed. A report on its past activities is published in this Bulletin.

As of November 1995, ESARDA has created a new Working Group on the "Back-end of the Fuel Cycle" (BFC). It will deal with safeguards problems related to this part of the fuel cycle, with special focus on the long term storage of spent fuel, on spent fuel conditioning facilities and on final geological repositories. Mr. M. Dionisi, of the Italian ANPA, has been appointed Convenor.

ESARDA Symposia Proceedings

Every two years ESARDA Organizes a Symposium on "Safeguards and Nuclear Material Management". The Proceedings of the Symposia are distributed free of charge to the participants. They can be purchased by non-participants at the price of 50 ECU per copy. For orders, please contact Mrs. F. Genoni (address in the 2nd page of the cover).

ESARDA also organizes, every two years, an "Internal Meeting" of the Association. Proceedings may be published or not, according to a case-to-case decision. The distribution is in principle limited to the ESARDA Partners and Working Groups Members only.

Who's Who in ESARDA?

(as of 1st March 1996)

Chairman 1996 *P.P. De Regge*, CEN/SCK, Mol, Belgium
Secretary *C. Foggi*, EC, JRC, Ispra, Italy

Steering Committee

G. Andrews, Dept. of Trade and Industry, London, UK
C. Beets, Ministry of Foreign Affairs, Liege, Belgium
C.P. Behrens, Kernkraftwerk Philippsburg, Germany
J.C. Charrault, EC, Brussels, Belgium
M. Cuypers, EC, JRC, Ispra, Italy
F. De Cormis (Mrs), EDF, Paris, France
P.P. De Regge, CEN/SCK, Mol, Belgium
D. Flory, CEA, Fontenay-aux-Roses, France
J. Fuger, EC, JRC, Karlsruhe, Germany
F. Garcìa González (Mrs), CIEMAT, Madrid, Spain
W. Gmelin, EC, ESD, Luxembourg
G. Grossi, ANPA, Rome, Italy
R. Howsley, BNFL, Risley, UK
R.F. Ingels, Belgonucléaire, Dessel, Belgium
G. Le Goff, CEA, Paris, France
F. Maccazzola, ANPA, Rome, Italy
B.H. Patrick, UKAEA, Harwell, UK
F. Pozzi, ENEA, Saluggia, Italy
J. Régnier, COGEMA, Velizy-Villacoûblay, France
H. Remagen, BMBF, Bonn, Germany
G. Stein, KFA, Jülich, Germany
A.M. Versteegh, ECN, Petten, The Netherlands
R. Weh, WKK, Bonn, Germany

Executive Committee

P.P. De Regge, CEN/SCK, Mol, Belgium
G. Grosssi, ANPA, Rome, Italy
R. Howsley, BNFL, Risley, UK
W. Kloeckner, EC, ESD, Luxembourg
G. Stein, KFA, Jülich, Germany
A.M. Versteegh, ECN, Petten, The Netherlands

Coordinators

R. Carchon, CEN/SCK, Mol, Belgium
M. Cuypers, EC, JRC, Ispra, Italy
M. Dionisi, ANPA, Rome, Italy
F. Garcìa González (Mrs), CIEMAT, Madrid, Spain
R.J.S. Harry, ECN, Petten, The Netherlands
W.D. Lauppe, KFA, Jülich, Germany
H. Lefèvre, CEA, Fontenay-aux-Roses, France
H. Nackaerts, EC, ESD, Luxembourg
M.D. Ward, UKAEA, Risley, UK

Working Group Convenors

Techniques and Standards for Non-Destructive Analysis (NDA)
S. Guardini, EC, JRC, Ispra, Italy

Techniques and Standards for Destructive Analysis (DA)
P. De Bièvre, EC, JRC, Geel, Belgium

Containment and Surveillance (C/S)
R. Richter, KFA, Jülich, Germany

Low-Enriched Uranium Conversion and Fuel Fabrication Plants (LEU)
F. Mousty, EC, JRC, Ispra, Italy

Mixed Oxide Fuel Fabrication Plants (MOX)
R.F. Ingels, Belgonucléaire,Dessel, Belgium

Back-End of the Fuel Cycle (BFC)
M. Dionisi, ANPA, Rome, Italy

ESARDA Bulletin Editors

C. Foggi, F. Genoni (Mrs), EC, JRC, Ispra, Italy

LB-AB-96-026-EN-N