EUR 4576 e **KFK 1100**

ASSOCIATION
EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM
GESELLSCHAFT FÜR KERNFORSCHUNG KARLSRUHE

JOINT INTEGRAL SAFEGUARDS EXPERIMENT (JEX 70) AT THE EUROCHEMIC REPROCESSING PLANT, MOL, BELGIUM

January 1970 - July 1971

Edited by

R. KRAEMER and W. BEYRICH
Projekt Spaltstofffflußkontrolle

zu KFK 1100
bzw. EUR 4576e

List of Errata in the Present Edition of EUR 4576e;KFK 1100

1) page 2-22 : replace equation (2-3) by :

$$(2\text{-}3)\quad \delta^2_{flow} = (\ \delta^2_c + \delta^2_r/n\ )_{volume/mass} + (\ \delta^2_c + \delta^2_r/nm)_{analysis}\ [\%RSD]^2$$

2) page 5-62 : replace equation (5-19) by :

$$(5\text{-}19)\qquad \delta_M = (\mathrm{var}\ M_a)^{1/2}/\ M_a \quad ; \qquad \delta_x = (\mathrm{var}\ x_a)^{1/2}/\ x_a$$

3) page 7-130 : replace line 13 from bottom by :

"centration (density) of the i-th sample, $\mu_i = \mu + a_i$,and the expectation"

4) page 7-130 : replace line 11 from bottom by :

"the interlab error). $e_{ij\nu}$ is the reproducibility of the ν-th measurement of

5) page 7-130 : replace line 8 from bottom by :

"ν-th measurement (scan) of the j-th run of the i-th laboratory. a_i is the"

6) page 7-132 : replace line 9 from top by :

"density) are significantly different, i.e. whether there is a "

7) page 7-132 : replace equation (II,3) by :

$$y_{j\nu} = \hat{\mu} + b_j + e_{j\nu} \qquad (II,3)$$

8) page 7-133 : replace in the second equation from bottom :

$(y_{\kappa\nu} - y_\kappa\ )^2$ by the correct term: $(y_{\kappa\nu} - y_{\kappa .})^2$

9) page 7-136 : replace in the first line of section II.4 :

b_{ij} by the correct symbol: a_i

10) page 7-138 : replace in equation (II,22):

s by the correct symbol: s_i

11) page 7-138 : replace in equation (II,23):

$Y_{ij\nu}$ by the correct symbol: $y_{ij\nu}$

12) page 7-138 : in equation (II,24) the factor: $1/N^2$ has to be multiplied with the total following expression.

$$\mathrm{var}\ \hat{\mu} = 1/N^2(\sum_{i=1}^{r} \cdots\cdots\cdots\cdots\cdots\ N\sigma^2_e) \qquad (II,24)$$

13) page 7-138 : in equation (II,27) (i.e.first equation) the factor :

$1/(rsn)^2$ has to be multiplied with the total expression:

$$\mathrm{var}\ \hat{\mu} = 1/(rsn)^2\ (\sum_{i=1}^{r} \cdots\cdots\cdots\cdots + rsn\ \sigma^2_e)$$

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ABSTRACT

The report presents in detail the methods used and the results obtained in an integral safeguards experiment carried out in the EUROCHEMIC reprocessing plant as a joint undertaking in the framework of the association for safeguards: CEN, EURATOM, GfK, and with collaboration of other organisations (ACDA, AECB, IAEA, USAEC). The objectives of this safeguards exercise cover mainly problems associated with accountability of nuclear material in a reprocessing plant such as: identification techniques on spent fuel elements in the fuel storage pond with help of a special television camera device and of equipment for measuring divers gamma activity ratios of suitable fission products, verification of operators input data by means of isotope correlation techniques and extended interlaboratory tests on present analytical methods for U and Pu concentrations and determinations of isotopic compositions in realistic feed, product and waste flows. Special objective of this joint experiment was an experimental demonstration of a new physical inventory technique which correlates isotopic compositions of subsequent input and product batches. Detailed theoretical investigations using digital simulation models on U and Pu flow through the EUROCHEMIC plant were carried out in order to obtain quantitative statements on limiting conditions and accuracy of this new inventory technique.

The different subjects of this report are devided in 8 selfconsistant chapters containing individually summaries and conclusions.

KEYWORDS

EUROCHEMIC
SAFEGUARDS
ACCOUNTING
SPENT FUEL ELEMENTS
STORAGE
TELEVISION
GAMMA DETECTION
GAMMA RADIATION
FISSION PRODUCTS
URANIUM
PLUTONIUM
ISOTOPE RATIO
CORRELATION
RELIABILITY
DIGITAL SYSTEMS
MOCKUP

JOINT INTEGRAL SAFEGUARDS EXPERIMENT (JEX 70)
AT THE EUROCHEMIC REPROCESSING PLANT, MOL, BELGIUM

List of Contents

The running page numbers are given separately for each chapter in combination with the corresponding chapter number.

Preface and Acknowledgement

This joint integral safeguards experiment was made possible in the framework of the Association for safeguards of the Gesellschaft für Kernforschung (GfK), Germany, with the European Communities (EURATOM) and the Centre d'Etude de l'Energie Nucléaire (CEN), Belgium +), in cooperation with the following organisations:

ACDA	- United States Arms Control and Disarmament Agency as contractor for Batelle Memorial Institutes in Columbus (BMC) and Richland (PNL) as well as the Oak Ridge National Laboratory (ORNL)
AECB	- Atomic Energy Control Board of Canada
EUROCHEMIC	- European Company for Chemical Processing of Irradiated Fuels
IAEA	- International Atomic Energy Agency
USAEC	- United States Atomic Energy Commission.

The evaluation of the results of the Analytical Interlaboratory Tests was based on the data supplied by the following laboratories:

BCMN	- Bureau Central de Mesures Nucléaires, EURATOM, Geel, Belgium
CEN	- Centre d'Etude de l'Energie Nucléaire, Mol-Donc, Belgium
CCR	- Joint Research Center of EURATOM, Chemistry Division, Ispra, Italy
EUROCHEMIC	- European Company for Chemical Processing of Irradiated Fuels, Analytical Laboratory, Mol, Belgium
GfK	- Gesellschaft für Kernforschung, Institut für Radiochemie, Karlsruhe, Germany
IAEA	- International Atomic Energy Agency Laboratory, Seibersdorf, Austria
ORNL	- Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA
TU	- European Institute of Transuranium Elements, EURATOM, Karlsruhe, Germany

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+) During 1970/71, this association was extended to Comitato Nationale per l'Energia Nucleare (CNEN) and Reactor Centrum Nederland (RCN)

This report is not only the work of the indicated authors, but the result of the combined efforts of numerous participants who are listed in the following working groups according to their main activities:

I. Working group: Organisation and Intercommunication

Asyee, J.	(EUROCHEMIC)	Houck, F.	(ACDA)
Bartels, W.	(USAEC)	Kraemer, R.	(GfK)
Beyrich, W.	(EURATOM)	Kruys, P.	(EURATOM)
Boggio, G.	(EURATOM)	Lamouraux, A.	(EURATOM)
Bresesti, M.	(EURATOM)	Mattys, H.	(EURATOM)
Colling, A.	(EURATOM)	McDowel, S.	(USAEC)
Finzi, S.	(EURATOM)	Miranda, U.	(EURATOM)
Gaines, E.	(ACDA)	Rentschler, R.R.	(ACDA)
Gupta, D.	(GfK)	Schmets, J.	(CEN)
Häfele, W.	(GfK)	Sköldebrand, R.	(IAEA)
Hagen, A.	(GfK)	Stieff, L.	(ACDA)
Higinbotham, W.A.	(BNL)	v.d. Styil, E.	(EURATOM)
		Waligura, A.J.	(IAEA)

II. Working group: In-Plant Data Collection

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Detiffe	(EURATOM)	Otto, H.-E.	(GfK)
Fransen, F.	(EUROCHEMIC)	Sola, A.	(EURATOM)
Frippiat, J.	(EURATOM)		

III. Working group: Identification of Spent Fuel Elements

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Bemmelmans, P.	(CEN)	Stubbé	(CEN)

IV. Working group: Simulation and Inventory Experiment

Cocquyt	(CEN)	Hall, A.	(CNEN-EUREX)
De Greef, J.F.	(CEN)	Kraemer, R.	(GfK)
Drosselmeyer, E.	(GfK)	Müller, K.H.	(EURATOM)
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Farese, L.	(EURATOM)	v.d.Stricht, E.	(EURATOM)

V. Working group: Isotope Correlation Technique

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Foggi, C.	(EURATOM)	Smythe, D.	(AECB)
Moeken, H.	(EUROCHEMIC)	Stewart, K.B.	(BNWL)
Palmedo, P.	(USAEC)		
Ransbotyn, J.	(CEN)		

VI. Working group: Analytical Efforts

Angeletti, L.	(EURATOM)	Grünbaum, L.	(GfK)
Avenhaus, R.	(GfK)	Kammerichs, K.	(EURATOM)
von Baeckmann, A.	(GfK)	Koch, L.	(EURATOM)
Berg, R.	(EUROCHEMIC)	Kraemer, R.	(GfK)
Beyrich, W.	(EURATOM)	Le Duigou, Y.	(EURATOM)
Bokelund, H.	(EUROCHEMIC)	Mainka, E.	(GfK)
Cameron, A.E.	(ORNL)	Mannone, F.	(EURATOM)
Debus, G.H.	(EURATOM)	Ruf, H.	(GfK)
De Regge, P.	(CEN)	Schuelein, V.L.	(IAEA)
Facchetti, S.	(EURATOM)	Singh, H.	(BARC)[1]
Frittum, H.	(IAEA)	Thiele, D.	(BAM)[2]

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[1] Bhabha Atomic Research Center, Bombay, India, delegated to GfK

[2] now Bundesanstalt für Materialprüfung, Berlin, Germany

This joint experiment was a fruitful experience in many respects. The results and data so obtained will be significant for the further development of a rational and effective safeguards system. It also came out to be a proof how successfully international groups that are engaged in a scientific subject can cooperate.

Particular thanks have to be given to all participants. It will not be possible to name them all. Special thanks, however, have to be extended to the management and the operators of the European Company for Chemical Processing of Irradiated Fuel. Without their cooperation and enthusiasm the experiment would not have become a success.

W. Häfele

The editors would like to express their thanks to Monika Mäule, Renate Tonk and Edith Wortmann for their diligent assistance in the typing and correction of the manuscript and in the preparation of the technical drawings.

1. INTRODUCTION

During the year 1969 an increasing interest on integral experiments could be observed among the international scientific community engaged on safeguards activities in the peaceful sector of nuclear energy. The results of a number of integral experiments became available /‾1-1 - 1-4_7 and the importance of such experiments was well recognized. The necessity of integral experiments was also emphasized in a number of IAEA panel meetings /‾1-5, 1-6_7 during this period.

At approximately the same time a number of safeguards relevant methods which were been worked upon in different countries, required further experimental verification. On the whole, it appeared to be opportune and fruitful to carry out an integral experiment in a reprocessing plant with international participation during the year 1970.

The possibility of the execution of such an experiment was discussed at a meeting of the Steering Committee of the Association on Safeguards [+)] (at that time consisting of EURATOM and GfK) on 6.11.1969. It was established that the EUROCHEMIC reprocessing plant at Mol, Belgium, would be well suited for an integral experiment provided some appropriately sized campaigns were scheduled for reprocessing during 1970.

Further investigations on this point and preliminary inquiries amongst the probable participants indicated that both the time schedule at the EUROCHEMIC plant and the response for participation would be favourable. A meeting of the probable participants (see preface) was accordingly held at Karlsruhe on the 14th, 15th and 16th January 1970 to discuss the time schedule of the EUROCHEMIC plant, the available experience for the execution of an integral experiment on an international level, the area and extent of cooperation and coordination amongst the participants and the choice of possible objectives for an integral experiment.

[+)] The Association, at present consisting of the partners EURATOM-CEN-CNEN-GfK-RCN, coordinates the R+D-activities of the partners in the field of safeguards.

It is to be noted that "integral experiment" means a safeguards exercise in an existing nuclear facility for a production campaign over a significant period of time. The principal objectives for an integral experiment are to close the material balance for these actual campaigns, to evaluate the measurement errors, the operating losses, to test different measurement instruments and other methods and techniques and to evaluate safeguards efforts.

In retrospect, the conclusions drawn at the above mentioned meeting and the preliminary objectives established, throw some interesting light on the different subjects finally taken over in the present report. The preliminary objectives chosen were: a) Physical Inventory Determination (PID), b) Applicability of Minor Isotope Correlation Techniques (MIST), and c) Interlaboratorium Tests for relevant analytical measurement methods. The only suitable operation campaign at the EUROCHEMIC plant which was scheduled to be reprocessed in 1970 consisted of about 10-12 tons of natural uranium CANDU +) type fuel elements with a fairly long cooling time. The fuel elements had different burn-ups.

a) <u>Identification of fuel elements</u>

For the application of the PID method, different concentrations of a particular isotope in two consecutive batches are required /¯1-7_/. On the basis of the shipper's data it was concluded that such a difference in concentration might be expected in different fuel elements because of their different burn-ups. However, they had to be arranged in a particular sequence to maximise the isotope concentration difference between the two batches (step signal). For that purpose the fuel elements had to be identified. Besides a photographic method of checking the serial numbers of the fuel elements, a γ-spectrometric method (suggested by the IAEA) was also considered as an alternative, as it was feared that the identification numbers might have been corroded away because of the long cooling time. In the course of the experiment it was found that the γ-spectrometric method would produce a large volume of additional information which could be of interest from the safeguards point of view. Although later on, no identification of CANDU type fuel was necessary because of a changed operation schedule (see below), γ-spectrometric measurements were made

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+) Different reactor types, explained in chapter 2.

on VAK [+)] and BR-2 type fuels to gather and test this information. The results of the analysis of this information are discussed in chapter 3. Some comments have also been made on the identification of the VAK [+)] fuel elements by photographic method.

b) Simulation

Another subject which turned out to be of importance because of the initial objectives set, was the simulation of process flow. During the planning stage of the experiment it was not possible to envisage whether PID could be made successfully. It was therefore, proposed to simulate the process flows relevant to the integral experiment and investigate the influence of various process parameters on this method. The results of this simulation were to be made available to the planning committee before the commencement of the integral experiment so that the PID could be dropped from the objectives in case it could not be applied. However, because of the changed operation schedule and on the basis of the preliminary results of the simulation it was found that the PID could be expected to be carried out with reasonable accuracy. Therefore, this was retained as one of the main objectives of the integral experiment. The simulation was however, found to be a powerful tool in analysing a wide spectrum of influences relevant to the PID method and therefore, was elaborated during the course of the experiment. A detailed description of the subject and an analysis of the results of simulation are to be found in chapter 4.

c) Physical Inventory Determination (PID)

PID based on the use of an isotopic step function /‾1-7_7 was expected to be the most important objective of the integral experiment. As mentioned earlier only one campaign (i.e. with CANDU fuel) was foreseen for this experiment during the planning stage. A change in the operation schedule of the EUROCHEMIC plant however, required successive reprocessing of fuels from four different reactors namely CANDU [+)], VAK [+)], CDN [+)], TRINO [+)]. Although this changed the original planning of the experiment, it provided a unique possibility for the application of PID (without any intermediate washout) a number of times during the experiment, as each of these fuel types had different

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[+)] Different reactor types, explained in chapter 2.

concentration of isotopes. A short description of the method and a detailed analysis of the results, which indicate the successful application of this method in a reprocessing plant under a variety of operating conditions, are presented in chapter 5.

d) Minor Isotope Correlation Techniques (MIST)

This technique is gaining rapidly in importance as a safeguards tool. It was recognized that the present integral experiment would provide realistic conditions to test and establish correlations between different isotopes in fuels coming from different types of reactors. As shown in chapter 6, fairly simple linear relations could be shown to exist between the depletion of uranium and the build-up of plutonium for the CANDU type fuel. Similar relations which were known to exist for similar type of reactors were corroborated broadly for the rest of the reactor types also.

e) Interlaboratorium Test

Initially proposed to be carried out as an interlaboratorium test for measurement of isotopic ratios only, the test was extended later to the methods for uranium and plutonium concentrations by chemical and X-ray fluorescence methods as well as by isotopic dilution methods. An analysis of efforts indicated later, that the largest part of analytical and manpower efforts spent in the framework of the integral experiment was required for this test. Detailed descriptions of this test and an elaborate analysis and comparison of the results from this test are to be found in chapter 7 of this report.

All the input data required for the planning, execution, and evaluation of the integral experiment are collected and presented in chapter 2 of this report.

It is to be noted from the foregone description that the conditions and the expected operation data changed in course of the planning phase of the experiment. As a result the objectives of the experiment changed also. In view of the subject matter discussed in this report the objectives of the present integral experiment may be redefined as follows:

1. Identification of irradiated fuel elements.
2. Simulation of fissile material flow to ascertain the influence of relevant process parameters on the physical inventory determination using an isotopic step function.
3. Experimental demonstration of the physical inventory determination using an isotopic step function.
4. Application or isotopic correlation techniques to the different fuels processed during the integral experiment.
5. Interlaboratorium comparison of measurement methods for the concentration and isotopic ratios of uranium and plutonium.

The execution of the different phases of the present integral experiment extended over the period January-June 1970. Fig. 1-1 gives an idea on the time spent by the different participants at the EUROCHEMIC plant in connection with this experiment.

It should be noted here that the present integral experiment has been reported to in the literature quite often as the Mol III experiment (since it was the third integral experiment at EUROCHEMIC, Mol) or the JEX-70 experiment (Joint integral experiment, 1970). Both these terms are equivalent.

The present integral experiment has proved to be a dynamic and a challenging venture. It required skillful and bold actions at almost every phase of the experiment from all the participants. It is to be expected that this experiment will be counted to those events which may contribute to the successful application of international safeguards.

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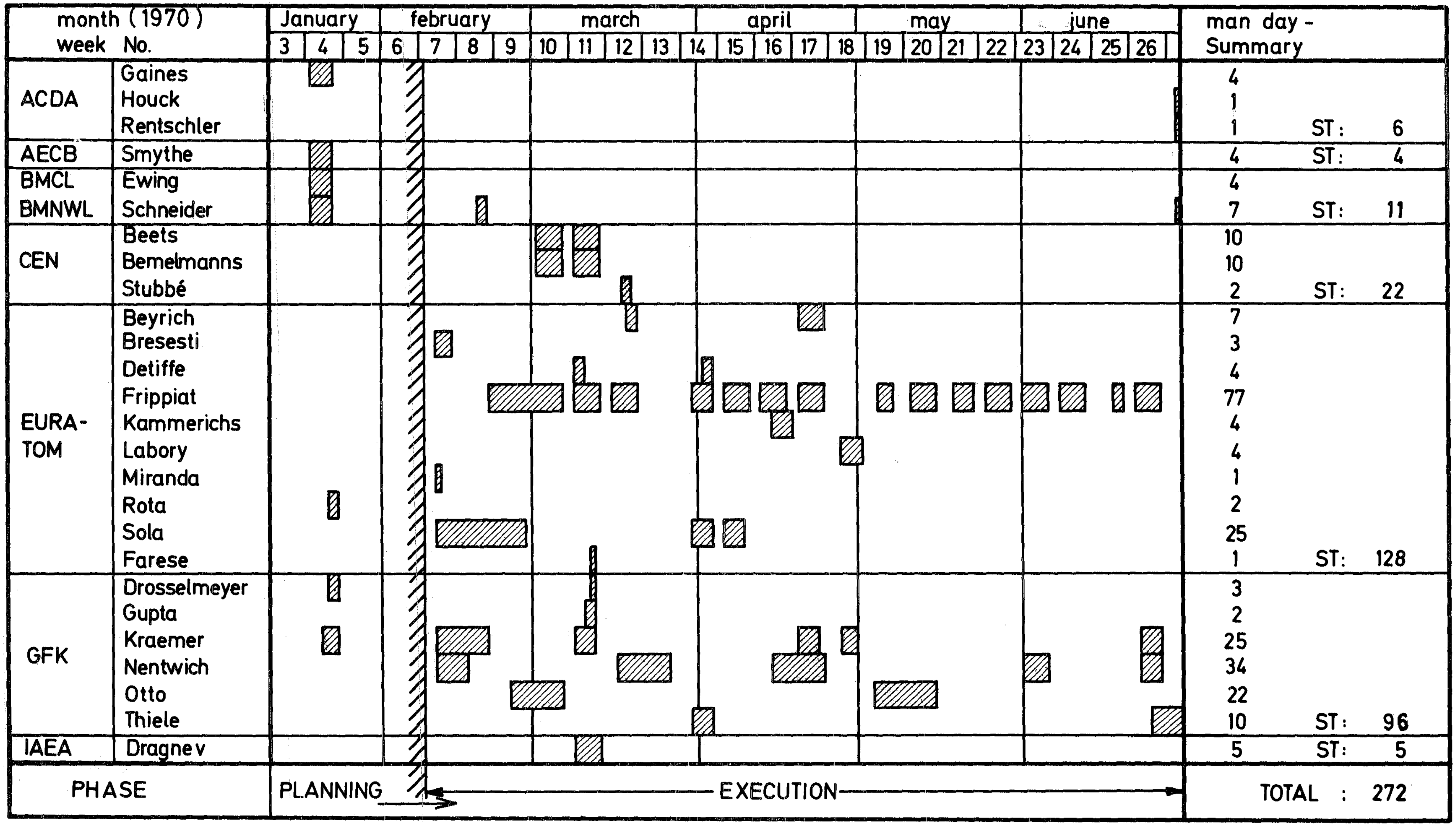

Fig. 1-1 Review of visits at EUROCHEMIC, Mol, Belgium during the joint experiment (JEX -70)

Chapter 2

Layout and Data Acquisition of JEX-70

by

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Abstract

This chapter headed "Layout and Data Acquisition of JEX-70" is to be understood as a collection of all information and data relevant for the following chapters.

The first part covers a general description of EUROCHEMIC plant layout followed by details about the defined material balance area system and relevant nuclear material flows inclusive their accountancy system as used for the establishment of a nuclear material balance both of Plutonium and Uranium.

The second and main part summarizes the data acquisition on

i) shipper and receiver data of spent fuel from four different reactors to be processed during JEX-70 and

ii) actual campaign data on input, product and waste flows which were partly subject of independent verification procedures.

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2.1 Plant Layout and Description of the Process

The EUROCHEMIC site is situated on the territory of the communities of Dessel and Mol in the northern part of Belgium, about 50 km east of Antwerp. The reprocessing plant (see Fig. 2.1-1)[1] which is located in the "active" section of the site comprises among others the Main Process Building (1), the Fuel Reception and Storage Building (2), the Analytical Laboratory (3), two Product Storage Buildings (6a and 6b) and five structures for waste treatment and storage (5,22,21,8,23).

The sequence of operations for Low Enriched Uranium (LEU) process is as follows (see Fig. 2.1-2 for the U-cycle schematic flowsheet and Fig. 2.1-3 for the Pu-cycle schematic flowsheet)[2].

Irradiated fuel elements which have been stored in the water-filled ponds of the Reception and Storage Building are, after an eventual mechanical treatment, loaded into a heavily shielded charging machine and transferred to a platform on top of the dissolver cells.

The cladding dissolution takes place in tank 221 for fuel with enrichments up to 1.6 % only and in tank 226 for fuel with enrichments up to 5 %. After the decladding of the fuel is complete the dissolver (unit 221) is cooled and the decladding solution is transferred to vessel 221-5 by steam jet. Here the solution is sampled and finally transferred to the clarification unit (223). The dissolver is then rinsed with water.

After the decladding operation is completed, the fuel dissolution takes place in the dissolver (226-1/2) using fresh or recovered nitric acid. After the dissolution is completed the dissolver is cooled and the unadjusted active fuel (AFU) is transferred to input accountability tanks 221-4 and 221-6. The dissolver is rinsed with nitric acid and water which is added to the AFU. After sampling and volume determination the AFU is sent to unit 223 (tanks 223-6a/6b)

Here, the active feed is adjusted to the correct concentration in acid and uranium and thereafter the solution is siphoned to tank 231-1, the feed tank to the extraction unit. The insoluble residues obtained during the adjustment operation are resuspended in water via sample tank 223-13, tanks 223-4 and 223-5 to the Medium Lowel Waste (MLW) Storage.

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[1] taken from /̅2.1-1_/

[2] taken from /̅2.1-2_/

In the first extraction cycle and concentration unit (unit 231), uranium and plutonium are first separated from the bulk of the fission products by means of solvent extraction, using as the solvent a 30% solution of TBP (tributylphosphate) in a kerosene type diluent. A gross fission product decontamination factor (DF) of about $2 \cdot 10^4$ is obtained, while the U and Pu losses are estimated to be 0.3 % and 0.1 % respectively.

As the contamination of the U leaving the first cycle is too high to meet the specification for the end product, a second cycle is necessary for further decontamination. A gross fission product DF of at least 50 is expected in the second extraction cycle and concentration unit (unit 232).

The concentrated uranium solution obtained as an output from the second cycle is finally purified by being passed through a column packed with silica-gel. This column absorbs fission products, particularly Zr/Nb, and retains insoluble matter. The purified stream coming from the top of the columns is collected in vessels 241-4a or b. As the uranium solutions of enrichment between 1.6 and 5 % have to be controlled by concentration or mass, the final uranium concentration is checked in 241-4a/b prior to transfer to the product blend tank 241-6 in building 6a and to the product storage tanks (unit 242).

After the solution in each tank has been mixed (recirculation by centrifugal pump), accountability control is done by sampling and level measurement.

The uranium solutions are then pumped into the transport containers (unit 243) for shipment.

The plutonium solution leaving the extraction column goes to product receiver tank 231-58. Final purification is obtained with a battery of mixer settlers (unit 237). The evaporator 236-2a/b concentrates the plutonium coming from the extraction unit, the concentrate being placed in tank 2436-1. A dry cycle is then performed in unit 238 which yields, after calcination, a final product under the form of Pu oxide powder.

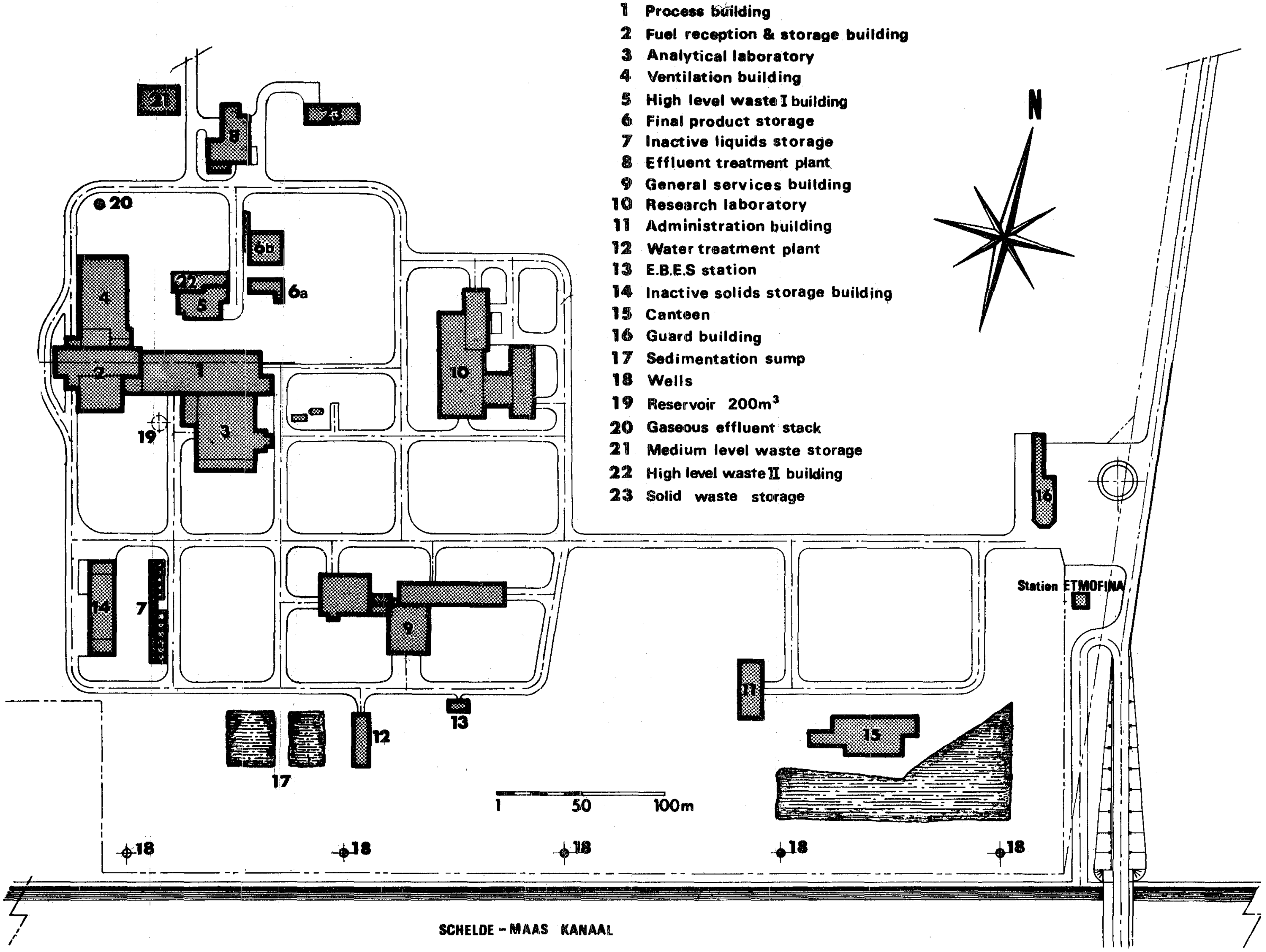

Fig. 2.1-1: **Eurochemic Site Lay-out**
(ref. /_2.1-1_/)

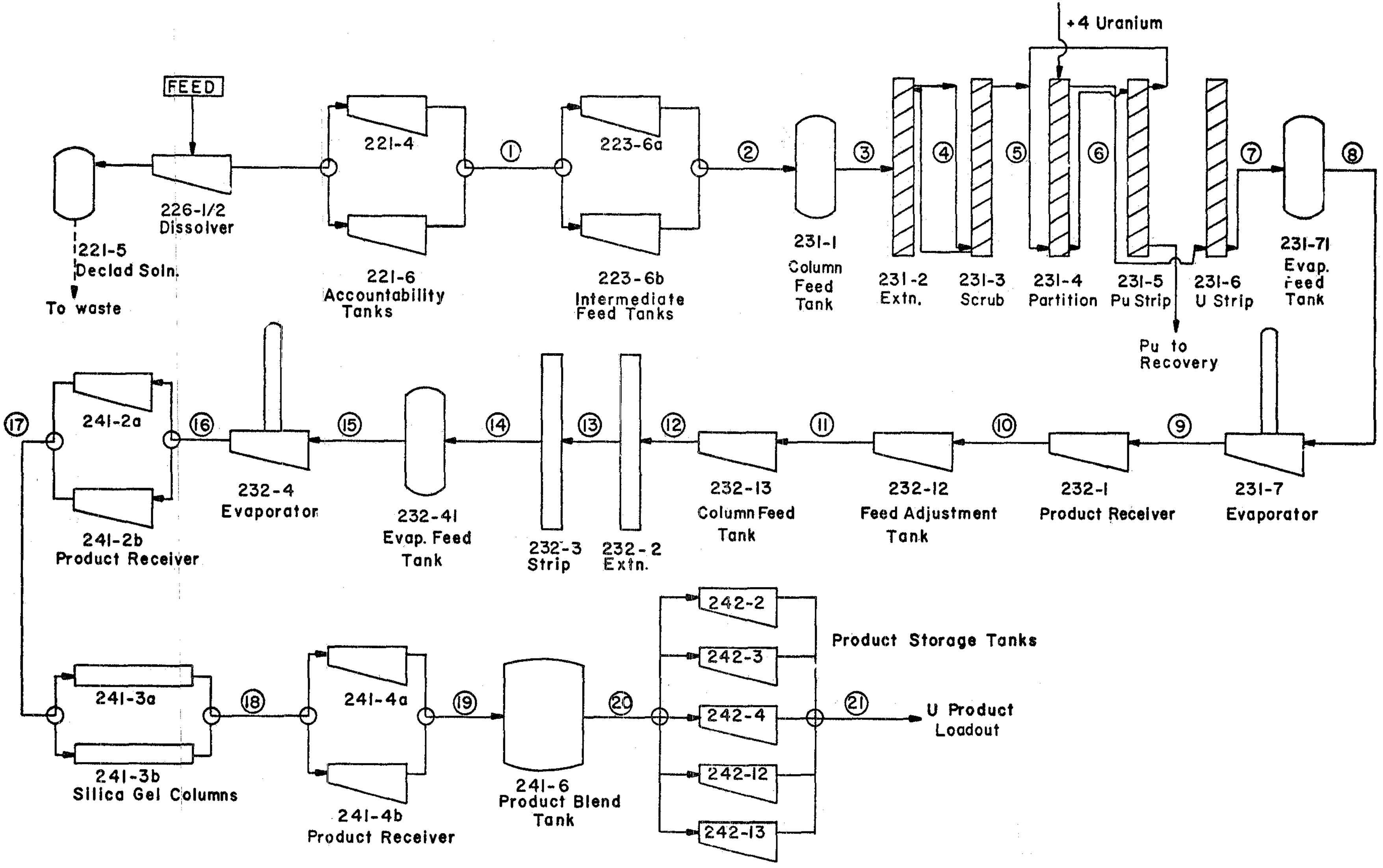

Fig. 2.1-2: SCHEMATIC FLOWSHEET EUROCHEMIC PLANT-U Cycle

Feb.9, 1970

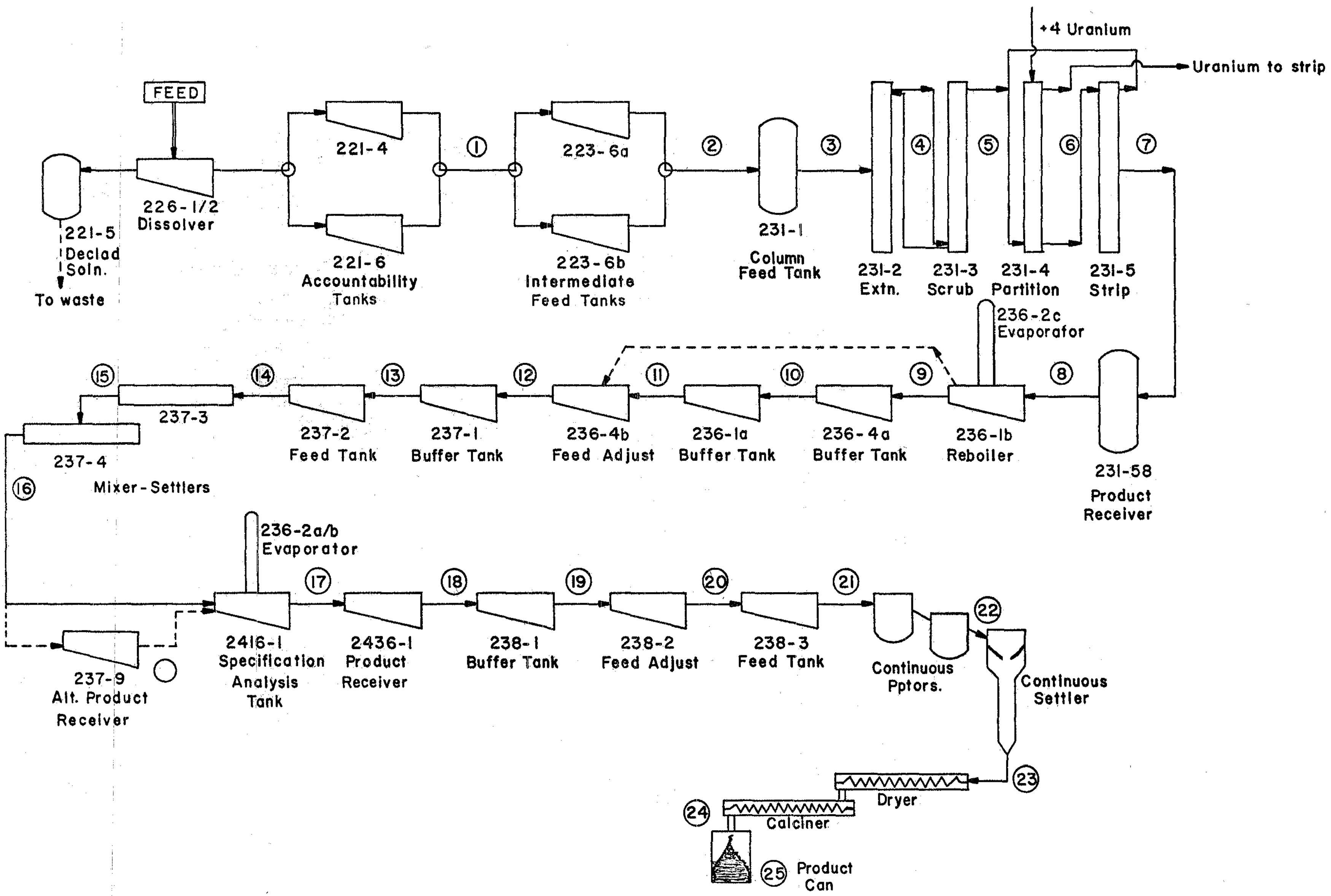

Fig. 2.1-3: SCHEMATIC FLOWSHEET EUROCHEMIC PLANT - Pu Cycle

Feb. 9, 1970

2.2 Definition of the Material Balance Areas (MBA) and of Controlled Fissionable Material Flows

In accordance with the objectives defined in chapter 1 and with plant layout section 2.1 the MBA-system shown in Fig. 2.2-1 for uranium flow and in Fig. 2.2-2 for Pu-flow respectively was defined at the beginning of the experiment. One of the main objectives of this joint exercise which influenced to a high extent the choice of the MBA was the experimental demonstration of the physical inventory determination by use of isotope analysis. This method requires a MBA which covers only the process part because one wants to follow certain isotopic signals of the main material flow through the process and to avoid the time delay and the great homogenisation which is associated with material management in storage facilities.

The application of isotope correlation technique (MIST) required an additional MBA only covering the dissolver(MBA 12 in Fig. 2.2-1 and 2.2-2). With help of this MBA one is able to account the quantities of nuclear material in the dissolved fuel elements and to correlate them with the initial figures as mentioned in the fabrication plant.

The different nuclear material flows crossing the boundaries of the MBA-system such as feed, product, waste and recycled material are specified in Table 2.2-1 and correspond with operators' codes as indicated in Fig. 2.2-1 and 2.2-2. Table 2.2-1 shows also the independent verification procedures on operators' accountability data received from the accountability section of EUROCHEMIC. With respect to transfer measurements JEX-70 observers were to establish a synchron volume-time plot of each interesting flow indicated in Table 2.2-1 (column 4) as transfer recording. This procedure is of great help for safeguards in reprocessing plants for the calculation of a running book inventory and the plot replaces completely special observer log-books because all interesting indications and remarks can be clearly entered in this diagram.

Independent analysis of U and Pu and their isotopes was covered either by composite sample technique or by single batch analysis in case the system response to an isotope step input signal was interesting with respect to the inventory experiment. These samples were partly subject of the interlaboratory test (chapter 7).

The definition of MBA 21 involved the accountability of an additional U-input stream (BXR) in the order of 5-10 % of AFU, which is required in the separation unit as reducing agent. This flow was partly recycled from an other MBA and partly internally recycled within MBA 21. Thus in the latter case no material transfer had to be accounted whereas the external recycle must be accounted. This external recycle represents in fact an additional input stream which is mixed with the main stream. Thus the product signal becomes a mixture of two dispersed input signals. As shown in chapter 4 these two input signals have to be corrected to one input signal otherwise the evaluation of the U-inventory by means of isotope analysis is not possible.

The Pu-product signal was followed in the 2BP-flow which passes the last accountability station before conversion into Pu-oxide. This MBA-system involved the accountability of the recycled mother liquor (3AW) from the Pu-precipitation unit. The analysis of the 3 AW-flow was covered by composite sample analyses. The analysis of 2 BP-flow compared with the PFP (Pu-oxide in containers) had the advantage that there was a considerable reduction of samples to be analysed for its isotopic composition.

On the other hand PFP data were completely made available from the operator, thus a very useful comparison of the two Pu-product flows could be established.

When using PFP-data for the inventory experiment both MBA 21 and 22 had to be considered whereas the use of 2 BP data reduces the balance area to MBA 21. Both alternatives are shown in Fig. 2.2-2.

Table 2.2-1: Nuclear Material Flows relevant for JEX-70

Operator's code	Definition	Accountability Tank no.	Independent verification procedures on operator's accountability data
1	2	3	4
AFU	Active feed unadjusted	221-4/6	Transfer recording, preparation and analysis of diverses composite samples (U and Pu totals and their isotopes
RAR	Recovered acid recycle	221-7	Transfer recording
UD	Undissolved discards	-	-
JD	Jacket (decanning) dissolution	226-2/221-5	-
BXR	Uranium (IV) recycle	building 10	Transfer recording
3 UP	Uranium product (3rd cycle)	241-4a/b	Transfer recording, analysis of single batch samples (U-total and isotopes)
2 BP	Pu battery product	2436-1	Transfer recording, analysis of single batch samples (Pu-total and isotopes)
PFP	Pu final product	product cans (PC)	Transfer recording
3 AW	Recycled mother liquor from precipitation	238-5	Preparation and analysis of 2 composite samples (Pu total and isotopes)
HAW	High active waste	251-1 a/b/c	-
SRW	Solvent recovery waste	234-22b/239-5	-
RIN	Rinse solutions	252-11/241-5	-
LLW	Low level waste	CEN	-

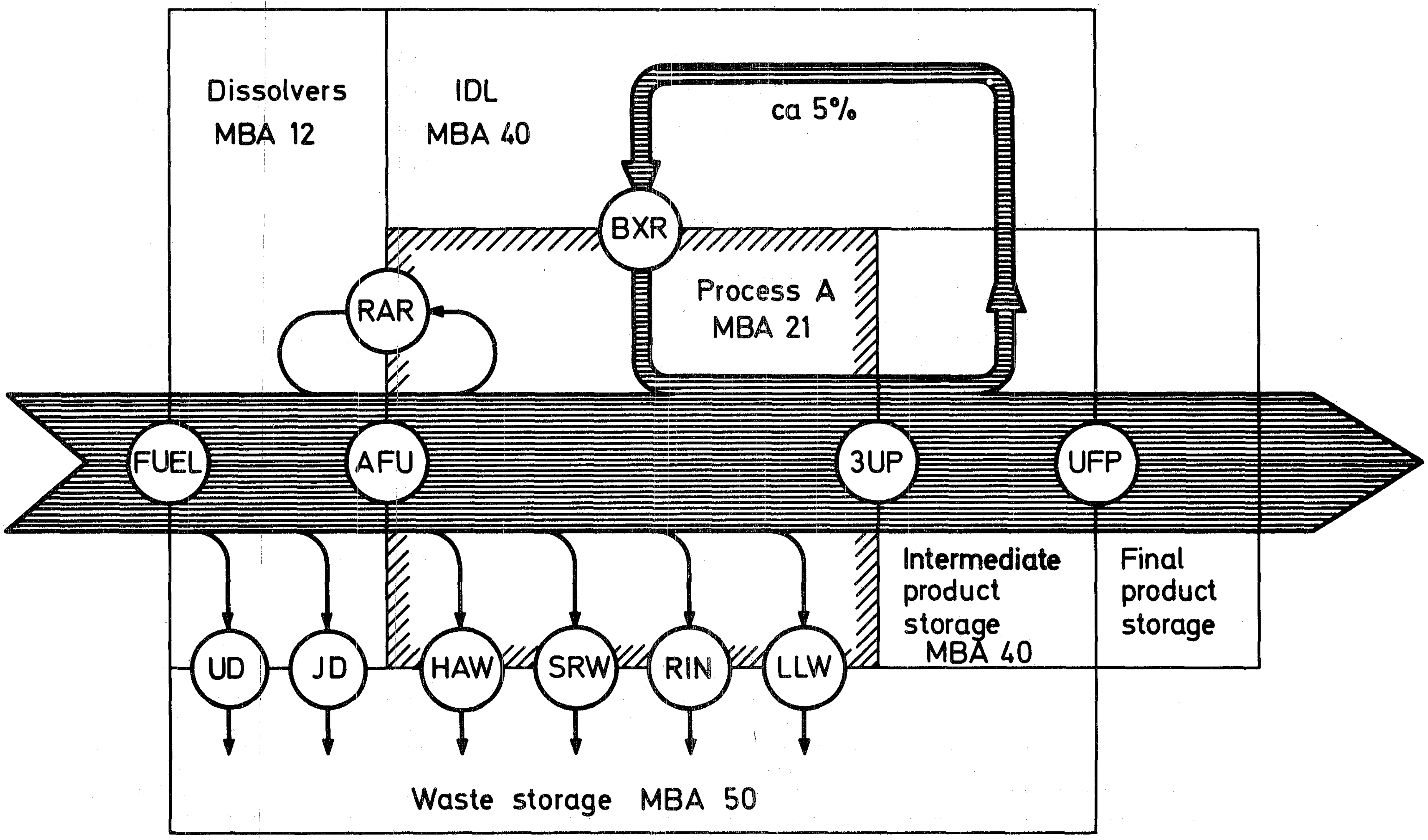

Fig. 2.2-1 Scheme of U-flow and MBA-system defined for JEX 70 in EUROCHEMIC, MOL, BELGIUM

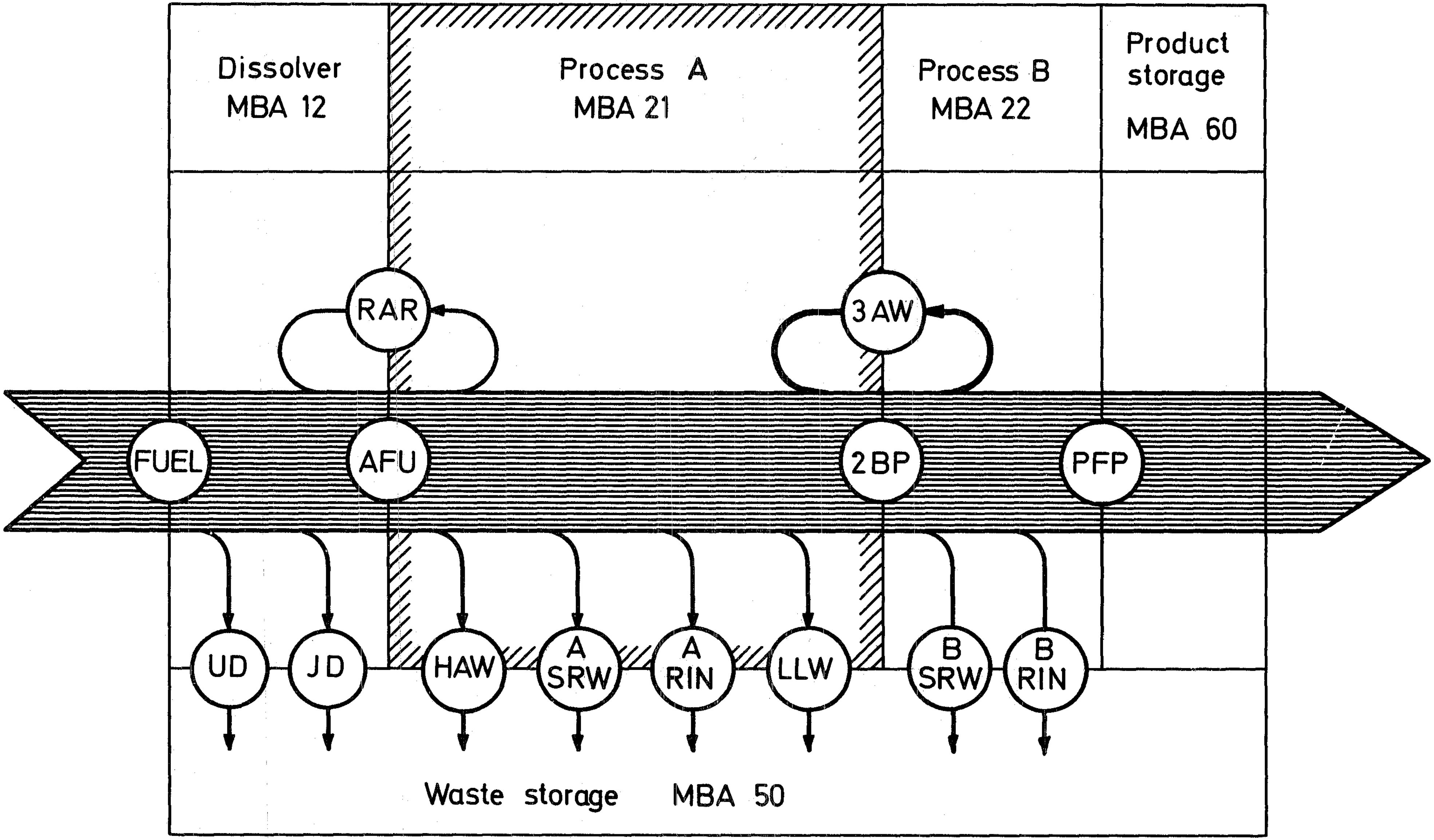

Fig. 2.2-2 Scheme of Pu-flow and MBA-system defined for JEX 70 in EUROCHEMIC, MOL, BELGIUM

2.3 Accountability of Nuclear Material

The quantity of nuclear material in one accountability batch is determined by measuring two components:

i) Mass or temperature corrected volume of transferred solution and

ii) Representative concentration of heavy nuclei (e.g. U, Pu and their isotopes) as mass fraction or per liter solution. In the latter case one has to pay attention that i) and ii) correspond in their reference temperature.

In the following a short description is given about the transfer measurement system, sampling technique, and analytical equipment installed at EUROCHEMIC (see also ref. /‾2.1-1_7).

2.3.1 Transfer Measurements

A detailed description of the transfer measurement system and its calibration procedures in case of input accountability tanks installed at EUROCHEMIC is given in /‾2.3-1_7. The same principle is applied there at all important accountability tanks for waste. Final product batches are normally weighed on a brutto-tara difference basis.

The quantity of solution in a tank is determined on the basis of a purely geometrical relationship, volume as a function of height. The "height" of the filled part of the tank, i.e. the liquid level, is measured by means of a calibrated system of dip-tubes installed in the tank. A stream of air with constant flowrate is pushed through these tubes and the pressure needed to keep this flow (the hydrostatic pressure at the reference level in the tank) is measured. At the same time, the density of the liquid is determined from the hydrostatic pressure differential on a calibrated height difference.

Fig. 2.3-1 [1] shows the characteristics of two input tanks (221-4 and 221-6). The level and density measurement instrumentation consists of a dip-tube system for determination of pressure differences. The reference point for pressure measurement is just on top of the tank in order to minimize the influence of the air flow-rate on the pressure measurement. The instrumentation of the tanks is shown in Fig. 2.3-2 [1].

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[1] Taken from reference /‾2.3-1_7

Level and density pressure differences are measured by U-tube manometers, 2 metres long, filled with TBE = tetrabromoethane (specific gravity approx. 2.95) and water, respectively and/or by transmitted electrical signals on recorders at the panel.

Regarding the more accurate U-tube manometer readings density of the tank solution is determined by equn. (2-1)

$$(2\text{-}1) \qquad \rho = \rho_m \cdot h_D / \hat{h} \qquad [\text{kg/l}]$$

where ρ_m is the temperature corrected density of the manometer liquid (H_2O), h_D the manometer reading, and $\hat{h}$ the constant difference in height of the two density diptubes.

The liquid level is obtained by equn. (2-2)

$$(2\text{-}2) \qquad h = h_l \;\; \rho_m / \rho \qquad [\text{mm}]$$

where ρ_m is the temperature corrected density of the manometer liquid (TBE), ρ from equn. (2-1) and h_l the level manometer reading.

Correlation between volume and level is given by the tank calibration curves which represent a least square fit to the different calibration points. Following formulas have been used as a consequence of the geometrical shape of the tank:

$$(2\text{-}3) \qquad v_1 = a_o + a_1 h + a_2 h^2 \; ; \quad h \leq h_1$$

$$(2\text{-}4) \qquad v_2 = a_3 + a_4 h \qquad ; \quad h_1 < h \leq h_2$$

where h_1 and h_2 limit the parabolic and linear range respectively.

The quality of the calibration (e.g. number of calibration runs, instrumentation used etc.) is according to the accuracy required. Input accountability tanks for example have highest specifications on the calibration. In this case equn. (2-3) and (2-4) are replaced by calibration tables as given in [2.3-1] which fit more closely to the different calibration points.

The information concerning a transfer from one tank to another are reported on a nuclear Material Transfer Report (NMTR). A NMTR is identified by a reference number and refers to a RSTA (see below); it indicates the batch identification number, between which tanks the transfer takes place and in which tank the measurements are made.

The density, the level and the temperature are measured before and after transfer; the readings made on each branch of the manometer are indicated, as well as the value of an eventual correction when the two branches of the manometer are not at the same temperature. These data allow the evaluation of the transferred mass or volume of solution (see specimen NMTR).

Attention has to be paid on the mode of transfer whether it is interesting to account the receiving or the leaving batch in a special accountability tank. The first mode is important for input accountability in order to keep the identity of nuclear material in dissolved fuel elements as required for the establishment of shipper receiver differences and isotope correlation technique (chapter 6). The leaving batch accountability is more simple because no attention has to be paid on different heel concentrations.

The information about sampling and analysis is reported on a "Report of Sample Transfer and Analysis" (RSTA) identified by a reference number and with reference to the corresponding NMTR number.

In case analyses for accountability purposes are requested U- and/or Pu concentrations and if requested weight percents of corresponding isotopes are entered in this form. The same form is also used for information required for process control and specification analyses of fission product concentrations.

NSD-AS-3A
FE 4-4-67

SPECIMEN

NUCLEAR MATERIAL TRANSFER REPORT N° [illegible]

RUN CODE: LEU/72 CANADIAN
TRANSFER FROM: 226-2 TO: 221-4 BY [✓ JET]-PUMP-SYPHON-AIR LIFT N° 226-J-203.
END OF TRANSFER DATE 6-3-70 TIME: 05h45
CORRESPONDING RSTA N°: 40181
BATCH IDENTIFICATION: AFU-500

Measurements in tank n° 221-4	BEFORE TRANSFER Instrument Readings		BEFORE TRANSFER Panel indications	AFTER TRANSFER Instrument Readings		AFTER TRANSFER Panel Indications	REMARKS (Indicate here type and n° of instrument used)
TEMPER. OF SOLUTION			13 °C			35 °C	−2/+2 → 0
DENSITY	PD −2 mm/ +2 mm		ρt / kg/l	PD 164 mm/ 1195 mm		ρt 1,43 kg/l	−2⁵/+2⁵ → 0
LEVEL	PL −2 mm/ +2 mm		0 %	PL 777 mm/ 779 mm		82 %	
MANOMETER TEMP.	25 °C			15 °C		/	
TANK CONTENT RELEASED BY N.S.D				Checked by Shift Supervisor (signature)			
DATE ____ TIME ____ SIGNATURE:							

For N.S.D.-A.S. calculations

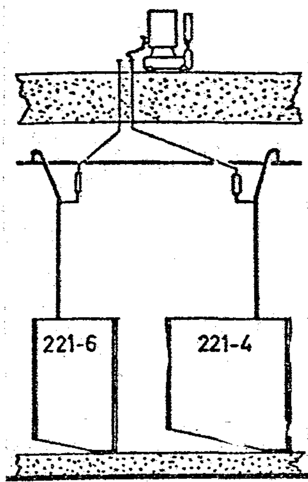
CORRECTED DENSITY IND.	PD 0 mm		PD 3335 mm		acc to 334.5 × 0.99707
CORRECTED LEVEL IND.	PL 0 mm		PL 4589.1 mm		acc. to 1558 × 2.9455
ACTUAL DENSITY	ρt 1.3315 kg/l		ρt 1.4101 kg/l		$\rho t = \frac{P_D}{h}$ with h = 236⁵ (stand. dist. of D. dip tubes)
ACTUAL LEVEL	ht / mm		ht 3254.5 mm		$ht = \frac{P_L}{\rho t}$
ACTUAL VOLUME	V_A 0.6 L		V_A 2714.1 L		calc. acc. to: bef. trans. table / aft. trans. table
STANDARD DENSITY	ρ25 0.8 kg/l		ρ25 3827.2 kg/l		
STANDARD VOLUME	V_S L		V_S L		$V_S = V_A \cdot \frac{\rho t}{\rho 25}$

	AVERAGE ANALYTICAL CONCENTRATION				ISOTOPIC PLUTONIUM COMPOSITION
TOTAL U	176.3 g/kg		1424.7 g/kg		Pu 239 74.77 P8 0.12 Pu 241 3.15
U-235	0.335		0.305		Pu 240 21.63 Pu 242 0.34
TOTAL Pu	491.9 mg/kg		513.9 mg/kg		U4 0.005 U6 0.065 U8 99.62
	QUANTITIES OF NUCLEAR MATERIALS				QUANTITIES TRANS. FROM MBA 12 TO MBA 21
TOTAL U	141.0 g		685402.2 g		TOTAL U 685 261 g
U-235	0.5 g		2148.8 g		U 235 2148.3 g
TOTAL Pu	0.4 g		1929.8 g		TOTAL Pu 1929.4 g

CALCULATED BY: CC DATE: 16/3/70

LINING UP FOR CALIBRATIONS

Scale: 1/200



DIMENSIONS (in mm)

TANK N°	a	b	c	d	e	f	g	h	i
221-4	421	1359.5	1310	895.5	236.5	20	96	295	3210
221-6	421	1359.5	1310	895.5	239.0	20	96	295	2210

1+3 : Level dip tubes
1+2 : Density dip tubes
4 : Inlet air for sampling
5 : Sample outlet
6 : Sample return line
7 : Air sparging line
8 : Steam line for int. dec. jet
9 : Ventilation line

221-4 :
3 Feed lines
5 Removal lines

221-6 :
4 Feed lines
9 Removal lines

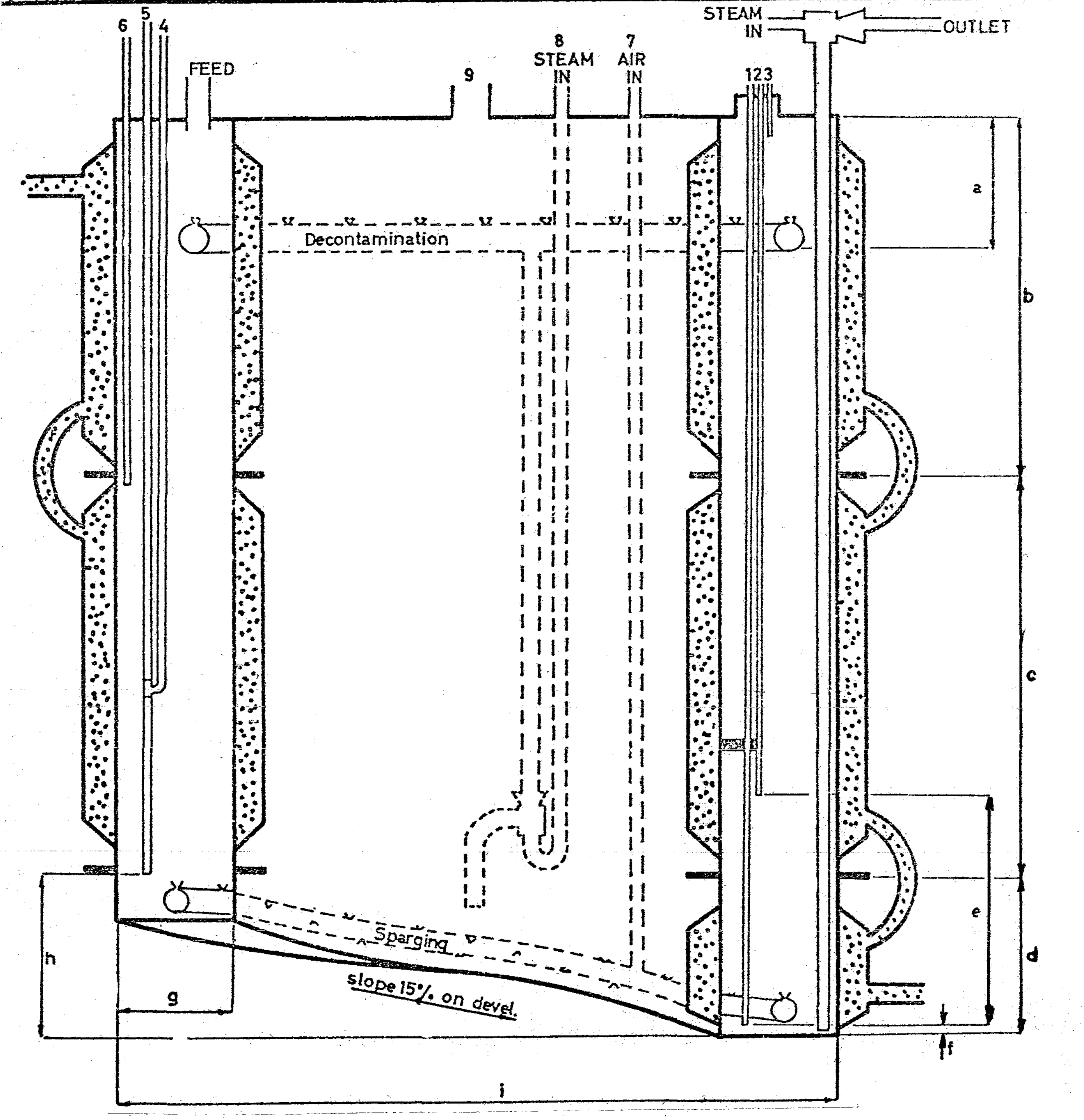


Fig. 2.3-1: CHARACTERISTICS OF INPUT ACCOUNTABILITY TANKS AT EUROCHEMIC

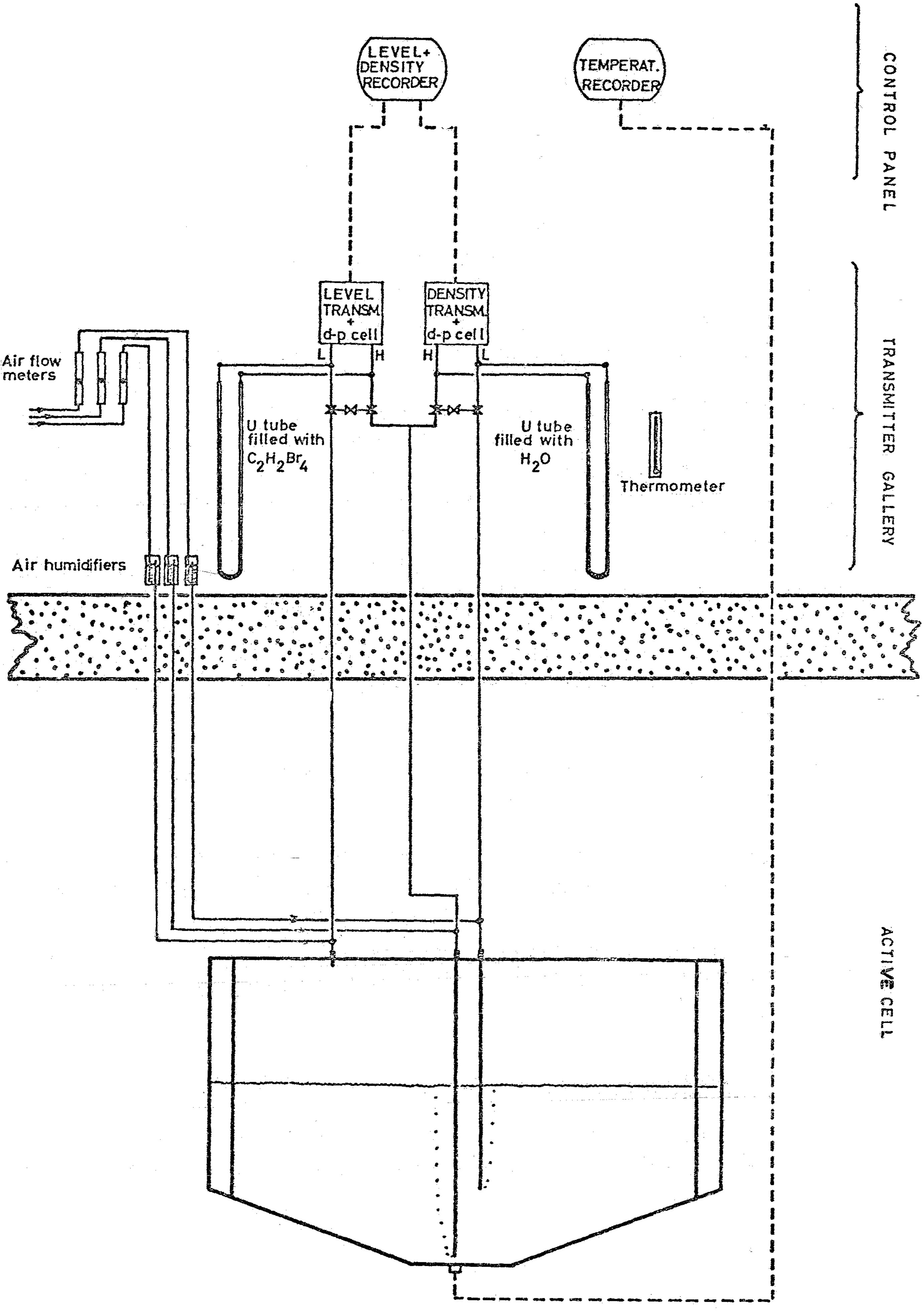


Fig. 2.3-2: SCHEME OF INSTRUMENTATION SET-UP FOR VOLUME DETERMINATION

2.3.2 Sampling Techniques (see also chapter 7; fig. 7.2-1 and /‾2.1-1_7)

The main sampling system is essentially an "air-lift" system.
The liquid to be sampled is lifted from a tank by a vacuum up a lifting pipe into which the air of the air-lift is introduced. The air circulates the liquid when the vacuum has created sufficient submergence. The air-liquid mixture is lifted up the pipe, passes through the sampling bottle and arrives at the drain line of a separator pot. The liquid returns to the vessel by gravity and the air passes to the vacuum system.

The samples are taken in 13 special shielded cells (blisters) each containing 8 sampling points. The samples are contained in small sealed glass bottles which are placed in plastic containers. A pneumatic dispatch system transports samples of radioactive material from the blisters to a distribution box in the Analytical Laboratory and from there either to the aliquot boxes in the box chain for high activity samples, or to the laboratory for low activity samples.

A system is provided to inform the receiving station in the Analytical Laboratory that a sample has been dispatched from the plant. The arrival of each sample is also indicated. Thus it is possible to discover at once if a cartridge is stuck in the line.

Direct sampling is also applied to solutions of low activity in the LLW (Low Level Waste) intermediate storage:

An evacuated sample bottle is connected to a long needle, dipping directly into a sampling pot containing the solution to be sampled. The liquid is thus sucked into the bottle. The sampling pot is filled by pumping liquor from the tank to be sampled. Other sampling systems, for occasional sampling, exist too; the samples obtained are transported to the Analytical Laboratory in shielded containers.

2.3.3 Analytical Laboratory

The Analytical Laboratory contains equipment for receiving samples and distributing them to shielded boxes, α-boxes and fume cupboards for analytical determinations.

In the high activity laboratories there is a chain of 13 shielded air tight boxes and of 10 unshielded boxes. Solutions are pipetted and analytical determinations are carried out in these boxes. Various analytical techniques are used, such as potentiometric titration, spectrophotometry, weighing, dilution and extraction. The shielded chain of boxes is used for analysing samples containing γ-emitters in quantities requiring shielding.

Preparation for counting is done in two fume cupboards in each high activity laboratory.

In the α-laboratory, located in the low activity area, α-active samples are analysed. Among others, the analysis of the final uranium and plutonium product streams is carried out here. The laboratory has seven conventional glove boxes, two benches and one fume cupboard. One glove box is used for sample storage.

The low activity laboratory is used for radiochemical analyses and preparative work involving small quantities of radioactive material. It is equipped with twelve benches, two reception boxes and six fume cupboards. If required, up to four conventional glove boxes can be installed.

The thermal emission mass spectrometer, loacted in the inactive area, is an important instrument in the spectro-analysis laboratory, as it is used to measure the isotopic composition of uranium and plutonium samples from the input and output tanks of the plant. Concentrations may also be determined accurately using isotope dilution mass spectrometry.

An emission spectrograph with auxiliary equipment is used to determine the traces of impurities in the uranium and plutonium final products.

Sample preparation for the instruments is done in the α-laboratory or in the target preparation laboratory, which has a bench and two fume cupboards. The fume cupboards are used for solidifying small amounts of plutonium and uranium solutions onto the filaments of the ion source bead for mass spectrometry, for evaporating solutions in the porous cup electrodes for emission spectrography and for other target preparation work.

2.3.4 Error Analysis on Nuclear Material Flow Measurements

A major effort from the view point of safeguards has to be paid on the error analysis associated with nuclear material flow measurements. These efforts result in a statement on any significance of MUF [2.3-2].

Supporting data on estimated relative standard deviations (RSD) associated with transfer measurements and analysis are compiled in table 2.3-1. These data result from operator's quality control and are supplemented by interlabtest results (chapter 7). Subdivision in calibration (δ_c) and random error (δ_R) respectively is due to their different treatment with respect to the accumulated RSD of the total flow which follows equn. (2-3) provided each batch shows equal volume and concentration. For reasons of simplicity this can be roughly assumed.

$$(2\text{-}3) \qquad \delta_{flow} = \left(\delta_c^2 + \frac{\delta_r^2}{n}\right)_{volume/mass} + \left(\delta_c^2 + \frac{\delta_r^2}{n \cdot m}\right)_{analysis} \qquad [\%\ \mathrm{RSD}]$$

where c and r denote calibration and measurement respectively,
n = number of batches and m = number of analyses per batch.

The variance of MUF results in accounting the absolute variances of flows and physical inventories.

The statistical technique used for the evaluation of any significance of MUF is described in detail in [2.3-2] and in chapter 5.6.

Table 2.3-1: Estimated Relative Standard Deviations Associated with Transfer Measurement and Analysis

		TRANSFER MEASUREMENT			PU-ANALYSIS			U-ANALYSIS		
Stream	Tank	Instr. 1)	δ_c %	δ_R %	Method 2)	δ_c %	δ_R %	Method 2)	δ_c %	δ_R %
AFU	221-4	DT/UM	0.1	0.25	IDA 3)	0.3	0.7	IDA 3)	0.1	0.5
	221-6	"	0.15	0.25	IDA	0.3	0.7	"		0.5
RAR	221-7	DT/UM	1	2	α-count. IDA	5. (0.3)	5. (0.7)	colorimetry	0.5	0.5
JD	221-5	DT/UM	1	2	α-court.	5	20	colorimetry	10	10
	226-2	DT/R	5	5	"		20			
Liqu.W.	-	DT/R	10	10	α-count.	5-10	20	colorimetry	10	10
Sol.W.	-	-	-	-	Neutron-count.	10	20	-		-
2 BP	2436.1	DT/UM	1	2	α-count.	5	5	-		-
3 AW	238-6	DT/R	5	5	α-count.	5	10	-		-
PFP	Pu-cont.	balance	0.05	0.1	potentiometry	0.1	0.1	-		-
3 UP	241-4a/b	DT/UM	0.2	0.5	-		-	gravimetry	0.2	0.1
UFP	SAFRAP	balance	0.02	0.05			-	gravimetry	0.2	0.1
PI	-	DT/R	5	5	α-count.	5	10	colorimetry	10	10
U^{IV}-Recycl.		balance	0.2	0.05	-		-	gravimetry	0.5	0.5

1) DT = Dip-tube-system
UM = U-tube-manometer for level and density
R = Recorder for level and density

2) Operator's system

3) IDA = Isotope Dilution Analysis

2.4 Overall Nuclear Material Balance of JEX-70

2.4.1 Shipper-Receiver Difference

The reprocessing program provided by EUROCHEMIC covered spent fuel elements from 4 different reactors to be processed in close sequence without any intermediate flushout. The isotopic changes between consecutive reactor batches were to be used for the inventory experiment. There were additional 11.8 kg Pu from a former campaign to be processed after the normal run which were already present in the rework unit as starting inventory. This material could be regarded as a fifth reactor batch containing only Pu.

Table 2.4.1 summarizes the main characteristics of the spent fuel as reported from the different fuel element shippers. More detailed data can be extracted from chapter 2.5.1. Table 2.4-1 includes also integrated shipper-receiver differences.

A comparison of the predicted and measured values of the U and Pu amounts indicates that for all the cases with U there is a close agreement between these two values. For Pu such close agreement can be observed only in the case of the CANDU type fuel. For the TRINO reactor this agreement is less which may be partly caused by the very small number of fuel elements (4) available for the establishment of a shipper-receiver difference. For both the test reactors VAK and CdN the difference between the predicted and measured values is the highest. This may be due to fluctuating mode of operation of these reactors compared to the relative stable modes of operation of power reactors.

It should be mentioned in this connection that no detailed analysis of this particular problem was made in the framework of this experiment.

2.4.2 Nuclear Material Balance Report

The balance period lasted from January 11, 1970 (beginning physical inventory) up to July 1, 1970 (ending physical inventory). This period is shown in Fig. 2.4-1 as cumulative Pu-flow plot which represents the relation of cumulating Pu quantities at the input and product accountability stations vs time. The difference of both curves is roughly equal to the running book inventory of MBA 21 and 22 as only the total waste is considered in this figure. The numbers associated with the input curve represent the dissolution batch identifications. Due to technical difficulties the time sequences between two consecutive input or product batches are considerably variable.

The Material Balance Report of the Joint Experiment is presented in Table 2.4-2: The Uranium data were taken in MBA 21 and the Plutonium data in both MBA 21 and MBA 22. Information on the values presented in this table are given in paragraph 2.5.

It is to be mentioned here that MBA 21 defined for the Uranium balance does not correspond with operator's MBA for accountability purposes which covers additionally the U final product storage. But for reasons pointed out in 2.2 operator's U final product accountability could not be used in the context of the new inventory technique which was to be demonstrated during JEX-70. The relative great (negative!) MUF for Uranium observed in MBA 21 may have its origin by a undetected bias in the U product accountability tank (241-4a/b) which was used in JEX-70.

Table 2.4-1: JEX-70 Spent fuel data and shipper-receiver difference

Fuel	CANDU[1)]	VAK[2)]	TRINO[3)]	CDN[4)]	Starting Inventory	Total
No.of fuel elements	719	38	4	1507	-	-
Burnup /‾MWd/kg_7	4-8	13-22	8-14	~10	-	-
Initial enrichment /‾W/o_7	0.71	2.33-2.60	2.72-3.9	4.-4.5	-	-
kg U calculated	9504	1961	1214	694	-	-
kg U measured	9416	1928	1179	873	873	14083
ΔU/U measured /‾%_/	+ 0.93	+ 1.71	+ 3.0	+ 1.02	-	-
kg Pu calculated	30.35	11.37	7.11	1.37	-	-
kg Pu measured	29.91	9.95	6.70	1.22	12.62	60.40
ΔPu/Pu measured /‾%_7	+ 1.49	+ 14.30	+ 6.18	+ 12.2	-	-

1) Douglas Point Nuclear Power Station, Canada (D_2O-Moderator)

2) Versuchsanlage Kahl/Main, Germany (LWR)

3) TRINO, Vercellese Nuclear Power Plant, Italy (LWR)

4) EL3-Reactor, France

Table 2.4-2: Material balance report of JEX-70 for MBA 21 and MBA 22

Balance period: January 11 - July 1st	URANIUM (kg) mean	 ± SD	Reference chapter	PLUTONIUM (g) mean	 ± SD	Reference chapter
MBA	21		2.2	21+22		2.2
Physical inventory on January 11	873	± 43	2.5.2	12 619	± 130	2.5.2
Corrected input - CANDU	9427	± 27	2.5.3	29940	± 174	2.5.3
- VAK	1928		2.5.3	9949		2.5.3
- TRINO	1179		2.5.3	6698		2.5.3
- EL-3	687		2.5.3	1219		2.5.3
- Others	33	± 2	-	-		
Make up	672	± 6	2.5.4	-		
Total Input	14799	± 51		60425	± 217	
Output	14753	± 54	2.5.5	55001	± 63	2.5.6
Wastes - Liquid	180	± 18	2.5.9	1500	± 200	2.5.9
- Solid	-			450	± 22	2.5.7
Physical Inventory on June 28/ July 1st	105	± 5	2.5.2	3225	± 41	2.5.2
Total Output	15038	± 57	-	60176	± 215	-
Material Unaccounted For (MUF)	- 239	± 77	-	+ 249	± 305	-
MUF/Total Input [%]	- 1.6		-	+ 0.41		-

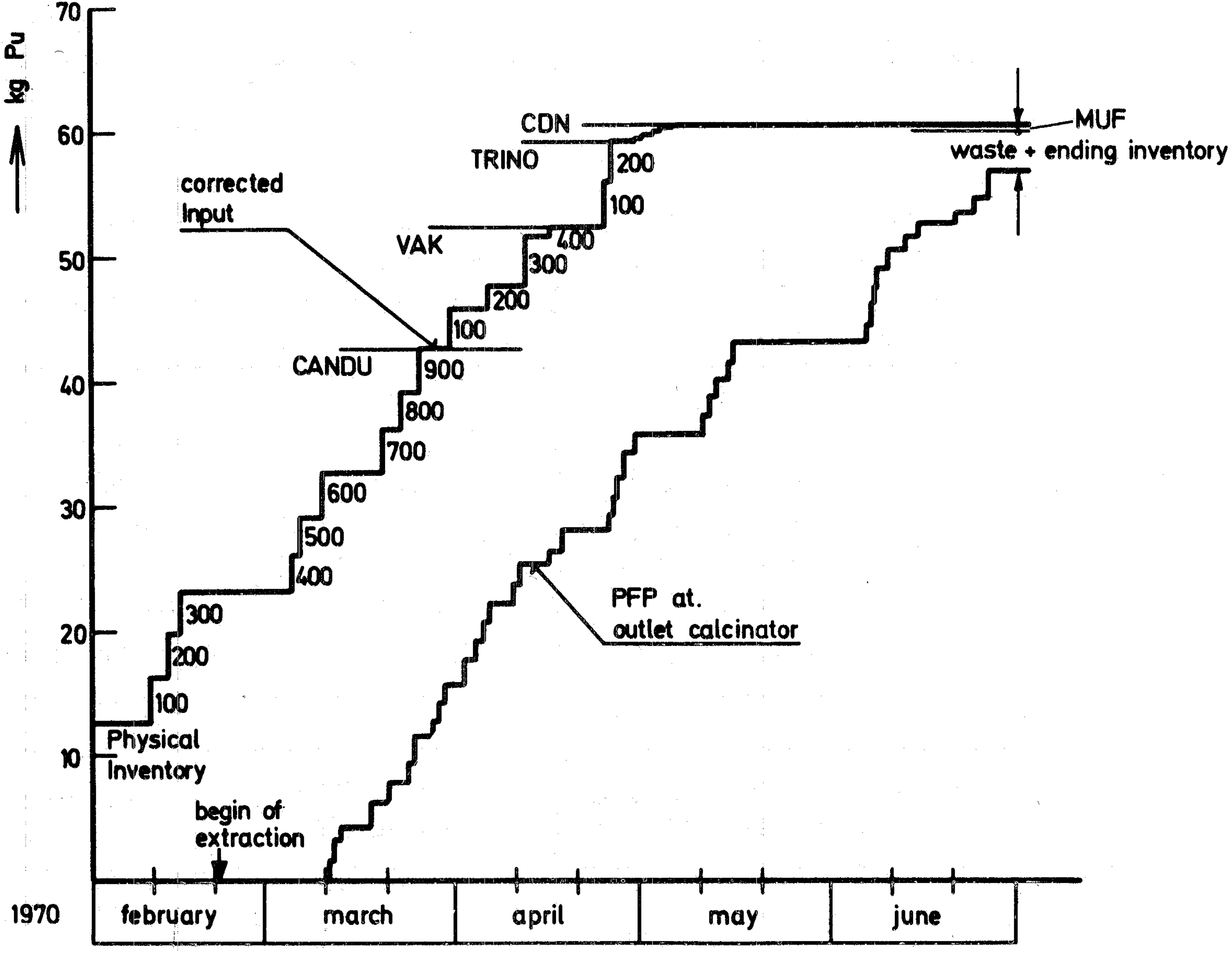


Fig. 2.4-1 Cumulative Pu-flow-plots of JEX-70

2.5 Data Acquisition

This paragraph summarizes all relevant data which were used for the nuclear material balance report (2.4). In addition a description of the dissolved fuel elements and their shipper's figures on calculated nuclear quantities is given.

2.5.1 Shipper's Data on Irradiated Fuels Elements. Description of the Fuel Elements

Fuel elements from the CANDU reactor, the VAK reactor, the TRINO reactor and the EL3 reactor were processed in JEX-70. These elements were shipped to the reprocessing plant together with shipper data providing information on the background and history of each fuel element. The shipper data were in turn used to determine how the fuel elements should be distributed to homogenize the dissolution batches with respect to the inventory experiment.

2.5.1.1 CANDU reactor (NPD)

A description of the CANDU reactor may be found in ref. /‾2.5-1_7. The fuel rods are filled with pellets (one end dished for differential thermal expansion) contained in Zircaloy-2 tube 0.6 in (1.52 cm) od. The length of a finished rod is 19.5 in (49.5 cm). The fuel consists of natural uranium in form of sintered UO_2; clad with 0.015 in (0.38 mm) Zircaloy-2. Subassemblies are made of 7 and 19 rods forming a 3.225 in (8.17 cm) od. and 19.5 in (45 cm) long bundle.

The shipper's data provide the following information

a) Reference number of the bundle.

b) Type of elements: this number refers to a code which specifies the fuel design. Types 1, 5 and 6 are 19 elements design; type 7 and 8 are 7 elements design.

c) Total weight in grams of the uranium contained in the bundle. The values vary from 13275 to 13674 for type 1; from 13195 to 13631 for type 2; from 12155 to 12915 for type 6; from 13395 to 13635 for type 7 and from 13635 to 15954 for type 8.

d) Calculated weight of uranium 235 (from 88 gm to 100 gm).

e) Weight of the bundle (about 16 to 17 kg).

f) Irradiation time in MWD/TU (megawatt days per ton of initial uranium): from 2700 to 8000, the average value being about 6000.

g) Removal date from the reactor (from 1964 to 1969).

h) Estimated weight of Pu, Pu-239, Pu-240, Pu-241, and Pu-242 in the bundle (in grams): the weight of Pu varies from 20 to 55 with an average of about 40.

i) Irradiation time at full power days: from 262 to 1617 with two exceptions à 53, the average being about 700.

j) Cooling time in days; the exact cooling time can be obtained as the difference between the date of removal from the reactor and the date of reprocessing in the plant (from February to April 1970).

k) Average power in kw of the bundle: from 25 to 200 with the two exceptions mentioned above at 630 and 760; the average being about 90.

l) Decay factor corresponding to the cooling time: from 0.8 to $5.6 \cdot 10^{-4}$ with the two exceptions at $6.75 \cdot 10^{-6}$; the average being about $1.8 \cdot 10^{-4}$.

m) Decay heat in watts: from 5 to 45 with an average of about 20.

Fuel element bundles were shipped for reprocessing in baskets, each basket containing about 60 bundles. Table 2.5.1-1 gives a summary of some of the shipper data for all the baskets together with some values calculated from these data. The first shipment was made of baskets 1,2,3,6,7 and 8 and the second shipment of baskets 1,2,3,4,5 and 6. The number of bundles in each basket, the total amount of Pu (in grams), the % weight of Pu-239, Pu-240, Pu-241 and Pu-242, the average irraditation time in MWD/TU and the total amount of uranium (in kgs) before irradiation: These data have been used to compute the total amount of uranium (Uf in kgs) left in the bundle after irradiation, the % weight of U-235 left in the bundle after irradiation and the % amount of U-235 left in the bundle after irradiation with respect to the amount of U-236. In addition there are given the average Pu/U ratio and average exposure.

As indicated in chapter 3 the identification of most of the CANDU fuel elements did not prove to be feasible. Out of the 9 batches made with the elements complete identification was obtained for batches 1, 2, 3; all the fuel elements except 9 were identified for the fourth batch and no identification was possible for the last five batches.

2.5.1.2 VAK reactor

A description of the German VAK reactor may be found in ref. [2.5-1]. The fuel elements are made of pellets, 1.27 cm od; 1.59 cm long; 48 pellets form a segment; and two segments form a rod; the rod diameter is 1.45 cm. The fuel consits of 2.4 to 2.6 % enriched uranium in form of sintered UO_2, clad with 0.85 mm Zircaloy-2. Subassemblies are made of 6x6 fuel rods contained in a square channel.

The shipper's data provide the following information:

a) Reference number of the fuel element. Three types of fuel elements were used: the 23 elements of type A had an enrichment of 2.33 %; the 8 elements of type B had an enrichment of 2.60 %; one element of type N had an enrichment of 2.48 %.

b) Various information as: manufacturer of the fuel (IGEOSA for types A and B; NUKEM for type N); drawing used for the fabrication; chemical form of the fuel (UO_2); physical form of the fuel (sintered); other material present in the fuel (none); eventual presence of other fuel elements in the reactor before loading (none) and eventual damage shown by the fuel when discharged (none).

c) Weight in kgs of the uranium contained in a fuel element: 63,2837 for type A; 63,2204 for type B; 63,498 for type N.

) Weight of uranium-235 in kgs: 1.4746 for type A; 1.6466 for type B; 1.572 for type N.

e) Irradiation time in MWD/TU; the values appear in Table 2.5.1-2.

f) Removal date from the reactor: 12/12/67 for elements B-4 and B-25; 19/10/69 for elements A-14/15/21/22/30/33/34/36/40/41/47 and B-30; and 10/9/68 for all the others.

g) Number of days when a fuel element was in the reactor (of the order of 2700) together with the number of days where the reactor had no power (of the order of 1700). The difference of these two values gives the irradiation time in days for each fuel element: 820 for elements B-4 and B-25; 1040 for elements A-22/33/36/41/47; 1084 for elements A-14/15/21/30/34/40 and B-30; 330 for elements N-20; 1025 for element B-9/21/24/40/43 and 1017 for all the others.

h) Maximum specific power of the fuel element when discharged(17 watts/g U).

i) Estimated weight of Pu, Pu-239, Pu-240 and Pu-241 in grams (see Table 5.1.1-2).

j) Weight of uranium left in a fuel element of the discharge Uf (see Table 2.5.1-2).

k) Weight of uranium-235 left in a fuel after discharge Uf-235 (see Table 2.5.1-2).

l) Weight of U-236 (see Table 2.5.1-2).

For reason of space no more than about 12 to 14 elements could be introduced at the same time in the dissolver even after a mechanical treatment in which the top and bottom part of the unfueled part was removed.

It had been foreseen to make a batch consisting of the 11 elements A-12/16/18/19/21/22/35/38/41/43/54 and two batches made with the other elements, these last two batches being mixed after dissolution. The expected U and Pu concentration (in %) would then have been:

First batch: U-235/U = 1.07; U-236/U = 0.23
Pu-239/Pu = 66.75; Pu-240/Pu = 18.30; Pu-241/Pu = 12.70.

2nd and 3rd batch: U-235/U = 1.08; U-236/U = 0.25
Pu-239/Pu = 65.36; Pu-240/Pu = 18.25; Pu-241/Pu = 13.56.

Unfortunately technical difficulties caused time delays during the dissolutions of the reactor batches which made the blending operation of the last two batche impossible.

The second batch consisted of the 8 elements A-5/15/17/30/31/36/47/55, the expected values of the concentration for this batch being (in %):

Second batch: U-235/U = 1.03 ; U-236/U = 0.23
Pu-239/Pu = 66.08; Pu-240/Pu = 18.43; Pu-241/Pu = 13.17.

The third batch consisted of the last 13 elements, with the following expected values:

Third batch: U-235/U = 1.10; U-236/U = 0.26
Pu-239/Pu = 64.98; Pu-240/Pu = 18.16; Pu-241/Pu = 13.81.

2.5.1.3 TRINO reactor

A description of the Italian Reactor ENRICO FERMI (Selni) reactor may be found in [2.5-2]. The fuel elements are made with UO_2 pellets placed in cylindrica rods which form either square or cruciform subassemblies. In the square subassemblies the pellets diameter is 0.890 cm, the rod length 274.37 cm (overall and the enrichment is 2.73 % in the inner region, 3.12 % in the intermediate region and 3.90 % in the outer region; in the cruciform subassemblies the pell diameter is 0.935 cm, the rod length 295.2 cm (overall) and the enrichment is 2.73 %. The cladding is type 304 stainless steel and is 0.0384 cm thick in the square subassemblies and 0.0732 cm thick in the cruciform subassemblies. The square subassemblies (19.99 x 19.99 each and 320.88 cm long overall) are made with 209 rods; the cruciform subassemblies (spare 37.191 and 32.443 cm, 295 cm long overall) are made with 28 rods.

The shipper's data provide the following information

a) Reference number of the fuel elements; the four elements which were treated were elements 509-017; 509-032; 509-049 and 509-104. (The data given in the following will correspond to these elements, in that order.)

b) Location in the reactor.

c) Loading date in the reactor: 1/10/64 for all the elements.

d) Removal date from the reactor: 28/4/67 for all the elements.

e) Weight of uranium at loading (in kg): 313.734; 313.559; 314.951 and 314.270.

f) Weight of U-235 (in g): 85.30; 85.26; 98.58 and 122.47.

g) Irradiation time in MWD/TU: 12945; 12465; 13980 and 8969.

h) Weight of uranium left after discharge (Uf, in kg): 307.648; 307.664; 308.337 and 310.058.

i) Weight of U-235 left after discharge (Uf-235, in g):4925; 5017; 5921 and 9365.

j) Estimated weight of

Pu-239(in g):	1421.76;	1431.13;	1509.42;	1127.87
Pu-240(in g):	312.96;	305.07;	314.87;	148.32
Pu-241(in g):	175.72;	167.90;	182.76;	88.82
Pu-242(in g):	9.61;	8.61;	24.38;	2.06
Pu (in g):	1920.05;	1912.71;	2031.43;	1367.07
Pu fissile (in g):	1597.48;	1599.03;	1692.18;	1216.69

k) Estimated weight of Np (in g): 3.27; 3.09; 3.69 and 1.86.

The four Trino fuel elements were dissolved in two batches: The first batch was made of the elements 509-032 and 509-049 and the second of elements 509-017 and 509-104, the expected values of the concentration being (in %):

First batch: U-235/U = 1.78
Pu-239/Pu = 74.59; Pu-240/Pu = 15.73; Pu-241/Pu = 8.89

Second batch: U-235/U = 2.31
Pu-239/Pu = 77.56; Pu-240/Pu = 14.03; Pu-241/Pu = 8.05

2.5.1.4 EL-3 reactor

A description of the French EL-3 reactor may be found in /‾2.5-3_7.

The fuel elements are made of pellets (5 or 8.9 mm in diameter; 12 or 8.9 mm long) contained in fuel pins (internal diameter 5 or 8.9 mm, thickness 1.2 mm, length 289.7 or 312.5 or 327.5 mm); the canning material is aluminium; a fuel element is made of 8 pins surrounding an axial tube. The fuel consists of uranium (natural, 1.5 %, 4 % and 4.5 % enriched) in form of UO_2.

The shipment contained 1507 spent fuel elements with a calculated amount of heavy nuclei of 694 kg U and 1.368 kg Pu. As there was no idendification of the single fuel elements possible only integral data are given here.

Table 2.5.1-1: CANADIAN FUEL SUMMARY SHEET

Shipment		No. of	Tot Pu	Weight %				MWD/T	Tot U_o	Tot U_f	Weight	% U_f
No.	BSK	Bdls.	GMS	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	AVE	KGM	KGM	^{235}U	^{236}U
1	1	59	2190.5	74.43	21.42	3.47	0.689	4958	775.69	769.79	0.3225	0.0596
1	2	60	2434.4	71.63	23.45	4.00	0.915	5630	794.09	787.18	0.2889	0.0646
1	3	60	2492.1	70.90	23.95	4.15	1.00	5757	801.65	794.44	0.2830	0.0656
1	6	60	2499.6	70.61	24.18	4.19	1.02	5892	792.20	784.99	0.2766	0.0666
1	7	60	2424.1	71.55	23.49	4.02	0.94	5580	795.25	785.44	0.2940	0.0643
1	8	60	2601.5	69.53	24.97	4.39	1.10	6316	789.67	782.01	0.2578	0.0694
2	4	60	2538.7	70.85	24.01	4.17	0.97	5887	805.08	797.75	0.2769	0.0665
2	5	60	2571.9	70.04	24.55	4.34	1.07	5943	810.61	803.15	0.2743	0.0669
2	1	60	2623.5	69.84	24.73	4.36	1.06	6162	808.57	800.89	0.2646	0.0684
2	6	60	2653.9	69.28	25.08	4.49	1.15	6229	812.52	804.72	0.2616	0.0688
2	2	60	2696.3	68.58	25.63	4.60	1.18	6515	801.58	793.56	0.2492	0.0769
2	3	60	2625.1	69.61	24.87	4.41	1.10	6173	808.17	800.49	0.2641	0.0685
	Σ	719	30351.6 grams						9595.1	9504.4 kilograms		

Pu, Average G/Tonne = 3193 end of life

Average MWD/Tonne = 5916 based on U_o

= 6003 based on U_f

Table 2.5.1-2: Calculated quantities of heavy isotopes in spent VAK fuel elements

Element No.	Exposure MWd/MTU	Tot Pu (g)	Pu-239 (g)	Pu-240 (g)	Pu-241 (g)	Tot U_f (kg)	U_f-235 (g)	U_f-236 (g)
1	2	3	4	5	6	7	8	9
A-5	15 844	357	235	66	47	61.847	639	143
A-12	15 108	348	232	64	44	61.923	666	139
A-14	18 280	380	241	71	56	61.748	555	155
A-15	18 031	377	240	71	55	61.756	563	154
A-16	15 096	347	232	63	44	61.925	667	139
A-17	15 909	357	235	66	47	61.842	636	144
A-18	15 835	357	235	66	47	61.849	639	143
A-19	15 668	353	234	65	46	61.866	645	142
A-21	18 259	380	241	71	56	61.749	556	155
A-22	13 835	330	227	60	38	62.044	715	132
A-30	18 216	380	241	71	56	61.750	557	154
A-31	15 992	357	235	66	47	61.833	633	144
A-33	13 400	325	225	58	37	62.069	725	129
A-34	18 652	383	241	72	58	61.732	544	156
A-35	15 072	347	232	63	44	61.928	668	139
A-36	13 215	322	224	57	36	62.089	739	127
A-38	14 192	336	229	61	40	62.017	701	134
A-40	17 802	375	240	70	54	61.764	570	153
A-41	13 928	333	228	60	39	62.036	711	132
A-43	15 154	348	232	64	44	61.918	664	139
A-47	13 965	333	228	60	39	62.034	710	132
A-54	15 123	347	232	63	44	61.921	666	139
A-55	15 735	354	234	65	46	61.859	643	143
B-4	15 853	353	239	63	44	61.790	787	153
B-9	18 150	379	246	69	53	61.612	701	167
B-21	18 538	383	247	70	55	61.582	686	170
B-24	21 832	414	253	77	67	61.336	578	186
B-25	15 903	353	239	63	44	61.786	785	154
B-30	18 686	383	247	70	55	61.570	680	171
B-40	18 433	390	246	70	54	61.588	690	169
B-43	21 847	412	252	77	66	61.333	577	186
N-20	9 450	256	194	39	18	62.584	989	103
Σ:32		11449	7536	2091	1520	1978.680	21285	4726

2.5.2 Physical Inventory before and after Campaign

2.5.2.1 Physical inventory before campaign

The beginning physical inventory was determined at January 11, 1970 and relevant data can be extracted from table 2.5.2-1.

As the layout of JEX-70 covered only MBA 21 and MBA 22 no attention has been paid on other MBA's.

There are a couple of units which cannot be inventorized adequately because of the lack of measurement and sampling equipment. In this case the operator was estimating the hold-up. Fortunately the main part of physical inventory both for U and Pu could be collected in adequate accountability tanks.

There were 16 units and 10 units to be inventorized with respect to U inventory and Pu inventory respectively.

2.5.2.2 Physical inventory after campaign

The ending physical inventory was taken at July 1st, 1970 for U and June 26, 1970 for Pu. The relevant data are compiled in table 2.5.2-2. The ending Pu inventory of MBA 22 includes two final product batches PC 163 and PC 164 as indicated in table 2.5.6-1 which contain 1899 g Pu. The ending U inventory was mainly collected in the dissolver tank (226-2).

Table 2.5.2-1: Physical Inventory a) before and
b) after the campaign

MBA	21		22
Date	kg U	g Pu	g Pu
a) January, 11	872.8	12061.	558.
b) June 29, and July 1	104.7	1163.	2061.

2.5.3 Corrected Input Data

2.5.3.1 Operator's data

As pointed out in 2.2 and 2.3.1 operator's MBA system keeps identity of of nuclear material in spent fuel elements forming one dissolution batch for reasons of establishment of adequate shipper-receiver differences and the application of the isotope correlation technique. "Corrected Input Data" representing the actual dissolved nuclear material in each dissolution batch are accounted for by using MBA 12 (see Fig. 2.2-1/2) according to equation (2-4).

$$(2\text{-}4) \qquad \text{Total} = \text{JD} - \text{RAR} + \text{AFU}\,(00) + \text{AFU}(10) + \text{UD} \qquad [\text{kg U, Pu}]$$

- JD corresponds to the input jacket dissolution; the isotopic composition of Uranium and Plutonium in JD was considered to be the same as in the corresponding AFU.
- RAR corresponds to the recovered acid recycle; the amount of heavy isotopes in recycled acid was directly determined.
- AFU(00)and AFU(10) correspond to the active feed unadjusted; the input fuel solution is accounted in two parallel input tanks: the transfer from tank 226-2 to tank 221-4, for batches 100, 200 ..., is indicated by the symbol (00); the transfer from tank 226-2 to tank 221-6, for batches 110, 220, ..., is indicated by the symbol (10).
  AFU(00)-batch normally contains the main part of fuel solution from dissolver 226-2 whereas AFU(10) contains the supplement and dissolver rinse solutions.
- UD corresponds to the undissolved discards.

Tables 2.5.3-1 to 2.5.3-4 show the actual data of the campaign; denoted LEU-1-70 (CANDU fuel), LEU-2-70 (VAK fuel) and LEU-3-70 (TRINO and EL-3 fuel) for the 9 CANDU batches (table 2.5.3-1), the 4 VAK batches (table 2.5.3-2), the 2 TRINO batches (table 2.5.3-3) and the 5 EL-3 batches (table 2.5.3-4).

Operator's input accountability data are shown for each batch in table 2.5.3-1; the values indicated under the mention "Total" are calculated according to formula (2-4). The values indicated under the mention "shipper's" are the Uranium preirradiation data as calculated from the shipper's data; as indicated in paragraph 2.5.1.1 some of these values are only estimations due to the lack of identification of the fuel elements. The values JRC (jacket recycle concentrate) correspond to the total amount of solid particles which were not dissolved during the jacket dissolutions. These solids were collected and dissolved in a special dissolution.

"Shipper's Initial" and "Shipper's Final" in table 2.5.3-2 represent shipper's pre and post irradiation data; those data do not appear for the fourth batch representing undissolved fuel from first three batches.

"Shipper's Initial" and "Shipper's Final" data in table 2.5.3-3 are slightly different from the values given in paragraph 2.5.1.3, this is due to the fact that some rods were taken out of the fuel elements for reasons of small sample analysis.

Since the complete fuel elements were dissolved during a single operation, there are no data for JD and RAR for the EL-3 batches in table 2.5.3-4.

2.5.3.2 Verification efforts on operator's input data

Considerable efforts were spent on verification of operator's input accountability by independant analyses using composite sample technique. Composite sample technique was also applied at a preceding integral safeguards exercise at EUROCHEMIC /‾ 2.5-4 _7 on original samples of active feed. As the efforts for transportation and handling of undiluted active sample solutions were experienced to be unreasonable high a dilution with nitric acid of 1:250 by volume on all samples was carried out by the operator before composing which has the advantage that the stability of samples is guaranteed during storage time.

Ten composite samples on diluted active feed solutions were composed by Dr.Thie and Mr. Kammerichs[2] using a Methrom-Mikro-Dosimat (type E 412-1-G-P) in combination with an automatic control unit: Metrhom-Dosifix (type E-442). Equipment and procedures are described in detail in ref. /‾ 2.5-4 _7.

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[1] BAM =Bundesanstalt für Materialforschung, Berlin

[2] European Transuranium Institute, EURATOM, Karlsruhe

Each composite sample was closely homogenized before distributing required sample material to single laboratories with request for analysis of U and Pu concentrations using isotope dilution technique. Each laboratory was to spike the received samples independently.

Table 2.5.3-5 summarizes all relevant data inclusive reference concentrations calculated on the basis of operator's single batch analysis whereas table 2.5.3-6 and 2.5.3-7 show single realisations of verification analyses on U and Pu from different laboratories relative to their corresponding reference values defined in table 2.5.3-5.

Significant deviations indicate those realisations which exceed roughly a ± 2 % limit. Realisations on composite sample C and D are compiled in table 2.5.3-6 and 2.5.3-7 for reasons of completeness. As indicated in table 2.5.3-5 the primarily used plastic bottles did not hit specifications on required tightness. Composite samples indicated as E-I represent dried samples according to a new technique developed in the European Transuranium Institute, EURATOM, Karlsruhe, which is described in detail in chapter 8.

The reported realisations of composite samples have a significant trend to overestimate U and Pu concentrations compared with the corresponding single batch analyses. This was also experienced in a previous experiment on composite samples /¯ 2.5-4 _7. The reasons thereof are not clearly identified.

Possible error components are the following:

i) Composite errors
ii) Sample preparation, spiking and dilution
iii) Aging effects due to autoradiolysis, evaporation, polymerisation and plating out.

i) and ii) should be of random nature in this consideration whereas aging effects may have caused this trend though considerable efforts were spent for stabilizing sample solutions immediately after sampling (see chapter 7.5).

Table 2.5.3-1: Operator's Input Accountability Data of CANDU-Fuel (LEU-1-70) /GMS heavy nuclei7

Ident.	U (tot)	U 234	U 235	U 236	U 238	Pu (tot)	Pu238	Pu 239	Pu 240	Pu 241	Pu 242	Remarks
JD 100	1277	0.1	3.5	0.9	1272.5	2.7	0.0	2.0	0.6	0.1	0.0	
RAR 100	- 2958	- 0.2	- 25.9	- 1.4	- 2930.5	- 9.1	0.0	- 7.2	- 1.3	- 0.5	- 0.1	
AFU 100	671357	33.5	1826.1	490.1	669007.3	2224.9	3.1	1596.0	518.8	83.2	23.8	
AFU 110	406101	20.3	1100.5	288.3	404691.9	1324.2	1.9	949.8	308.8	49.5	14.2	
Total	1075777	53.7	2904.2	777.9	1072041.2	3542.7	5.0	2540.6	826.9	132.3	37.9	
Shipper's	1090600 2)		7754. 2)			3542.9		2471.1	877.8	155.4	38.5	
JD 200	1309	0.1	4.0	0.9	1304.0	2.5	0.0	1.8	0.6	0.1	0.0	
RAR 200	- 19540	- 1.2	- 171.4	- 9.2	- 19358.2	- 59.9	- 0.2	- 47.1	- 8.8	- 3.3	- 0.5	
AFU 200	703890	35.2	2034.7	485.7	701334.4	2299.8	3,2	1645.7	535.6	90.2	25.1	
AFU 210	384947	19.2	1124.5	281.0	383522.3	1257.7	1.8	900.0	292.9	49.3	13.7	
Total	1070606	53.3	2991.8	758.4	1066802.5	3500.1	4.8	2500.4	820.3	136.3	38.3	
Shipper's	1088100 2)		7736. 2)			3513.9	-	2447.9	872.1	155.2	38.7	
JD 300	552	0.0	1.4	0.4	550.2	1.4	0.0	1.0	013	0.1	0.0	no RAR!
AFU 300	676146	33.8	1717.3	493.6	67390113	2302.4	3.2	1624.6	554.4	93.0	27.2	
AFU 310	353959	17.7	894.1	269.0	352778.2	1206.7	1.7	851.4	290.6	48.8	14.2	
Total	1030657	51.5	2612.8	763.0	1027229.7	3510.5	4.9	2477.0	845.3	141.9	41.4	
Shipper's	1052200 2)		7481. 2)			3542.1	-	2428.6	908.5	162.8	42.1	
JD 400	731	0.0	2.5	0.4	728.1	1.5	0.0	1.2	0.3	0.0	0.0	
RAR 400	- 275	- 0.4	- 38.7	- 4.1	- 231.8	- 17.1	- 0.1	- 13.5	- 2.5	- 0.9	- 0.1	
AFU 400	647743	32.4	2196.1	395.1	645119.4	1807.1	2.0	1373.3	368.3	51.0	12.5	
AFU 410	397822	19.9	1356.7	234.7	396210.7	1097.1	1.2	833.8	223.6	30.9	7.6	
Total	1046021	51.9	3516.6	626.1	1041826.4	2888.6	3.1	2194.8	589.7	81.0	20.0	
Shipper's	1056300 2)		7510. 2)			2974.2	-	2196.7	647.4	107.9	22.2	

Table 2.5.3-1: Operator's Input Accountability Data of CANDU-Fuel (LEU-1-70) [GMS heavy nuclei]

Ident.	U tot.	U 234	U 235	U 236	U 238	Pu tot.	Pu 238	Pu 239	Pu 240	Pu 241	Pu 242
JD 500	899	0.0	2.8	0.6	895.6	2.9	0.0	2.2	0.6	0.1	0.0
RAR 500	- 62075	- 1.9	- 235.9	- 47.8	- 61789.4	- 35.2	- 0.1	- 26.4	- 6.6	- 1.7	- 0.4
AFU 500	695261	34.8	2148.3	451.9	692626.0	1989.4	2.4	1477.3	430.3	62.7	16.7
AFU 510	424215	17.0	1302.3	271.5	422624.2	1220.4	1.5	906.2	264.0	38.4	10.3
Total	1058300	49.9	3217.5	676.2	1054356.4	3177.5	3.8	2359.3	688.3	99.5	26.6
Shipper's	1102600 2)		7839 2)			3294.0	-	2377.7	758.1	129.7	28.6
JD 600	1314	0.1	3.7	1.0	1309.2	6.2	0.0	4.4	1.5	0.2	0.1
RAR 600	- 9329	- 0.5	- 28.0	- 6.1	- 9294.4	- 23.3	- 0.1	- 16.6	- 5.2	- 1.1	- 0.3
AFU 600	599991	30.0	1685.6	468.0	597807.4	1960.9	2.5	1404.5	459.6	72.9	21.4
AFU 610	433474	21.7	1187.6	320.8	431943.9	1430.0	1.9	1024.1	335.2	53.2	15.6
Total	1025450	51.3	2848.9	783.7	1021766.1	3373.8	4.3	2416.4	791.1	125.2	36.8
Shipper's 1)	1039100 2)		7486 2)			3374.0	-				
JD 700	382	0.0	1.0	0.3	380.7	1.2	0.0	0.9	0.3	0.0	0.0
RAR 700	- 4854	- 0.2	- 14.5	- 3.2	- 4836.1	- 41.3	- 0.1	- 30.3	- 8.8	- 1.7	- 0.4
AFU 700	611220	24.4	1656.3	458.4	609080.9	2060.5	2.7	1467.9	488.5	78.5	22.9
AFU 710	391786	15.7	1061.7	286.0	390422.6	1316.5	1.7	937.9	312.1	50.2	14.6
Total	998534	39.9	2704.5	741.5	995048.1	3336.9	4.3	2376.4	792.1	127.0	37.1
Shipper's 1)	1063400 2)		7661 2)			3537.					
JD 800	1465	0.1	4.0	1.1	1459.8	2.8	0.0	2.0	0.7	0.1	0.0
RAR 800	- 1831	- 0.1	- 5.5	- 1.2	- 1824.2	- 44.5	- 0.1	- 31.8	- 10.0	- 2.1	- 0.5
AFU 800	635868	31.8	1748.6	464.2	633623.4	2051.6	2.7	1471.4	480.7	75.3	21.5
AFU 810	360759	18.0	977.6	252.5	359510.9	1167.3	1.5	837.2	273.5	42.8	12.3
Total	996261	49.8	2724.7	716.6	992769.9	3177.2	4.1	2278.8	744.9	116.1	33.3
Shipper's 1)	1013200 2)		7300 2)			3270.					

Table 2.5.3-1: Operator's Input Accountability Data of CANDU-Fuel (EEU-1-70) /GMS heavy nuclei/

Ident.	U tot.	U 234	U 235	U 236	U 238	Pu tot.	Pu238	Pu 239	Pu 240	Pu 241	Pu 242
JD 900	1252	0.1	3.8	0.8	1247.3	2.7	0.0	2.0	0.6	0.1	0.0
RAR 900	- 2596	- 0.1	- 11.2	- 1.3	- 2583.4	- 40.3	- 0.1	- 29.7	- 8.6	- 1.5	- 0.4
AFU 900	700443	35.0	2115.4	462.3	697830.3	2159.6	2.6	1577.6	484.4	73.6	21.4
AFU 910	414636	20.7	1268.9	261.2	413085.2	1275.0	1.5	931.4	286.0	43.5	12.6
Total	1113735	55.7	3376.9	723.0	1109579.4	3397.0	4.0	2481.3	762.4	115.7	33.6
Shipper's 1)	1089700 2)		7841. 2)			3303					
JRC tot.	752	-	2.1	-	749.9	2.4	-	1.7	0.7	-	-
TOTAL	9416093	457.0	26900.0	6566.4	9382169.6	29906.7	38.3	21626.7	6861.7	1075.0	305.0
Shipper's	9595100 2)	-	68608.0 2)	-	-	30351.6	-	21396.9	7359.6	1284.4	310.7

1) Estimated data because fuel elements could not be identified.

2) Preirradiation data.

IDENT.	U^{TOT}	U^{234}	U^{235}	U^{236}	U^{238}	Pu^{TOT}	Pu^{238}	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}
JD 100	1152	0.1	12.2	2.6	1137.1	8.4	0.1	5.6	1.9	0.6	0.2
RAR 100	-8489	-0.4	-29.3	-5.2	-8454.1	-129.9	-0.2	-94.2	-29.2	-5.0	-1.3
AFU 100	619028	74.3	6541.5	1411.4	611000.8	3102.3	18.5	2102.6	686.5	233.6	61.1
TOTAL 100	611691	74.0	6524.4	1408.8	603683.8	2980.8	18.4	2014.0	659.2	229.2	60.0
SHIPPER'S: INITIAL	696121	-	16220.6	-	679900.4	-	-	-	-	-	-
SHIPPER'S: FINAL	681175	-	7298.0	1653.0	672224.0	3826.0	-	2554.0	700.0	486.0	-
JD 200	4550	0.5	46.4	10.6	4492.5	59.5	0.4	39.2	13.7	4.8	1.4
RAR 200	-5497	-0.3	-19.0	-3.4	-5474.3	-84.1	-0.1	-61.0	-18.9	-3.3	-0.8
AFU 200	415914	49.9	4238.1	973.2	410652.8	2109.5	13.3	1393.0	484.3	170.4	48.5
RAR 210	-760	-0.0	-2.6	-0.5	-756.9	-11.6	-0.0	-8.5	-2.6	-0.4	-0.1
UD 100 200	1235	0.1	12.6	2.9	1219.4	6.3	0.0	4.3	1.4	0.5	0.1
AFU 210	11219	1.3	114.3	26.3	11077.1	62.7	0.4	41.4	14.4	5.1	1.4
TOTAL 200	426661	51.5	4389.8	1009.1	421210.6	2142.3	14.0	1408.4	492.3	177.1	50.5
SHIPPER'S: INITIAL	506270	-	11797.0	-	494473.0	-	-	-	-	-	-
SHIPPER'S: FINAL	495010	-	5120.0	1141.0	488749.0	2837.0	-	1872.0	522.0	373.0	-
JD 300	1887	0.2	19.5	4.9	1862.4	23.6	0.2	15.4	5.5	1.9	0.6
RAR 300	-29949	-1.8	-94.0	-21.3	-29831.9	-202.7	-0.3	-147.2	-45.6	-7.5	-2.1
AFU 300	501986	60.2	5187.2	1300.1	495438.5	2770.2	20.6	1810.3	645.7	226.6	67.0
AFU 310	267745	32.1	2766.1	696.1	264250.7	1475.4	10.9	964.2	343.9	120.7	35.7
UD 300	731	0.1	7.7	1.7	721.5	8.5	-	5.9	1.8	0.6	0.1
TOTAL 300	742400	90.8	7886.5	1981.5	732441.2	4075.0	31.4	2648.6	951.3	342.3	101.3
SHIPPER'S: INITIAL	804812	-	20198.2	-	784613.8	-	-	-	-	-	-
SHIPPER'S: FINAL	785250	-	8638.0	2014.0	774598.0	4706.0	-	3050.0	853.0	650.0	-
JD 400	5698	0.7	62.0	13.3	5622.0	46.6	0.2	31.9	10.1	3.6	0.8
RAR 400	-3984	-0.4	-37.2	-7.2	-3939.2	-7.3	-0.0	-5.2	-1.6	-0.4	-0.1
AFU 400	144220	17.3	1569.3	337.5	142295.9	701.4	3.7	479.1	151.8	54.3	12.5
UD 400	868	0.1	9.2	2.0	856.7	10.1	0.1	6.9	2.2	0.8	0.2
TOTAL 400	146802	17.7	1603.3	345.6	144835.4	750.8	4.0	512.7	162.5	58.3	13.4
TOTAL	1927554	234.0	20404.0	4745.0	1902171.0	9948.9	67.8	6583.7	2265.3	806.9	225.2
SHIPPER'S: INITIAL	2007203	-	48215.8	-	1958987.2	-	-	-	-	-	-
SHIPPER'S: FINAL	1961435	-	21056.0	4708.0	1935571.0	11369.0	-	7476.0	2075.0	1509.0	-

Table 2.5.3-3: Operator's Input Accountability Data of TRINO Fuel (LEU-3-70)

IDENT.	U^{TOT}	U^{234}	U^{235}	U^{236}	U^{238}	Pu^{TOT}	Pu^{238}	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}
JD 100	1814	0.3	32.6	4.5	1776.6	19.6	0.1	14.8	3.1	1.4	0.2
RAR 100	-8431	-0.9	-78.8	-15.3	-8336.0	-15.5	-0.1	-10.9	-3.4	-0.9	-0.2
AFU 100	338147	47.3	6073.1	835.2	331191.4	2094.1	9.2	1580.0	329.6	150.4	24.9
AFU 110	237270	33.2	4211.5	595.5	232429.8	1460.8	6.4	1102.2	229.9	104.9	17.4
TOTAL 100	568800	79.9	10238.4	1419.9	557061.8	3559.0	15.6	2686.1	559.2	255.8	42.3
SHIPPER'S: INITIAL	611869	-	17882.0	-	593987.0	-	-	-	-	-	-
SHIPPER'S: FINAL	599699	-	10638.0	-	-	3838.4	-	2861.8	603.4	340.6	31.9
JD 200	482	0.1	11.1	1.1	469.7	4.8	0.0	3.8	0.7	0.3	0.0
RAR 200	-1304	-0.2	-13.4	-2.3	-1288.1	-8.1	-0.0	-6.0	-1.6	-0.4	-0.1
AFU 200	301724	42.2	6956.4	684.9	294040.5	1549.6	5.6	1220.1	218.0	92.0	13.9
AFU 210	309056	43.3	7128.7	692.3	301191.7	1592.5	5.7	1253.8	224.1	94.6	14.3
TOTAL 200	609958	85.4	14082.8	1376.0	594413.8	3138.8	11.3	2471.7	441.2	186.5	28.1
SHIPPER'S: INITIAL	624981	-	20659.0	-	604322.0	-	-	-	-	-	-
SHIPPER'S: FINAL	614729	-	14200.0	-	-	3274.0	-	2538.8	459.8	263.1	11.6
TOTAL	1178758	165.3	24321.2	2795.9	1151475.6	6697.8	26.9	5157.8	1000.4	442.3	70.4
SHIPPER'S: INITIAL	1236850	-	38541.0	-	1198309.0	-	-	-	-	-	-
SHIPPER'S: FINAL	1214428	-	24838.0	-	-	7112.4	-	5400.6	1063.2	603.7	43.5

Table 2.5.3-4: Operator's Input Accountability Data of EL-3 Fuel (LEU-3-70)

IDENT.	U^{TOT}	U^{234}	U^{235}	U^{236}	U^{238}	Pu^{TOT}	Pu^{238}	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}
AFU 100	178886	35.8	5378.2	500.9	172971.1	315.2	0.2	274.0	36.1	4.3	0.6
AFU 200	131376	21.0	3859.7	381.0	127114.3	238.4	0.2	203.4	30.7	3.6	0.5
AFU 300	198472	35.7	5868.8	559.7	192007.8	358.0	0.2	310.2	42.3	4.8	0.5
AFU 400	167987	28.6	5253.1	428.4	162276.9	288.8	0.2	252.2	32.6	3.4	0.4
AFU 500	10710	1.9	316.7	30.2	10361.2	18.8	0.0	16.3	2.2	0.3	0.0
TOTAL	687431	123.0	20676.5	1900.2	664731.3	1219.2	0.8	1056.1	143.9	16.4	2.0
SHIPPER'S											
INITIAL	705694		31611.0								
FINAL	693802		21208.0			1368.0					

Table 2.5.3-5: Survey on Composite Samples of Active Feed in JEX-70

Composite Sample	A	B	C	D	E	E - I	F	G	H
1	2	3	4	5	6	7	8	9	10
Fuel	CANDU		CANDU		VAK			TRINO	TRINO + CDN
AFU-Batch	700-910		100-610		100-400			100-210	100-210+100-500
Total mass of sol. (tons)	17.138		37.147		13.023			8.284	22.815
Pipetter capacity (ml)	4		4		4			4	2
10^6 Aliquot factor	4.7	3.1	1.3496		1.471			2.2	0.7
Volume dilution factor	248.2 →								
Ref.Sol.Density[1] (g/ml)	1.4218		1.3992		1.3806			1.3233	1.3138
Ref.Dil.Density[2] (g/ml)	1.17415 →								
Ref. U-conc.[1] (mg U/g dil)	0.8870		0.8199		0.7134			0.6498	0.3702
Ref.Pu-conc.[1] (µg Pu/g dil.)	2.828		2.600		3.720			3.601	1.540

Table 2.5.3-5: Survey on Composite Samples of Active Feed in JEX-70 (continuation)

Ref.Pu/U 1) (o/oo)	3.188	3.171	5.214	5.542	4.160
Reference 234 1)	0.0047	0.005	0.012	0.014	0.016
U-isotope 235	0.283	0.291	1.041	2.054	2.405
abundances 236	0.070	0.070	0.242	0.237	0.251
as (W/%) 238	99.643	99.635	98.705	97.696	97.328
Ref.Pu-238 1)	0.127	0.131	0.660	0.400	0.348
isotope 239	72.010	72.495	66.432	77.027	78.534
abund. 240	23.182	22.773	22.765	14.939	14.446
(W/%) 241	3.628	3.594	7.933	6.586	5.764
242	1.047	1.006	2.214	1.050	0.911
Remarks:	Samples stored in glass vials and used for interlabtest. A-aliquots taken from the same dilution as used for single batch analysis of the operator. B-aliquots taken from dilution of independant ref. samples.	Samples primarily stored in plastic bottles which showed wall difusion losses and were therefore rejected for the interlabtest. C and D samples correspond to A and B samples respectively.	E and E-I samples taken from the same dilution but independantly composed. E and F samples correspond to A and B samples respectively. Only glass bottles used. E-I-samples were dried in Al.-capsules.	Correspond to A-samples. Only glass bottles used.	Correspond to A-samples. Great differences in concentrations of single batches (Factor 200). Only glass bottles used.

1) Based on single batch analysis of the operator
2) Determined at EUROCHEMIC analytical laboratory
3) Not measured. Ref. density was estimated as the mean of other composite samples due to the great solution factor.

Table 2.5.3-6: U-concentrations by Isotope Dilution Analysis normalized to Operator's Single Batch Analysis = 100 % (Reference Value in Table 2.5.3-5)

Numbers in brackets represent realisations rejected by the corresponding laboratory.

Composite sample	A	B	C	D	E	E - I	F	G	H
Laboratory I	99.2	103.0	101.4	102.9	-	-	-	-	-
	103.3	100.8	103.2	(99.2)					
Laboratory II	98.7	98.9	-	-	-	-	-	99.4	104.4
	98.4	98.3							
Laboratory III	101.1	101.3	-	-	(102.6)	102.0	102.7	103.4	105.7
	100.4	101.2			(102.7)	101.7	103.0	104.0	106.9
	103.3				101.6	102.2	102.2		
	103.2				101.5	101.9	102.5		
						102.3			
						103.0			
						103.1			
Laboratory IV 1)	100.8	-	104.1	102.4	-	-	-	-	-
	101.4		104.0	102.2					
	101.1		104.4	102.2					
	101.8		104.5	102.4					
Laboratory V	101.8	-	-	-	-	-	-	-	-
Mean	101.1	100.6	103.6	102.4	101.6	102.3	102.6	102.3	105.7
RSD %	1.6	1.7	1.1	0.3	0.1	0.5	0.3	2.4	1.2

1) Using X-ray fluorescence spectroscopy

Table 2.5.3-7: Pu-concentrations by Isotope Dilution Analysis normalized to Operator's Single Batch Analysis = 100 % (Reference Value in Table 2.5.3-5)
Numbers in brackets represent realisations rejected by the corresponding laboratory.

Composite sample	A	B	C	D	E	E - I	F	G	H
Laboratory I	99.7 (82.0)	97.6 93.0	99.6 98.5	98.5 (88.1)	-	-	-	-	-
Laboratory II	100.8 102.1	101.1 100.1	-	-	-	-	-	101.9	100.3
Laboratory III	(99.6) (99.8) 103.1 103.6	101.9 102.2	-	-	(105.6) (104.2) 101.9 102.6	103.6 102.0 100.3 99.9 103.3 105.8	104.5 104.8 103.5	105.0 106.0	105.4 106.0
Laboratory V	102.5	-	-	-	-	-	-	-	-
Mean RSD %	102.0 1.4	99.3 3.5	99.1 0.8	- -	102.3 0.5	102.5 2.2	103.7 1.2	104.3 2.0	103.9 3.0

2.5.4 Recycled Uranium (BXR)

The partition column (231-4) was fed by a reducing agent in form of U(IV) solution from make up (tank 262-26) as pointed out in chapter 2.2 and Fig. 2.1-3. These batches were transferred from another building in plastic bottles and filled in tank 242-4 and 242-3. The single increments are compiled in table 2.5.4-1. This material does not represent the total amount of recycled BXR but only the external recycle which has to be accounted for. A considerable part of BXR was internally recycled within MBA 21 thus no material accountancy was required. The special problems associated with this recycle in the context of inventory experiment are described in chapter 5.3.2.

Table 2.5.4-1: U(IV) Uranium used for make-up

No.	DATE	ORIGIN.TANK	U QUANTITY (kg)	U-235 (W/o)
1	2	3	4	5
SATR 1041	12/2/70	242-4	49.3	0.701
" 1097	17/2/70	242-4	61.6	↓
" 1098	18/2/70	242-4	54.5	
" 1102	24/2/70	242-4	63.0	
" 1105	4/3/70	242-4	49.3	
" 1107	9/3/70	242-4	64.1	
" 1108	11/3/70	242-4	54.2	
" 1109	11/3/70	242-4	17.5	
" 1110	13/3/70	242-3	25.2	0.31
" 1111	18/3/70	242-3	77.8	"
" 1113	20/3/70	242-3	90.6	"
RSTA 1115	26/3/70	Bldg. 6B	102.0	1.47
" 1118	8/4/70			
" 1508	28/5/70	"	11.3	0.31
" 1512	12/6/70	"	11.2	"
" 1514	12/6/70	"	11.2	"
TOTAL			742.8	
U removed to building 6B			- 70.3	
Total Uranium fed into MBA 21			672.5	

2.5.5 Uranium Product from 3rd Cycle (3UP)

The Uranium product flow at the output of MBA 21 was measured in relatively small product receiver tanks (241-4a/b) with a normal hold up of 1100 l and 450 kg U respectively. 3 UP is sampled by the operator for specification analysis and there is no request for an accurate accountability analysis as the operator performs this analysis at Uranium Final Product (UFP). The layout of the U inventory experiment however required to follow the U isotopic system response in 3 UP in order to avoid the great homogenisation in the following final product storage tanks. The 3 UP batches represent the increments thereof. To realize adequate accountability of this 3 UP batches duplicate samples from each batch were requested to be analysed for total Uranium concentration and isotopic abundances in the laboratories of the Joint Reserach Center EURATOM, Ispra. All together 167 Uranium determinations and 70 density determinations have been carried out there.

An error analysis of the U-concentration determinations resulted in a value of the precision per single analysis which includes also possible sampling errors because the results of the duplicate samples have been combined for the evaluation of their variance. However sampling errors in this flow were experienced to be not significant (see chapter 7.1). Relevant data of this analysis are compiled in table 2.5.5-2.

Table 2.5.5-1: Uranium product from 3rd extraction cycle (3UP) accountability tank 241-4a/4b

	Reactor	Batch Identification	NMTR No.	RSTA No.	Date/hour of transfer end	Weight of transferred solution [kg]	Sample density 1) [g/ml]	2)1) mg U / g sol	kg U	Σkg U	U-isotopic comp. [w/o] 234	235	236	238	Remarks
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	-	-	-	-	19.2/	-	-	- 4)	338.4	338.4	-	0.910	-	-	5)
2	-	-	-	-	19.2/	-	-	- 4)	310.3	648.7	-	0.910	-	-	5)
3	NPD	3 UP-100	5611	39961	1.3/16.30	1689	1.5177	254.45	429.8	1078.5	-	-	-	-	
4	NPD	3 UP-200	5614	40087	3.3/10.45	1610	1.5895	273.35	440.1	1518.6	-	-	-	-	
5	↓	3 UP-300	5616	40095	4.3/20.30	1719	1.5697	273.62	470.4	1988.9	-	-	-	-	
6		3 UP-400	5620	40106	6.3/13.40	1625	1.5698	271.35	440.9	242.99	-	-	-	-	
7		3 UP-500	5624	40026	8.3/0.25	1746	1.5776	275.45	480.9	2910.8	-	-	-	-	
8		3 UP-700 3)	5707	40654	16.3/10.00	1453	1.5825	277.79	403.6	3314.4	-	-	-	-	
9		3 UP-800	5708	40773	17.3/4.40	1647	1.6067	283.05	466.2	3780.6	-	-	-	-	
10		3 UP-900	5850	40856	18.3/14.15	1653	1.5953	281.52	465.4	4246.0	-	-	-	-	

1) measured in CCR-Ispra

2) duplicate samples

3) batch NPD-3UP 600 was recycled within MBA 21

4) EUROCHEMIC process analysis

5) from beginning physical inventory

Table 2.5.5-1: Uranium product from 3rd extraction cycle (3UP) accountability tank 241-4a/4b (continued)

	Reactor	Batch Identification	NMTR No.	RSTA No.	Date/hour of transfer end	Weight of transferred solution [kg]	Sample density$^{1)}$ [g/ml]	$^{2)1)}$ mg U / g sol	kg U	Σkg U	U-isotopic comp.$^{1)}$ [w/o]				Remarks
											234	235	236	238	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	NPD	3UP-1000	5855	40866	20.3/5.10	1649	1.5883	275.22	453.8	4699.8	0.005	0.334	0.059	99.602	
2	↓	3UP-1100	5857	41055	21.3/14.15	1714	1.5755	276.83	474.5	5174.3	0.005	0.344	0.059	99.592	
3		3UP-1200	5859	41064	22.3/17.15	1640	1.5999	281.22	461.2	5635.5	0.005	0.313	0.061	99.621	
4		3UP-1300	5862	41226	24.3/19.00	1713	1.5716	274.28	469.8	6105.3	0.006	0.297	0.068	99.629	
5		3UP-1400	5866	41239	26.3/8.45	1703	1.5958	277.58	472.7	6578.0	0.005	0.273	0.066	99.656	
6		3UP-1500	5868	41252	27.3/10.00	1704	1.6076	283.44	483.0	7061.0	0.005	0.279	0.064	99.652	
7		3UP-1600	5871	41255	28.3/17.15	1696	1.6199	285.04	483.4	7544.5	0.006	0.310	0.066	99.618	
8		3UP-1700	5806	41264	31.3/2.30	1686	1.5548	269.69	454.7	7999.1	0.006	0.295	0.067	99.632	
9		3UP-1800	5809	41279	31.3/21.45	1709	1.6151	284.80	486.7	8485.9	0.005	0.289	0.066	99.640	
10	↓	3UP-1900	5878	41296	4.4./4.00	1706	1.6215	286.87	489.4	8975.3	0.005	0.291	0.066	99.638	

Table 2.5.5-1: Uranium product from 3rd extraction cycle (3UP) accountability tank 241-4a/4b (continued)

	Reactor	Batch Identification	NMTR No.	RSTA No.	Date/hour of transfer end	Weight of transferred solution [kg]	Sample density 1) [g/ml]	2)1) mg U / g sol	kg U	Σkg U	U-isotopic comp. 1) [w/o] 234	235	236	238	Remarks
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	NPD	3UP-2000	5881	41548	6.4/9.00	1674	1.6086	283.78	475.0	9450.3	0.005	0.284	0.065	99.646	
2	↓	3UP-2100	5886	41903	8.4/18.10	1750	1.5949	281.5 4)	492.6	9942.9	-	-	-	-	
3	↓	3UP-2200	5889	41909	9.4/22.15	1900	1.4746	240.47	456.9	10399.8	0.005	0.293	0.067	99.635	
4	VAK	3UP-100	5898	41916	15.4/17.20	1706	1.5317	260.06	443.7	10843.5	0.011	0.883	0.172	98.934	
5	↓	3UP-200	5675	43130	16.4/9.30	1729	1.5969	280.15	484.4	11327.9	0.011	0.997	0.200	98.792	
6	↓	3UP-300	5684	43031	21.4/19.20	1693	1.6004	280.17	474.3	11802.2	0.011	0.966	0.185	98.838	
7	↓	3UP-400	5692	43220	26.4/22.50	1520	1.5768	272.90	414.8	12217.0	0.011	0.984	0.222	98.783	
8	↓	3UP-500	5696	43408	28.4/12.45	1694	1.5247	256.47	434.5	12651.5	0.013	0.996	0.217	98.774	
9	↓	3UP-600	5697	43417	28.4/20.15	617	1.2656	154.43	95.3	12746.8	0.012	0.993	0.213	98.782	
10	TRINO	3UP-100	5601	43691	1.5/14.30	1167	1.2728	159.99	186.7	12933.5	0.012	1.582	0.225	98.181	

Table 2.5.5-1: Uranium product from 3rd extraction cycle (3UP) accountability tank 241-4a/4b (continued)

	Reactor	Batch Identification	NMTR	RSTA No.	Date/hour of transfer end	Weight of transferred solution [kg]	Sample density 1) [g/ml]	mg U / g sol 2)1)	kg U	Σ kg U	U-isotopic comp. 1) [w/o]				Remarks
											234	235	236	238	
1	TRINO	3UP-200	5603	43615	2.5/6.10	1414	1.2523	149.34	211.2	13144.6	0.013	1.649	0.222	98.116	
2		3UP-300	5607	43807	3.5/5.15	1552	1.2454	144.52	224.3	13368.9	0.014	1.848	0.227	97.910	
3		3UP-400	5609	43756	4.5/4.40	1410	1.2443	144.56	203.8	13572.8	0.015	2.049	0.224	97.712	
4		3UP-500	5612	43877	6.5/6.30	1366	1.2901	165.57	226.2	13798.9	0.017	2.195	0.223	97.565	
5		3UP-600	5731	44719	22.5/2.30	1222	1.2071	125.76	153.7	13952.6	0.016	2.227	0.224	97.533	
6		3UP-700	5733	44723	22.5/17.00	715	1.1311	83.79	59.9	14012.5	0.016	2.255	0.224	97.564	
7	CDN	3UP-100	5621	44013	10.5/14.45	1509	1.3142	167.91	253.4	14265.9	0.018	2.752	0.259	96.971	
8		3UP-200	5632	43397	13.5/11.30	963	1.3302	170.17	163.9	14429.8	0.019	2.862	0.262	96.857	
9		3UP-300	5643	44628	17.5/18.30	1357	1.3016	163.85	222.3	14652.1	0.019	2.860	0.263	96.858	
10		3UP-400	5648	44701	19.5/3.00	540	1.2188	127.87	69.0	14721.2	0.019	2.843	0.263	96.875	
11		3UP-500	5728	44707	19.5/5.30	401	1.1332	79.54	31.9	14753.1	0.019	2.844	0.263	96.874	

Table 2.5.5-2: **Survey on U-determinations of 3UP samples performed by the laboratory of the Joint Research Center EURATOM, Ispra**

Fuel	CANDU	VAK	TRINO	CDN
No. of batches	21	6	7	5
No. of samples per batch	2	2	2	2
No. of analyses per sample	2-3	3	3	2
Mean concentration /‾mg U/g_7	275.5	250.7	139.1	141.9
Precision /‾% RSD_7	0.20	0.19	0.32	0.34

2.5.6 Pu-Final Product (PFP)

Contrary to Uranium final product PFP was used to follow the isotopic system response of MBA 21 and 22 because there is no preceding large product sampling tank installed at EUROCHEMIC which causes intolerable homogenisation. The Pu-containers (PC) which were directly filled from a continuous operating calcinator represent ideal batch sizes for the use of the new inventory technique as described in chapter 5. Relevant batch data are compiled in table 2.5.6-1.

Date and time when each Pu container was filled and replaced by an empty one at the outlet calcinator, which was considered to be the boundary of the MBA 22, are given in column (1) to (3). The values given in column (4) correspond to the weight of the PuO_2 in a Pu-container before any sampling; the Pu weight percent, the weight of Pu and the cumulative weight of Pu are shown in columns (5) to (7); the Pu-isotope-weight-fraction and the Pu-isotope weight appear in columns (8) to (17). The first product batch, PC 118, was apparently material from a former campaign because its isotope vector does not fit at all with the CANDU plutonium isotope vector.

Table 2.5.6-1: Pu-Final-Product (PFP) Batches Inclusive Sample Material

PC	Date	Hour	g PuO_2	Pu %	g Pu	Σ g Pu	Pu-isotope-weight-fraction [%]					Pu-isotopes [g]				
							238	239	240	241	242	238	239	240	241	242
118	11.3	06.00	1932.65	86.47	1671.16	1671.16	0.427	69.32	22.57	6.05	1.63	7.14	1158.45	377.18	101.11	27.24
143	12.3	15.30	1601.03	87.16	1395.46	3066.62	0.135	72.13	23.02	3.69	1.02	1.88	1006.54	321.23	51.49	14.23
121	13.3	06.00	1346.96	86.43	1164.18	4230.80	0.144	72.35	22.87	3.63	1.01	1.68	842.28	266.25	42.26	11.76
122	18.3	15.00	2213.52	86.88	1923.11	6153.90	0.137	72.68	22.56	3.63	0.995	2.63	1397.71	433.85	69.80	19.13
124	21.3	02.00	1870.68	86.81	1623.94	7777.84	0.134	72.92	22.41	3.57	0.967	2.18	1184.18	363.92	57.97	15.70
123	23.3	12.00	1849.98	86.60	1602.08	9379.92	0.138	73.10	22.22	3.59	0.953	2.21	1171.12	355.98	57.51	15.27
126	24.3	12.50	1910.24	87.09	1663.63	11043.55	0.129	73.03	22.33	3.55	0.962	2.15	1214.95	371.49	59.06	16.00
125	28.3	10.00	1827.71	87.11	1592.12	12635.67	0.118	72.92	22.45	3.55	0.967	1.88	1160.97	357.43	56.52	15.40
131	29.3	21.00	1705.60	87.13	1486.09	14121.76	0.128	72.55	22.73	3.59	1.01	1.90	1078.16	337.78	53.35	15.01
132	30.3	21.00	1911.34	87.27	1668.03	15789.79	0.130	72.66	22.68	3.55	0.990	2.17	1211.99	378.31	59.21	16.51
134	2.4	02.00	2072.66	87.32	1809.85	17599.63	0.134	72.53	22.75	3.59	0.996	2.43	1312.68	411.74	64.97	18.03
135	4.4	22.45	1843.33	87.49	1612.73	19212.36	0.130	72.48	22.80	3.59	0.999	2.10	1168.91	367.70	57.90	16.11
136	5.4	16.30	1767.13	87.72	1550.13	20762.49	0.126	72.12	23.03	3.67	1.05	1.95	1117.95	356.99	56.89	16.28
127	6.4	10.45	1783.32	87.60	1562.19	22324.68	0.129	72.47	22.81	3.55	1.04	2.02	1132.12	356.34	55.46	16.25
128	10.4	19.45	1814.75	87.43	1586.64	23911.31	0.124	72.57	22.77	3.54	0.996	1.97	1151.42	361.28	56.17	15.80

Table 2.5.6-1 (continued)

PC	Date	Hour	g PuO_2	Pu %	g Pu	Σg Pu	Pu-isotope-weight-fraction [%]					Pu-isotopes [g]				
							238	239	240	241	242	238	239	240	241	242
129	11.4	17.30	1777.69	87.15	1549.26	25460.57	0.123	72.73	22.67	3.48	0.987	1.91	1126.77	351.22	53.91	15.29
130	16.4	00.00	1034.43	86.47	894.47	26355.04	0.127	72.66	22.73	3.50	0.989	1.14	649.92	203.31	31.31	8.85
133	18.4	03.00	1968.93	86.56	1704.31	28059.35	0.345	70.44	22.54	5.26	1.420	5.88	1200.51	384.15	89.65	24.20
138	26.4	06.00	1664.22	86.52	1439.88	29499.23	0.432	69.32	22.54	6.07	1.640	6.22	998.13	324.55	87.40	23.61
139	26.4	22.00	1508.88	87.52	1320.57	30819.80	0.54	67.75	22.76	6.94	2.01	7.13	894.69	300.56	91.65	26.54
140	27.4	18.15	1772.91	87.69	1554.66	32374.47	0.62	66.78	23.05	7.35	2.20	9.64	1038.21	358.35	114.27	34.20
141	28.4	11.00	1884.23	87.71	1652.66	34027.12	0.62	66.38	23.08	7.62	2.31	10.25	1097.03	381.43	125.93	38.18
142	30.4	12.00	1944.77	87.55	1702.65	35729.77	0.70	66.28	23.06	7.65	2.31	11.91	1128.13	392.50	130.21	39.32
145	11.5	12.30	1954.86	88.13	1722.82	37452.59	0.47	74.49	17.14	6.56	1.34	8.10	1283.33	295.29	113.02	23.09
146	12.5	10.00	1848.96	87.83	1623.94	39076.53	0.42	75.72	16.42	6.24	1.20	6.82	1229.65	266.65	101.33	19.49
147	13.5	04.30	1444.16	87.86	1268.84	40345.37	0.47	74.61	16.98	6.65	1.29	5.96	946.68	215.45	84.38	16.37
148	14.5	05.00	1567.57	87.96	1378.83	41724.21	0.42	75.50	16.38	6.47	1.23	5.79	1041.02	225.85	89.21	16.96
149	16.5	06.00	2058.27	87.95	1810.25	43534.45	0.39	76.97	15.63	5.94	1.08	7.06	1393.35	282.94	107.53	19.55
155	7.6	03.00	1566.45	87.47	1370.17	44904.63	0.33	78.11	15.16	5.50	0.908	4.52	1070.24	207.72	75.35	12.44

PC	Date	Hour	g PuO$_2$	Pu %	g Pu	g Pu	Pu-Isotope-Weight Fraction [%]					Pu-Isotopes [g]				
							238	239	240	241	242	238	239	240	241	242
156	7.6.	21.00	1693.01	87.49	1481.21	46385.84	0.30	78.60	14.82	5.40	0.886	4.44	1164.23	219.52	79.99	13.12
157	8.6.	11.00	1582.85	87.48	1384.68	47770.52	0.32	78.54	14.86	5.39	0.885	4.43	1087.53	205.76	74.63	12.25
150	8.6.	19.00	1787.90	87.76	1569.06	49339.58	0.27	77.14	16.81	4.89	0.889	4.23	1210.37	263.76	76.73	13.95
158	10.6.	15.30	1704.95	87.53	1492.34	50831.92	0.31	78.62	14.78	5.39	0.891	4.62	1173.28	220.57	80.44	13.30
159	13.6.	01.00	1247.56	87.40	1090.37	51922.29	0.32	78.55	14.86	5.41	0.867	3.49	856.48	162.03	58.99	9.45
160	14.6.	01.00	1290.00	87.25	1125.53	53047.82	0.33	78.59	14.78	5.41	0.885	3.71	884.55	166.35	60.89	9.96
162	21.6	03.00	1059.18	86.99	921.38	53969.20	0.29	78.89	15.04	4.93	0.859	2.67	726.88	138.58	45.42	7.91
161	23.6.	09.00	1188.04	86.83	1031.58	55000.77	0.30	78.62	15.35	4.84	0.884	3.09	811.02	158.35	49.93	9.12
163	29.6	1)	641.37	87.72	562.61	55563.38	0.29	78.59	15.42	4.83	0.875	1.63	442.16	86.75	27.17	4.92
164	29.6		1613.58	82.81	1336.21	56899.59	0.33	75.31	18.11	5.37	0.886	4.41	1006.30	241.99	71.75	11.84

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1) Included in final physical inventory

2.5.7 Pu-Battery Product (2BP)

Pu battery product (2 BP) which hits specifications on impurities is collected in a product receiver (2436-1) in batches of 40-100 l for accountability measurements before being transferred into MBA 22 for precipitation and calcination. These batches are listed in table 2.5.7-1 showing all relevant batch data and isotopic determinations which were used for inventory determinations in MBA 21 (chapter 5). Batches which were out of specifications need reextraction for additional purification. They were entirely recycled via 2436-1 to buffer tanks preceding the mixer-settlers. On the other hand the operator was using a technique to feed additionally the mixer settlers with recycled product because the head end could not provide every time enough feed for steady state running mixer settlers.

As pointed out in table 2.2-1 2 BP-flow was subject of independant verification procedures such as:

i) Transfer recording in order to estimate the amount of recycled Pu as supporting data for simulation models.

ii) Sampling and analysis of Pu total concentration and isotopic determinations on relevant batch data.

In total 34 samples (in general 2 per batch) excluding those to be used for inter labtest (chapter 7) were taken and stabilized for transport and storage by dilution (appr. 1:1 by weight) with 10 M HNO_3.

As indicated in table 2.5.7-1, samples which were taken immediately before transport have not been diluted.

All samples were analysed in GfK (IRCh) for Pu-total concentration using following methods

a) X-ray fluorescence spectrometry
b) Coulometry
c) Oxidimetry (Ago)

As there was the chance to evaluate analyses on diluted as well as original samples it was of interest to investigate whether the sampling error of the diluted samples is significantly different from that of original ones. The RSD of sampling error calculated by use of analysis of variances (chapter 7, appendix II) are compiled in Table 2.5.7-2.

In case of X-ray fluorescence spectrometry and coulometry the sampling errors of the diluted samples were found to be greater than of the original ones whereas the opposite trend was observed for the measurements performed by oxidimetry. Therefore no clear conclusion can be drawn from this special error analysis. However the order of magnitude of the evaluated sampling error is about half of the corresponding value evaluated in chapter 7.2 1). The latter value is based on only one batch whereas the corresponding sampling errors compiled in Table 2.5.7-2 represent the average of 8 batches.

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1) Please note that the sampling error defined in this paragraph includes both components 'sampling' and 'sample' error as defined in chapter 7.2.

Table: 2.5.7-1 Pu-Battery-Product Batches (2 BP)

Batch ident.	NMTR	RSTA	Date/hour of transfer-end	Transfer-vol. [l]	Solution density kg/l	mg Pu / g sol. 1)	g Pu	Σg Pu	Pu-isotopic comp. w/o					Remarks
									238	239	240	241	242	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2BP-300	5493	39275	8.3./21.	43.3	1.1394	44.506	2195.7	2195.7	0.136	71.982	23.103	3.742	1.037	3)
2BP-400	5501	36522	11.3./12.	46.9	1.1475	40.800	2175.6	4371.3	0.132	72.501	22.747	3.629	0.991	3)
2BP-900	5531	39504	17.3./17.	80.1	1.1475	38.509	3539.5	7910.8	0.129	73.038	22.375	3.510	0.948	3)
2BP-1100	5536	39569	21.3./6.	70.4	1.1394	28.456	2282.6	10193.4	0.125	73.233	22.263	3.458	0.921	3)
2BP-1200	5776	39611	23.3./24.	42.4	1.1635	52.0 2)	2204.8	12398.2	-	-	-	-	-	2)
2BP-1300	5790	39658	27.3./12.	58.5	1.1654	41.304	2815.9	15214.1	0.126	72.491	22.781	3.599	1.003	3)
2BP-1400	5795	39757	28.3./14.	44.7	1.1155	39.388	1964.0	17178.1	0.124	72.372	22.835	3.648	1.021	3)
2BP-1500	5758	39683	30.3./14.	39.5	1.1774	48.932	2275.7	19453.8	0.126	72.523	22.743	3.597	1.011	3)
2BP-1600	5902	39796	5.4./4.	140.6	1.1555	26.694	4336.8	23790.6	0.121	72.485	22.887	3.509	0.999	3)
2BP-1700	5920	40418	9.4./24.	82.0	1.1555	36.572	3465.2	27255.8	0.121	72.477	22.920	3.493	0.989	3)→sample (1) 4)→sample (2)
2BP-1800	5443	40491	15.4./17.	61.0	1.1555	40.875	2881.1	30136.9	0.379	69.969	22.522	5.596	1.532	3)
2BP-1900	5450	40515	16.4./16.	47.2	1.1754	42.371	2350.7	32487.6	0.497	68.699	22.488	6.519	1.797	3)
2BP-2000	5475	41652	22.4./24.	74.2	1.1274	31.762	2657.0	35144.6	0.653	66.681	22.987	7.472	2.207	3)
2BP-2100	5490	41717	27.4./11.	87.7	1.1515	37.490	3786.0	38930.6	0.701	66.146	23.146	7.667	2.340	4)
2BP-3100	5777	42444	10.5./12.	104.1	1.1595	44.868	5415.7	44346.3	0.460	75.098	16.617	6.575	1.250	4)

Table: 2.5.7-1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2BP-3200	5793	42493	13.5./19.	106.5	1.1234	25.305	3027.5	47373.9	0.372	77.863	15.167	5.622	0.976	4)
2BP-3900	5868	44308	6.6./7.	59.0	1.1555	43.338	2954.5	50328.4	0.329	78.473	14.892	5.429	0.877	4)
2BP-4000	5875	44330	7.6./8.	64.3	1.1475	46.462	3428.2	53156.6	0.328	78.468	14.936	5.380	0.888	4)
2BP-4100	5886	44373	9.6./16.	87.5	1.1394	37.297	3718.4	57475.0	0.329	78.454	14.931	5.405	0.881	4)
2BP-4400	6038	44520	20.6./7.	38.9	1.1954	27.724	1289.2	58764.2	0.296	78.884	15.295	4.676	0.849	4)
2BP-4500	6048	-	22.6./12.	57.9	-	12.6 2)	729.6	59493.8	-	-	-	-	-	2)
2BP-4600	6050	45276	22.6./20.	24.3	1.0115	1.658	40.6	59534.4	0.298	78.636	15.443	4.757	0.866	4)
2BP-4700	6056	-	23.6./	320.1	-	0.71 2)	227.3	59761.7	-	-	-	-	-	2)
2BP-4800	6057	-		420.9	-	0.269 2)	113.2	59874.9	-	-	-	-	-	2)
2BP-4900	6059	-		336.7	-	0.037 2)	12.5	59887.4	-	-	-	-	-	2)
2BP-5000	6061	-		336.7	-	0.058 2)	19.5	59906.9	-	-	-	-	-	2)
2BP-5100	6072	-	24.6./	690.4	-	0.003 2)	2.1	59909.0	-	-	-	-	-	2)

1) Mean value of GfK-analyses by AGO, coulometry and X-Ray spectroscopy

2) Process analyses of EUROCHEMIC [g Pu/l]. No isotope measurement available.
No duplicate sample taken for the exercise.

3) Duplicate samples taken for the exercise were diluted approximately 1:1 by weight with 10 M HNO_3

4) Duplicate samples for the exercise were not diluted

Table 2.5.7-2: Survey on Pu-determinations of 2BP-samples performed by the Institut für Radiochemie, GfK

Method	X-ray fluorescence spectrometry		Coulometry		Oxidimetry (AgO)	
Samples [1]	diluted	original	diluted	original	diluted	original
No. of duplicate analyses	9	13	9	13	16	13
No. of batches with duplicate samples	8	5	8	5	8	5
Precision [% RSD]	0.56	0.38	0.20	0.16	0.34	0.14
Sampling error [2] [% RSD]	0.25	not significant	0.34	0.19	0.14	0.19

[1] Range of diluted samples: 13-24 mg Pu/g
" " original " : 25-46 mg Pu/g

[2] Includes dilution error for corresponding samples

2.5.8 Recycled Plutonium (3AW)

The mother liquor (3AW) from the precipitation unit recycled into MBA 21 is measured in a relatively small accountability tank (238-5) with an average batch size of 60-70 l corresponding to about 10 - 15 g Pu. A total number of 142 batches had to be accounted. Table 2.5.8-1 summarizes only integrated amounts relevant for book inventory determinations at the two step times and the total amount up to ending physical inventory.

Table 2.5.8-1: Integrated Pu-quantities in 3 AW-flow recycled into MBA 21 at different step times

Step	Time	g Pu
CANDU/VAK	April 4th, 12.00	837.
VAK/TRINO	April 24th, 14.00	952.
Total	up to June 29th	1834.

As indicated in table 2.2-1 3 AW flow was subject of independent verification analysis by means of composite sample technique. Relevant data on this test are compiled in table 2.5.8-2. This test was performed in order to prove the potential of the composite sample technique with respect to waste analysis where verification procedures can be decreased considerably due to the high number of waste batches. In addition, great differences in Pu concentrations of single batches were expected (factor 70) so that more sensitive results of the composite sample analysis compared with the calculated concentration using operator's single batch analysis could be waited for.

Composing of all together 103 single samples were performed by Dr. Thiele[1] using the same device as described in 2.5.3.2.

Two independant laboratories were analysing composite samples K and L using isotope dilution technique and the results are compiled in table 2.5.8-2 relative to calculated concentrations using operator's single batch analysis (α-counting). Remarkable agreement at sample K was achieved by lab.I[2] which

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[1] BAM = Bundesanstalt für Materialforschung, Berlin

[2] The laboratories are coded according to agreement of involved analysts.

hit exactly the theoretical value whereas verification of composite sample L was poor. Possible reasons may be either a bias of operator's single batch analysis or a composing error as both verification analyses indicate the same tendency and correspond within 3 %,thus no considerable bias occured at the independent analysis. The isotopic determinations of both laboratories agree within tolerable limits.

Table 2.5.8-2: **Survey on 3 AW-composite samples no. K and L**

Composite Sample	K 3)	L 4)
i) No. of samples composed	32	71
ii) Total volume of corresponding batches [l]	2056.3	4476.4
iii) Aliquotation factor 1)	2.7×10^{-5}	2.7×10^{-5}
iv) Calculated Pu-concentration according to single batch analysis of the operator (α-counting) [mg Pu/l]	181.1	130.0
v) Measured ref.density (Lab.II) [kg/l]	1.0618	1.0684
vi) Verification analysis 2) relative to iv) from Lab. I	100.0±0.62 %	92.6 ± 0.31 %
vii) Verification analysis 2) relative to iv) from Lab. II	outlier	88.9 %
viii) Pu isotopes [W/o] (238/239/240/241/242) Lab. I:	0.125/72.71/22.62/ 3.56/0.99	0.335/73.60/19.45/ 5.37/1.25
Lab.II:	0.127/72.50/22.69/ 3.67/1.02	0.364/73.42/19.53/ 5.41/1.28

1) Defined as ratio: pipetted sample volume vs standard volume of corresponding batch.

(pipetter capacity: 2ml and 4ml)

2) Using isotope dilution analysis.

3) Using batches transferred into MBA 21 from March 12 up to April 4 exclusive NMTR 5735, 5535, 5534.

4) Using batches transferred into MBA 21 from April 4 up to NMTR 6058.

2.5.9 Liquid and Solid Waste

Table 2.5.9-1 summarizes relevant data on waste accountability as reported by the operator. No verification efforts were spent on these data due to the small amounts of heavy material in a relative great number of batches and due to difficulties in handling and transportation of high active sample material. Information on used codes in column 1 is already given in table 2.2-1. Subdivision indicated as A and B refers to waste flows leaving process A and B which correspond to MBA 21 and MBA 22 respectively. RIN means Rinse-solutions.

Quantitative Pu determinations in solid waste drums were carried out on the basis of measuring the complex 0.38 MeV-Gamma emission from Pu-239 with help of a two channel analyser using a NaI(Te)-detector.

Main interference of this method was experienced to be the attenuation of the emitted radiation by drum contents and the contribution to the selected energy range by long lived fission products and U-237 which is in equilibrium conditions by α decay of Pu-241. The instrument settings and calibration procedures used allowed appropriate corrections. Estimated accuracy on the given results is ± 30 % RSD per drum.

Table 2.5.9-1: Survey on Measured Losses (liquid and solid waste)

Waste flow	Total No. of batches	Total volume transferred [m^3]	Average Concentration [g U/l]	Average Concentration [mg Pu/l]	Total heavy material transferred into MBA 50 [kg U] a/c 1)	Total heavy material transferred into MBA 50 [g Pu] a/b/c 1)
1	2	3	4	5	6/7	8/9/10
JW	24	62.9	0.72	4.8	13/45.	48/250/304
HAW	142	314.0	0.29	2.65	1/91.	130/175/831
A SRW	161	148.1	0.15	0.63	12/22.	12/14/93
B SRW	282	64.9	0.07	2.9	1/4	67/93/187
A RIN	14	-	0.83	6.7	13/16.	6/14/93
B RIN	2	0.4	0.09	8.5	-/-	4/4/4
LLW	cont. flow	3054.	5.1×10^{-3}	$3. \times 10^{-3}$	1/1.6	3/3/5
Solid Waste	88 drums	-	-	-	-/-	166/252/447
Total	7/3	-	-	-	41/180	436/805/1964

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1) Referring to periods from January 11 to: a) April 12, b) April 25, c) July 1st with respect to book inventory determination at different step times.

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JEX-70

Chapter 3

Identification of Irradiated Fuel Elements

by

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SUMMARY

Part I of the report deals with the material identification of irradiated fuel assemblies by making gamma spectrometry measurements. Using a very simple mechanical device for fuel scanning and Ge(Li) spectrometer, gamma measurements of two BR-2 fuel elements and 25 VAK fuel assemblies were carried out at the pond of Eurochemic Reprocessing Plant, Mol, Belgium.

Several fission products' activities and their ratios were used as burn-up and cooling time monitors, two of them were used for estimation of plutonium/uranium fission ratio.

Results showed that gamma measurements could be developed in a practical and satisfactory technique for safeguards authorities verification on operators statements about burn-up, cooling time and Pu/U fission ratio.

Part II of the report deals with the use of television cameras to identify the code number of the irradiated fuel assembly under water. The method has proved to be satisfactory in this particular case.

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GAMMA IDENTIFICATION OF THE IRRADIATED FUEL

3.1 Introduction

It is desirable to have possibilities of identifying the fuel elements as well as knowing the burn-up for each of these fuel elements independently for an easy application of the PID technique. Normally the application of this method is possible with the help of data supplied by the shipper of the fuel elements. However, occasionally because of operating conditions independent identification and determination of burn-ups might be necessary. As mentioned in the introduction to this report the application of the PID technique was supposed to be carried out with the CANDU type of fuel only. Since it was feared that the numbers of these elements could not be identified adequately the possibility of identification of these fuel elements by using γ-spectrometry was considered. Since the operation schedule was changed and a sequence of four fuel element types was processed during the integral experiment, the application of the PID technique became possible in a highly satisfactory manner without having to identify the CANDU fuel elements or to estimate their burn-ups. It should also be noted in this connection that an averaging effect could be obtained in the case of the CANDU fuel because of the very large number of fuel elements to be processed. In spite of this fact two different identification methods were investigated in the course of this integral experiment namely one based on a television method and the second based on γ-spectroscopy method. The fuel elements chosen for this investigation were those from the VAK type reactors. In part one of this report the method of the application of γ-spectrometry has been described and the results have been discussed. Part two deals with the description of the television cameras used to identify the VAK fuel elements.

There are several reported possibilities for non-destructive measurements of irradiated fuel:

a) Gamma spectrometry measurements of the radioactive fission products. [1]

b) Burn-up determination by 145 KeV gamma ray absorption. [2]

c) Burn-up determiantion through measurement of the 2.55 MeV gamma ray of 140 La using D (γ,n)p reaction as threshold detector of the gamma rays. [3]

d) Active neturon interrogation measurement of irradiated fuel. [4]

In any consideration of potential non-destructive techniques which might be applied to the assay of irradiated fuel, the measurement of the concentration of fission product nuclei by means of techniques of gamma spectrometry represents a promising approach for IAEA safeguards.

This report seeks to answer the following questions:

1. Is it possible, using non-destructive gamma spectrometry measurements of the irradiated fuel assemblies to verify the operators' statements which include the type of fuel (pre-irradiation enrichment), history of its irradiation and operational history of the reactor during the period when the measured fuel was in the core of the reactor.

2. Are these measurements of value for safeguards regarding reprocessing plant input?

3. What are the practical possibilities of carrying out such measurements from the IAEA safeguards point of view?

In order to avoid a risk of misunderstanding it is necessary to explain the term 'identification' of irradiated fuel assembly. [5] Gamma identification of irradiated fuel is a gamma spectrometry measurement of the fuel which enables one (an inspector) to identify the kind of measured fuel and to verify operators' statements about the irradiation history of the fuel.

Such measurements follow the modern trends in safeguards because they allow verification of a large part of the whole fuel cycle starting with the fuel fabrication plant through the reactor and finishing with the input of the reprocessing plant. The majority of countries do not have and are not likely to have fuel fabrication and fuel reprocessing plants. Thus, with such measurements it will be possible to monitor the total nuclear activities of these countries.

Gamma spectrometry measurements of fuel elements to obtain fission-products concentrations as indicators of fuel burn-up were among the first attempts at non-destructive fuel assay. Several methods and techniques for such measurements have been suggested and developed [1], [6], [7], [8], [9], [10], [11], [12], [13]. But published results from practical applications are limited, [10], [14], [15], [16].

There are also several reviews of this problem which compare and evaluate studies of non-destructive burn-up assay [17], [18], [19], [20], [21], [22]. A very interesting study of different semiconductor spectrometers is made in [23].

3.2. EXPERIMENTAL

The measurements were carried out in the pond of the Eurochemic reprocessing plant at Mol. The necessary instruments, a Ge(Li) detector, a pre-amplifier, a high voltage source, an amplifier, a multichannel analyzer and a printing device were taken to the site from CEN, Belgium.

A simplified sketch of the equipment set-up is shown in Fig. 3 - 1. A closed tube, six meters in length, inner diameter 5 cm was used as an air channel in the water. It was suspended on cords with lead weights at the lower end, 15 cm from the pond wall. The immersion angle was 45°. There was a collimator-filter only at the upper end of the tube in front of the Ge(Li) detector. The collimator diameter was 20 cm. Two filters, one 20 mm thick brass and one 5 mm thich lead, were used to reduce the intensities of low energy gamma rays. Nevertheless, gamma intensity of 0.42 years cooled fuel assemblies was higher than optimum for such measurement. The measured fuel assembly was suspended on the crane hook. No device for radial fixation of the measured fuel assembly was used.

The active volume of the Ge(Li) detector was approximately 4 cc. The resolving power of the whole system, detector, pre-amplifier, amplifier, analyzer was about 7 KeV for 662 KeV peak, so it was not possible to resolve the 757 KeV gamma ray peak of Zr-95 and the 77 KeV gamma ray peak of Nb-95. The detector efficiency was a little small for gamma rays with energy higher than 1 MeV. The open electrodes of the detector, which was located near the pond, caused some inconvenience because of the increase after 24 hours in electrical conductivity between the electrodes due to moisture pickup. Resolving power of the detector was maintained by periodically drying and cleaning the electrodes.

For the experiment a 4000 multichannel analyzer "Intertechnique" was used. However, use of 1000 channels is adequate for similar measurements. The ability of the analyzer to integrate the number of counts under any peak facilitated the data processing later and was a useful feature.

The on-site preparation and set-up of equipment, calibration of the instruments and preliminary measurements required about one day.

Routine measurements were carried out by one technician from CEN and one mechanic-operator from the Eurochemic plant (in one shift). The time necessary for one routine measurement, i.e. one point on a single fuel assembly, was twenty minutes - ten minutes measurement and ten minutes for printing of the data and crane changing of the fuel assembly. Control measurements which were made for higher accuracy ranged from 30 to 300 minutes.

3. DATA PROCESSING

The two spectra, taken from the BR-2 fuel elements, are shown in Fig.3-2. On the spectrum from the fuel element S-184 (cooling time 5.44 years) one can see only two peaks of Cs-134, 605 and 796 KeV and the only peak of Cs-137, 662 KeV. On the spectrum from the fuel element M-519 (cooling time 3.184 years) the peak of Pr-144, 696 KeV and peak of Rh-106, 622 KeV also can be measured.

The spectrum from the VAK fuel assembly A-35 (cooling time 1.58 years) is shown in Fig. 3- 3.

It is obvious from this spectrum that one can measure the intensity of many gamma peaks. The energy of most of these peaks are given in Table 3-- 1.

The energy calibration of the instruments was made using Co-60 and Ba-133 standard sources, using the method of least squares.

The energies of fuel element gamma peaks measured through this calibration and their energies from literature are given in Table 3 - 1.

Table 3 - 1. Comparison of Scanning vs Energy from Literature Data

A	Rh-106	Cs-134	Rh-106	Cs-137	Pr-144	Zr-95	Nb-95	Cs-134	Cs-134	Pr-144	Pr-144
E (KeV) (Lit)	511.9	604.6	622.0	661.6	696.3	724.2	765.8	795.9	1365.2	1489.5	2185.6
E (KeV) (Meas.)	511.8	604.4	621.8	661.7	696.4	724.1	765.9	795.8	1365.2	1489.7	2186.2

It is clear from the table that the determination of the gamma energies is reasonably accurate.

Repeated measurement of the background showed it to be negligible. Only two peaks of Co-60 appeared after a long measurement of the background. Shielding of the detector was not necessary.

Originally in planning the experiment, the intent was to measure only the ratios of two gamma peaks: 605 KeV peak of the Cs-134 and 662 KeV of the Cs-137. However, in order to obtain as much information as possible about all fuel assemblies and different approaches to gamma measurements, the whole spectra from 500 to 2500 KeV were taken.

The most important of the additional measurable gamma peaks are:

1. Two peaks of the Cs-134 with energy 796 KeV and 802 KeV which are measured together. These peaks are better isolated from other peaks and can be measured with higher accuracy than 605 KeV peak.

2. Several gamma peaks of the Rh-106 (512 KeV, 622 KeV, 873 KeV, 1128 KeV) and one well isolated peak of the Eu-154 (1274 KeV) which are mainly the results of Pu-239 fission.

3. Two gamma peaks 724 KeV of the Zr-95 and 766 KeV of the Nb-95 which show the cooling time of the fuel.

4. Three gamma peaks of Pr-144 with energy of 696.3 KeV, 1489 KeV and 2186 KeV. These peaks can be used for determination of fuel burn-up and cooling time. The measurements showed that **these gamma peaks** can be used successfully for some burn-up determination for a cooling period from three months to more than two years. The 2186 KeV **peak is also very important due to its high energy and the high** penetrability of its gamma rays. Moreover, this peak is well separated from other peaks and can be easily measured with high accuracy even with scintillation detectors and single channel analyzers. Because these instruments are easily portable, this is very important for safeguards purposes.

The areas of different full-energy peaks in the spectrum are related to the amount of corresponding gamma radioactive fission products in the measured fuel assembly. The Compton scattering mainly and some other effects create rather high continuum over which the full energy peaks appear. It is very difficult to take into account all these effects, particularly for the complex spectrum of irradiated fuel. Usually the full-energy peak is determined as a difference between the count under the peak and the estimated background. In order to receive high statistical precision relatively long time measurements are required. For such cases however, when only relative measurements of one or two groups of fuel elements with similar conditions of irradiation and cooling time are required it is possible to use another approach. This consists of taking the total amount of the counts between the boundaries of the full-energy peak as related to the amount of corresponding fission product. This approach was used for relative measurement of burn-up because of the short counting times. Results show that it is a better approach. For axial distribution of the burn-up, however, the full-energy peaks as such were used as representatives of fission product activities.

3.4. MEASUREMENTS OF AXIAL DISTRIBUTIONS OF BURN-UP

The relative axial distributions of the burn-up along the BR-2 fuel elements and VAK fuel assemblies were first measured because:

a) They provide the basic qualitative check of the capability of the method and measurements as roughly the axial distribution of integrated flux and burn-up was known in advance.

b) These measurements are necessary for the determination of the integrated burn-up of the fuel assembly.

The axial distributions of the burn-up along one BR-2 fuel element M-519 and three VAK fuel assemblies A-35, A-34 and A-41 with different degrees of burn-up were measured. The gamma spectra were taken at nine points of the fuel element or fuel assemblies - at 0/8, 1/8, 2/8, 3/8, 4/8, 5/8, 6/8, 7/8 and 8/8 parts of the active length of the fuel.

The following burn-up monitors were used for these measurements:

a) The intensity of Cs-137 gamma peaks with energy 662 KeV.

b) The intensities of Pr-144 gamma peaks with energies 696, 1489 and 2186 KeV.

c) The ratio between intensities of Cs-134 gamma peaks 605, 796 and 1365 KeV and Cs-137 gamma peak 662 KeV.

A quantitative value of the quality of measurements was made by using the variation coefficient of the ratios between intensities of different peaks from the same isotopes along the fuel elements and the fuel assemblies. In particular, the three peaks of Cs-134 and the three peaks of Pr-144 were used. The values of these ratios should be constant because the two peaks being compared are from one isotope and gamma ray absorption must be the same along the fuel element.

The data from BR-2 fuel element, M-519 are shown in Fig. 3 - 4. The variation coefficients of the intensity ratios of Cs-134 two peaks - 796 to 605 KeV and intensity ratios of Pr-144 peaks - 696 KeV and Cs-137 peaks - 662 KeV were found to be 4.5% and 3.7%. These two results demonstrate that the precision of these measurements is reasonable. The 3.7% coefficient shows also that there is no diffusion of Cs to the ends of the fuel element. The relative values of Cs-134 activities pronounced through the relative values of two peaks as well as the relative values of Cs-137 and Pr-144 activities for the same points are in agreement.

The data from VAK fuel assembly A-35 are shown in Fig. 3 - 5. Additional peaks and activity ratios were used for measurements of this fuel assembly as compared to the previous measurement.

In Table No. 3-2 the variation coefficients for corresponding intensity ratios are given. VC1 is for variation coefficients when all measured points are taken into account; VC2 - when the end points are excluded and VC3 is for variation coefficients when all measured points are taken into account and corresponding activity values are for net full-energy peaks. As it was expected, the variation coefficients for the last case are higher.

Table No: 3-2. Axial Distributions of Activity Ratios Along Fuel Assembly A-35 (VAK)

R VC	$\frac{796}{605}$	$\frac{1365}{605}$	$\frac{1365}{796}$	$\frac{1489}{696}$	$\frac{2186}{696}$	$\frac{2186}{1489}$
VC 1	3.3%	5.8%	6.5%	6.7%	9.4%	5.1%
VC 2	0.8%	3.5%	3.8%	2.2%	1.9%	2.0%
VC 3	7.9%	15.4%	10%			

The comparison between the VC1 and VC2 in Table No: 3 - 2. shows that variation coefficients increase by a factor of 2 to 3 when end points are included. This means that without a special device for fixation of the fuel assembly the measurements at the ends are not satisfactory. But they do not, however, strongly influence the integral value of burn-up for the whole fuel assembly.

It can be seen from Fig. 3-5 that the intensities of gamma peaks at the midpoint of the fuel assemblies are significantly lower. This is because VAK fuel assemblies comprise two separate fuel sections and there is a distance of approximately 4 cm between the two separated fuel sections where fissionable material is not present.

Attention should be paid to the fact that when the ratio of activities of Cs-134 to Cs-137 are used as a burn-up monitor they give the correct burn-up values despite the lack of fuel in the centre. This shows that geometrical factors of measurement are not so important for the **activity ratio** monitors and that the ratio of activities does not depend strongly on the quantity of the fissionable material at the measured point.

The relative values of the three measured activities as well as the relative values of two measured activity ratios are in agreement for different points. For the end points the differences are greater.

It must be pointed out also that variation coefficient is greater for intensity ratios in cases where the difference in energy of the related peaks is higher. The most probable reason for this is connected again with the geometrical instability of these measurements, due to the lack of any fixing device. As the effective absorption coefficient for gamma rays decreases constantly with increasing of their energy, it strongly affects the ratios when the difference between the energies of the two related gamma peaks is higher.

The axial distribution measurements of activities and activity ratios of Cs-134 to Cs-137 can be summarized as follows:

1. The axial distributions of activities and activity ratios as burn-up monitors follow qualitatively the distribution of the integrated neutron flux at different points of the reactor core.

2. The axial distribution of Cs-134 activities decreases steeply to the ends of the fuel assemblies which reflect the fact that Cs-134 accumulation is nearly proportional to the second degree of integrated neutron flux.

3. The precision of the measurements themselves, even in this preliminary case, is reasonable as can be seen from variation coefficients.

3.5 RELATIVE BURN-UP MEASUREMENTS OF VAK FUEL ASSEMBLIES

Since only two days were available for measurement of the 25 VAK fuel assemblies, measurement of 21 of the assemblies was limited to one specific location of these assemblies. (The remaining four assemblies were extensively measured to obtain the maximum amount of data.) Additionally, in those cases where burn-up measurements are being made on identical type fuel assemblies, a single place measurement is sufficient for relative burn-up determinations. This conclusion was one of the aims of the experiment. In these cases, however, it is important to select the optimal place along the fuel assembly for precise measurements.

The gamma spectroscopic data from fuel assemblies were divided in two groups according to their cooling times; data of fuel assemblies with a cooling time of 0.42 years, whose activity was essentially higher, and data from fuel assemblies with a cooling time of 1.58 years. The significantly higher activities of the shortly cooled assemblies made it difficult to make a mistake in assigning the individual fuel assemblies to their proper groups.

Table No:3-33summarizes the data for fuel assemblies having a cooling time of 1.58 years. The column code for this table is as follows:

Column No: 1 is for the identification codes of measured fuel assemblies.

No: 2 gives the calculated burn-up in MWd/ton.

Nos: 3 to 11 give activity ratios for the peaks named.

Nos: 12 to 14 give the relative values of corresponding activities in percentages for the measured fuel assembly to the same activities of the fuel assembly A-31.

A-31 was chosen as a relative standard because it had the highest calculated burn-up in this group.

Nos: 15 and 16 give the relative values of activity ratios R_1 and R_2 in percentages for measured fuel assembly to the corresponding activity ratios for the fuel assembly A-31.

Table No: 3-3 Data from VAK Fuel Assemblies with 1.58 years cooling time

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Code	B	$\frac{A_{2186}}{A_{696}}$	$\frac{A_{1489}}{A_{696}}$	$\frac{A_{2186}}{A_{1489}}$	$\frac{A_{1365}}{A_{605}}$	$\frac{A_{796}}{A_{605}}$	$\frac{A_{1365}}{A_{796}}$	$\frac{A_{766}}{A_{662}}$	$R_1=\frac{A_{605}}{A_{662}}$	$R_2=\frac{A_{796}}{A_{662}}$	$\frac{A_{605}(i)}{A_{605}(ii)}$	$\frac{A_{796}(i)}{A_{796}(ii)}$	$\frac{A_{662}(i)}{A_{662}(31)}$	$\frac{R_1(i)}{R_1(31)}$	$\frac{R_2(i)}{R_2(31)}$	$\frac{B_c(i)}{B_c(31)}$
N-20	~9450	0.106	0.170	0.626	0.0732	0.872	0.0885	0.375	0.790	0.654	99	102	105	95	98	59
A-38	14192	0.0790	0.136	0.581	0.0612	0.835	0.0733	0.361	0.811	0.677	87	90	90	97	101	89
A-35	15072	0.0843	0.144	0.587	0.0721	0.853	0.0845	0.417	0.820	0.698	42	44	43	98	104	94
A-35	15072	0.0844	0.144	0.586	0.0717	0.857	0.0837	0.400	0.808	0.693	42	45	42	97	103	94
A-16	15072	0.0889	-	-	0.0745	0.859	0.0868	0.434	0.837	0.719	40	42	39	100	107	94
A-12	15108	0.0697	0.124	0.558	0.0584	0.796	0.0733	0.369	0.838	0.667	78	78	78	100	100	94
A-54	15123	0.0716	0.124	0.576	0.0566	0.858	0.0659	0.328	0.820	0.704	94	100	95	98	105	95
A-43	15154	0.0697	0.124	0.562	0.0584	0.803	0.0728	0.352	0.800	0.636	76	76	78	96	95	95
A-19	15668	0.0758	0.134	0.564	0.0632	0.852	0.0742	0.368	0.795	0.677	63	67	66	95	101	98
A-55	15735	0.0712	0.133	0.537	0.0619	0.864	0.0716	0.358	0.803	0.694	70	75	72	96	104	98
A-18	15835	0.0799	0.143	0.559	0.0778	0.853	0.0912	0.519	0.986	0.841	24	25	20	118	126	99
A-5	15884	0.0755	-	-	0.0675	0.818	0.0825	0.419	0.858	0.702	44	45	43	103	105	99
A-17	15909	0.0673	0.119	0.56	0.0557	0.801	0.0695	0.362	0.849	0.680	95	95	93	102	102	100
A-31	15992	0.0670	0.121	0.555	0.0547	0.803	0.0682	0.340	0.834	0.670	100	100	100	100	100	100
$\bar{x}$		0.0757	0.131	0.566	0.0641	0.835	0.0767	0.376								
σ		0.0068	0.009	0.014	0.0074	0.025	0.0077	0.0337								
$\frac{\sigma}{\bar{x}}$		9.4 %	6.9 %	2.5 %	11.6 %	3.0 %	10 %	8.5 %								

No: 17 gives the ratios of calculated burn-up of measured fuel assemblies to the calculated burn-up of A-31 fuel assembly in percentages.

It is essential to consider the following in connection with this table:

a) The fuel assembly N-20 was partly decladded so the conditions for its measurement were different and it is difficult to compare N-20 measurements with other fuel assembly measurements.

b) A-35 fuel assembly was measured twice, the first time 50 minutes and the second time, after several other measurements, 300 minutes. The comparison of these two measurements showed that the precision and reproducibility of the measurements was quite satisfactory.

c) In addition to the previous quantitative values of activity ratio from the same isotopes for the quality of measurements a new one was used: Column No: 9 - the activity ratios of Nb-95 (766 KeV) to Cs-137 (662 KeV) activities. It is possible to use this activity ratio as quality monitor by assuming that all fuel assemblies have the same cooling time and nearly the same history of irradiation. The last months of irradiation, of course, are more important.

The last three lines of the table give:

1. the average value of corresponding ratios.
2. the absolute values of standard deviations.
3. the variation coefficients of the corresponding ratios.

It can be seen from the table that again the standard deviations and the variation coefficients are greater for the intensity ratios when the difference in energy of related peaks is higher.

The reason should be the same - the absence of a device to fix the radial movement of the assembly under measurement.

There is an agreement between two Cs-134 measurements, as well as between Cs-134 and Cs-137 measurements. There is also an agreement between two measurements of Pr-144 using 1489 and 2186 KeV peaks, but there is no agreement between Cs-137 and Pr-144. This can be explained by the higher penetrability of the Pr-gamma rays and the geometry of measurements. The relative values of two ratios are in sufficient agreement but the ratios 796/662 are usually several percent higher. Probably, the reason is the lower than average value of this ratio for A-31 fuel assembly, which gives higher relative values for other fuel assembly ratios.

There is a considerable difference between the data from A-18 and the data from other fuel assemblies. although the calculated burn-up is nearly the same. It must be noted also that A-18 activity ratios for Zr, Nb, Pr and Cs-134 peaks to the 662 KeV peaks of Cs-137 are more than three sigma higher than the average for all fuel assemblies. This anomaly may be due to a shorter cooling time of this fuel assembly, or relatively more intensive irradiation during the final period of irradiation.

Table No: 3 - 4 summarizes the data for fuel assemblies having a cooling time of 0.42 years. The data are listed again according to increasing calculated burn-up.

There is close agreement between Zr-95 and Nb-95 activities, as well as between Cs-137 and Pr-144 activities, the last being higher again because of the higher penetrability of these gamma rays. There is also an agreement between the relative values of the activity ratios burn-up monitor and the relative values of calculated burn-up. The calculated correlation factor for linear dependance between relative values of calculated burn-up and relative values of activity ratios Cs-134 to Cs-137 is 0.993 which confirms this agreement. The agreement between relative values of calculated burn-up and relative values of all the activities is not satisfactory, as can be seen from the table. Probably, the most essential reason for this is the unsuitable place of measurement along the fuel assemblies. This assumption is strongly confirmed by the fact that the relative values of all the activities are in satisfactory agreement between themselves.

The fuel assembly A-41 was measured twice. The first time measurement was made using a 5 mm thick*Pb-filter and the second time without this filter. This gives the possibility to calculate the attenuation of different energy gamma rays in the filter material. The calculated data are shown in Table No: 3-5.

Table No: 3-5. The Energy Dependance of the Counting Rates Ratio Without and With Absorber

$E_{(KeV)}$	605	662	724	766	796	1365	1489	2186
K_{att}	2.14	2.08	1.99	1.90	1.76	1.55	1.50	1.41

As expected in this energy range, the attenuation coefficient K_{att} constantly decreases when gamma energy increases.

Table No: 3-4 Data from VAK Fuel Assemblies with 0.42 years cooling time

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Code	B	$\frac{A_{2186}}{A_{1489}}$	$\frac{A_{1365}}{A_{605}}$	$\frac{A_{796}}{A_{605}}$	$\frac{A_{1365}}{A_{796}}$	$\frac{A_{724}}{A_{662}}$ T_{Zr}	$\frac{A_{766}}{A_{662}}$ T_{Nb}	$\frac{A_{2186}}{A_{662}}$ T_{Pr}	$R_1=\frac{A_{605}}{A_{662}}$	$R_2=\frac{A_{796}}{A_{662}}$	$\frac{A_{662}(i)}{A_{662}(34)}$	$\frac{A_{724}(i)}{A_{724}(34)}$	$\frac{A_{766}(i)}{A_{766}(34)}$	$\frac{A_{2186}(i)}{A_{2186}(34)}$	$\frac{R_2(i)}{R_2(34)}$	$\frac{B_c(i)}{B_c(34)}$
A-36	13215	0.432	0.0489	0.426	0.115	0.916	2.530	0.0237	1.285	0.548	32	36	38	42	87	71
A-33	13400	0.431	0.0431	0.388	0.111	0.881	2.357	0.0195	1.271	0.493	64	70	70	70	78	72
A-22	13835	0.448	0.0458	0.414	0.111	0.883	2.434	0.0215	1.283	0.531	57	63	65	69	85	74
A-41	13928	0.442	0.0537	0.443	0.121	0.893	2.315	0.0250	1.238	0.548	27	30	30	38	87	75
A-47	13965	0.435	-	0.401	-	0.889	2.330	0.0219	1.261	0.506	56	63	61	69	81	75
A-40	17802	0.422	0.0458	0.465	0.098	0.810	2.120	0.0189	1.300	0.604	57	58	56	60	96	95
A-15	18031	0.432	0.0444	0.441	0.101	0.833	2.316	0.0192	1.314	0.580	56	58	61	60	92	97
A-30	18216	0.416	0.0459	0.475	0.097	0.804	2.076	0.0181	1.294	0.615	80	71	68	72	98	98
A-21	18259	0.419	0.0458	0.459	0.100	0.830	2.194	0.0182	1.310	0.601	73	76	75	75	96	98
A-14	18280	0.415	0.0452	0.460	0.098	0.828	2.128	0.0180	1.285	0.591	78	83	79	80	94	98
A-34	18652	0.412	0.0448	0.585	0.092	0.800	2.144	0.0178	1.293	0.628	100	100	100	100	100	100
$\bar{x}$		0.428	0.0463	0.442	0.104	0.852	2.268	0.0202								
σ		0.011	0.0028	0.030	0.0095	0.039	0.138	0.0024								
$\frac{\sigma}{\bar{x}}$		2.6 %	6.1 %	6.7 %	8.7 %	4.6 %	6.1 %	11. 8 %								

3.6 COOLING TIME MEASUREMENTS

The measured VAK fuel assemblies had two different cooling times: 0.42 years and 1.58 years. Two BR-2 fuel elements (90% enrichment) having much longer cooling times, respectively 3.18 years and 5.44 years were also measured. Thus, two different types of fuel elements (VAK assemblies, 2.6% enrichment and highly enriched BR-2 fuel elements) having four different cooling times and a spread in the degrees of burn-up: 23% and 25% for BR-2 fuel elements and 10,000 to 19,000 MWd/ton (1 - 2% of all atoms) for VAK fuel assemblies were measured.

It was easy to distinguish the cooling times of the fuel elements qualitatively and quantitatively because:

a) Their radioactivities depend strongly on the cooling time and even the ratemeter of the multichannel analyzer was a reasonably good monitor of the cooling time.

b) The general character of the spectrum is also a good qualitative cooling time monitor. Experience in gamma spectrometric measurements of irradiated fuel enables one to determine roughly the cooling time of measured fuel from the general character of the spectrum.

c) Suitable quantitative monitors of cooling time, however, are the activity ratios of the following isotopes:

- i) La-140 ($T_{\frac{1}{2}}$=40.27 hours) to Cs-137 for very short cooling time, days and weeks;
- ii) Nb-95 and Zr-95 to Cs-137 for normal cooling times, months;
- iii) Pr-144 to Cs-137 for long cooling time, many months and even years.

All these ratios depend also on some other factors but by using several of these ratios a reliable and accurate cooling monitor can be achieved.

A more independant monitor of cooling time may be obtained by using activity ratios of genetically related isotopes. These ratios give definite information if it is known that they were in saturation immediately before the shut-down of the reactor. For practical application the most suitable such ratios are:

1. For short cooling times the activity ratios of La-140 to Ba-140. The 537 KeV gamma rays of Ba-140 should be used for measurement of Ba activities. There are several suitable gamma peaks (487 KeV, 816 KeV, 925 KeV, 1597 KeV, 2522 KeV) of La-140 gamma rays which can be used for determining its activity. The cooling time dependance of La-140 to Ba-140 activity ratio is shown in Fig. 3.- 6.

2. The activity ratio of Nb-95 to Zr-95. The use of this ratio was first proposed in [24]. This ratio is very suitable because it covers practical range of cooling times. However, it is not easy to resolve the 577 KeV Zr-95 gamma peak and 766 KeV Nb-95 gamma peak. In such cases it is recommended that the ratio of these two intensities together to the intensity of 724 KeV gamma rays of Zr-95 be used.

The dependence of the last ratio from the cooling time is shown in Fig.3-7. On both Figs. 6 and 7 the full lines are for the ratios after shutdown from constant power (equilibrium) and dotted lines for the ratios after shutdown from power burst. These ratios can be used as well:

a) To determine if the reactor was shut down from constant power or not in case the cooling time of the fuel is known; and

b) To state definitely that the cooling time is longer than the period for which the ratios reach constant value in time, if it is so for the measured case.

The data from reported measurements are given in Table 3 - 6 As can be seen from the table, all ratios steeply increase when the cooling time decreases. The ratio of 757 and 766 KeV gamma intensities to 724 KeV gamma intensity in the case of 1.58 years is 5.99 instead of the calculated 6.10 and in the case of 0.42 years 5.97 instead of 5.75. This is quite reasonable for such measurements.

Table No: 3 - 6. Cooling Times Estimation

Activity ratios / Cooling times	$\frac{724}{662}$	$\frac{757 + 766}{662}$	$\frac{696}{662}$	$\frac{757 + 766}{724}$	$\frac{605}{662}$	$\frac{796}{662}$
5.44			0.005		0.045	0.032
3.18			0.028		0.090	0.068
1.58	0.024	0.14	0.033	5.99	0.42	0.65
0.42	1.40	8.34	0.097	5.97	0.55	0.84

Another illustration of the cooling time estimations is given in Table 3-7.It is divided into two parts.

The top half of the table shows the correlation between the different activity ratios which indicate the variations of the fuel element cooling time in the 1.58 year range.

The lower half shows the same for fuel elements in the 0.42 year range.

It is clear from both halves of the table that there is a strong correlation between Nb-95 and Zr-95 ratios and satisfactory correlation between them and Pr-144 ratios. The cooling time factor, however, is not dominant in the case of Cs-134 (R_2) ratios and the cooling time correlation with the other three ratios is not evident.

Table No: 3 - 7. Correllations Between Different Cooling Time Monitors

	A-54	A-31	A-43	A-55	A-38	A-17	A-19	A-12	$A\text{-}35_I$	$A\text{-}35_{II}$	A-5	A-16	A-18
$T_{Nb} = \frac{A_{766}}{A_{662}}$	0.33	0.34	0.35	0.36	0.36	0.36	0.37	0.37	0.40	0.42	0.42	0.43	0.52
$T_{Zr} = \frac{A_{724}}{A_{662}}$	0.20	0.21	0.21	0.22	0.215	0.22	0.22	0.22	0.25	0.25	0.25	0.26	0.32
$T_{Pr} = \frac{A_{2193}}{A_{662}}$	0.017	0.017	0.018	0.018	0.020	0.018	0.020	0.019	0.024	0.025	0.023	0.028	0.030
$R_2 = \frac{A_{796}}{A_{622}}$	0.70	0.67	0.64	0.69	0.68	0.68	0.68	0.67	0.70	0.69	0.70	0.72	0.84
	A-30	A-40	A-14	A-34	A-21	A-15	A-41	A-47	A-33	A-22	A-36		
$T_{Zr} = \frac{A_{724}}{A_{662}}$	0.80	0.81	0.83	0.80	0.83	0.83	0.89	0.89	0.88	0.88	0.92		
$T_{Nb} = \frac{A_{724}}{A_{662}}$	2.08	2.12	2.13	2.14	2.19	2.31	2.32	2.33	2.36	2.43	2.53		
$T_{Pr} = \frac{A_{2193}}{A_{662}}$	0.018	0.019	0.018	0.018	0.018	0.019	0.025	0.022	0.020	0.022	0.024		
$R_2 = \frac{A_{796}}{A_{662}}$	0.62	0.60	0.59	0.63	0.60	0.58	0.55	0.51	0.49	0.53	0.55		

3.7. ESTIMATION OF Pu/U FISSION RATIO

Ce-Pr-144 to Ru-Rh-106 activity ratios were used for estimation of the ratio of total Pu to total U fissions [24]. This ratio is a sensitive measure because of the big difference in Ru fission yields from Pu and U fission and it does not vary strongly in time because of the close decay times of Ru and Ce.

The obtained values for measured fuel after the introduction of the decay time corrections was 11.6 for BR-2 fuel and 3.6 for VAK fuel. The small 3.6 ratio for the VAK fuel indicates that significant Pu production and burn-up has taken place during irradiation in the reactor.

Another very useful signature of Pu/U ratio may be the activity ratio of Eu-154 to Cs-137. The decay time of Eu-154 is very long (16 years). The energies and intensities of some of its gamma rays are also very suitable for non-destructive measurements (966 KeV, 1004 KeV and 1274 KeV).

However, this point has still not been sufficiently investigated.

Conclusions

1. A scanning device is necessary for a better accuracy of measurement. Such a device was later used in the cooling pond of the BR-2 reactor for the measurement of its fuel elements. It is shown in Fig.3 - 8.

2. For many control safeguard purposes single-place measurement along the fuel assemblies is enough. The choice of the proper measurement place in such cases is important.

3. The activity ratios are more reliable and accurate burn-up and cooling time monitors. The variation coefficients of some of the used ratios in the BR-2 experiment on one typical fuel element were:

$$\frac{A_{605}}{A_{662}} = 0.44\% \qquad \frac{A_{796+802}}{A_{662}} = 0.48\% \qquad \frac{A_{757} + A_{765}}{A_{724}} = 0.06\%$$

but for 662 KeV activity only it was 0.63%.

4. The most suitable burn-up monitor for relative measurements with scintillation detectors is ^{144}Pr-1286 KeV activity. [16]

5. The accuracy of measurement, even in this preliminary case, was reasonable. It depends upon the precision of the scanning device and the measurement time. Using a semiconductor gamma spectrometer with up-to-date resolution and a suitable scanning device, an accuracy of measurement of about 1-2% could be achieved, i.e. considering the ratio $\frac{A_{757} + A_{766}}{A_{724}}$ the difference between measured and calculated (knowing the cooling time) ratios divided by the calculated ratio was 0.7% for the typical BR-2 fuel element.

This means that such measurements can be used for an identification of the fuel limited by 1 - 2% accuracy.

6. The quantity of information which can be obtained from the gamma measurement depends on the cooling time at the moment of measurement. The shorter cooling time permits more

information to be extracted. Up to cooling times of 2 - 3 years, however, there is no difficulty in the determination of the irradiation history and isotope contents of interest from a safeguards point of view.

7. The most promising way to achieve the highest possible precision and accuracy is to use a semiconductor spectrometer with compton suppression and computer processing of the data. Using gamma spectrometry with suppressed compton continuum and digital computers only, it is possible to determine the relative and absolute values of different fission product activities, the effective attenuation of gamma rays in the fuel material and the radioactive isotope contents with an accuracy of 1 - 2%. Further improvements can be made by introducing an effective gamma detection coefficient as a correction factor.

It is really important for gamma identification of the irradiated fuel to use not only activities of one or two isotopes but the total gamma spectrum - practically from 0.3 to 3.0 MeV and to use the correlation between different activities and ratios for the introduction of correction in independant interpretations and assumptions [24].

In conclusion, we can answer the questions put at the beginning of this report:

1. Gamma spectrometric measurements are a reliable and practical method for irradiated fuel identification.
2. These measurements even now are of value for safeguards regarding reprocessing plant input but this aspect needs further development and, maybe, calibration of gamma measurements against results from destructive analysis.
3. IAEA safeguards can carry out such measurements with instruments on site or with portable instruments which are now under development.

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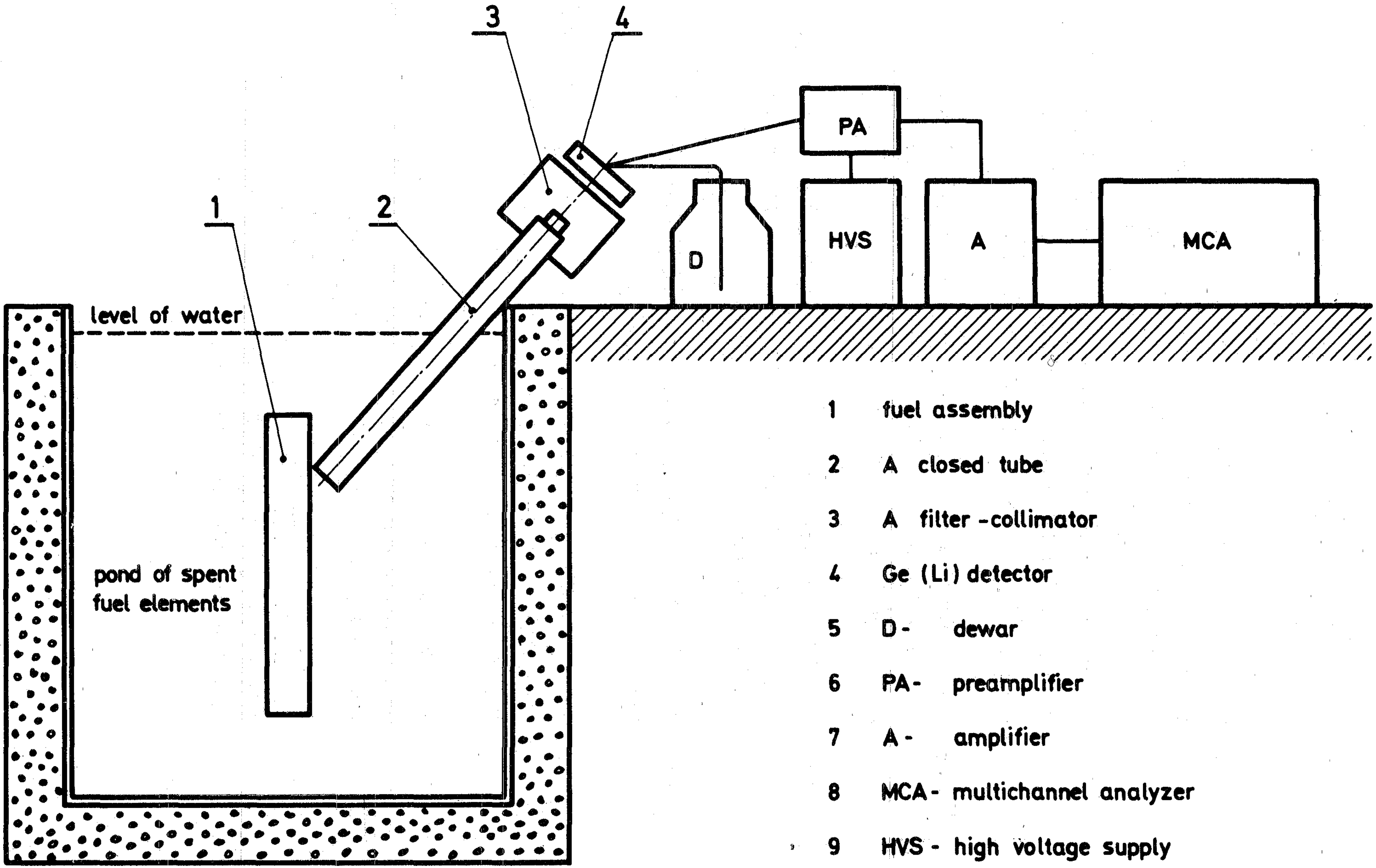


Fig. 3-1 A Scetch of Measurements of Spent Fuel Elements with Ge (Li) Detector

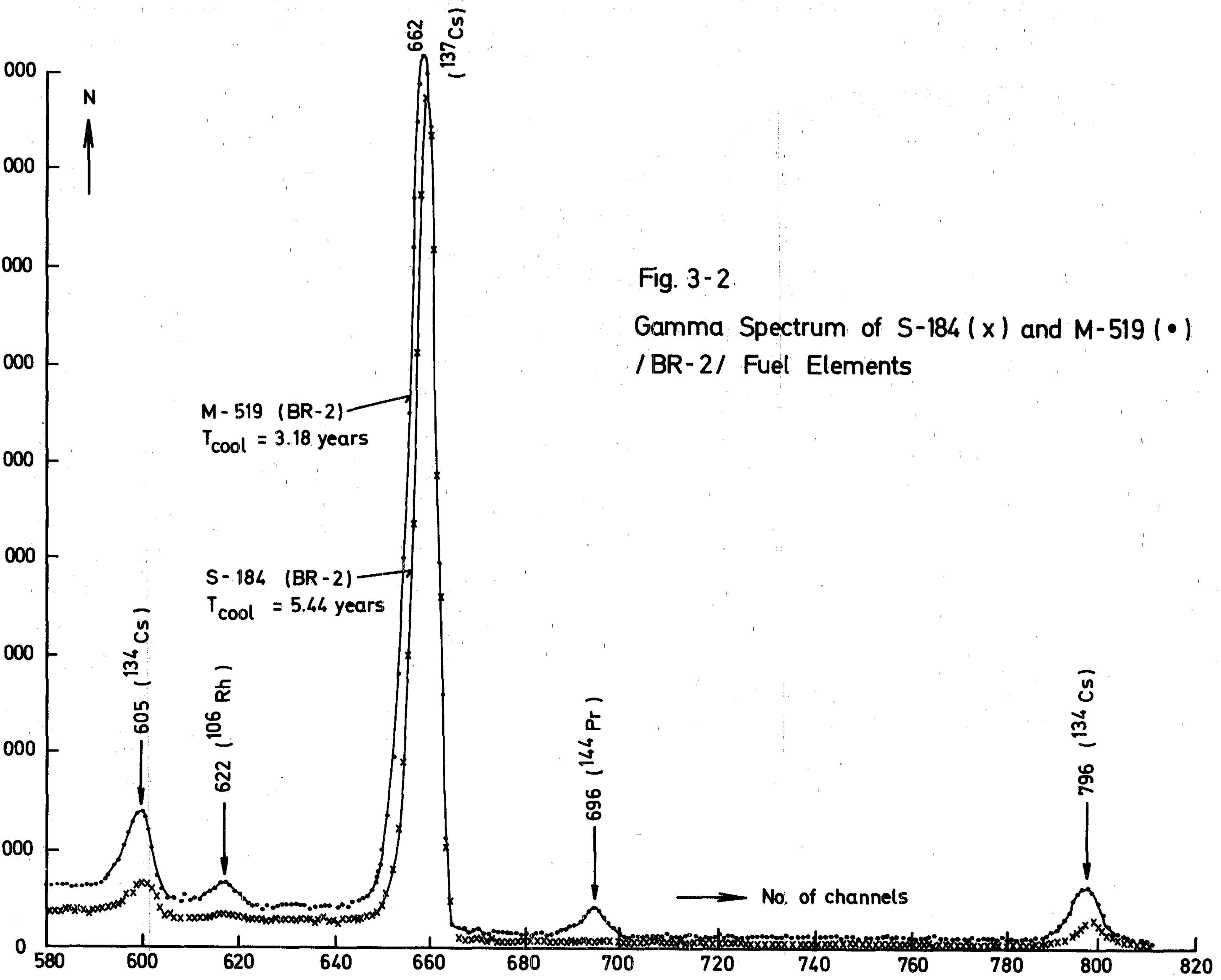


Fig. 3-2

Gamma Spectrum of S-184 (x) and M-519 (•) /BR-2/ Fuel Elements

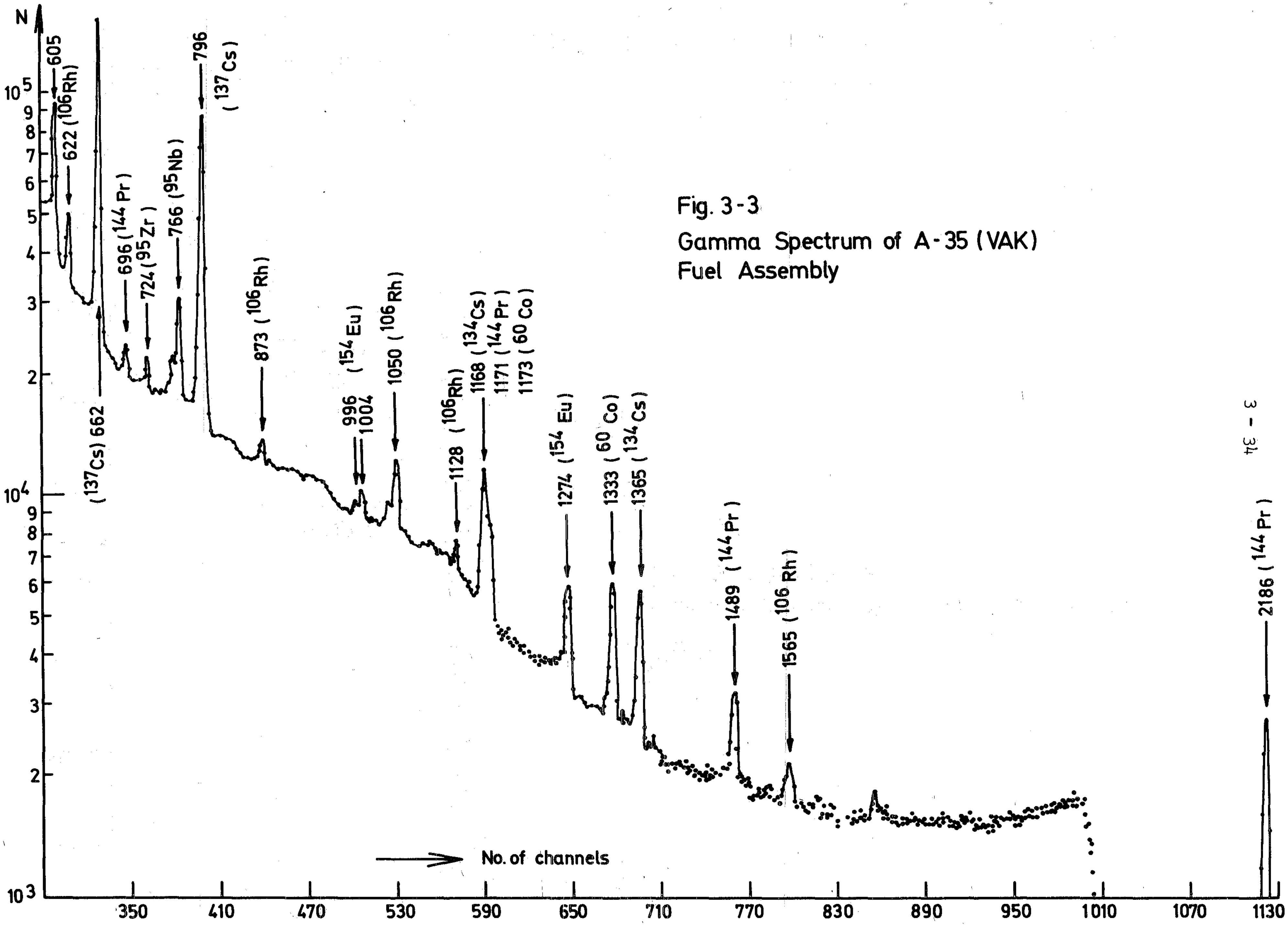


Fig. 3-3
Gamma Spectrum of A-35 (VAK)
Fuel Assembly

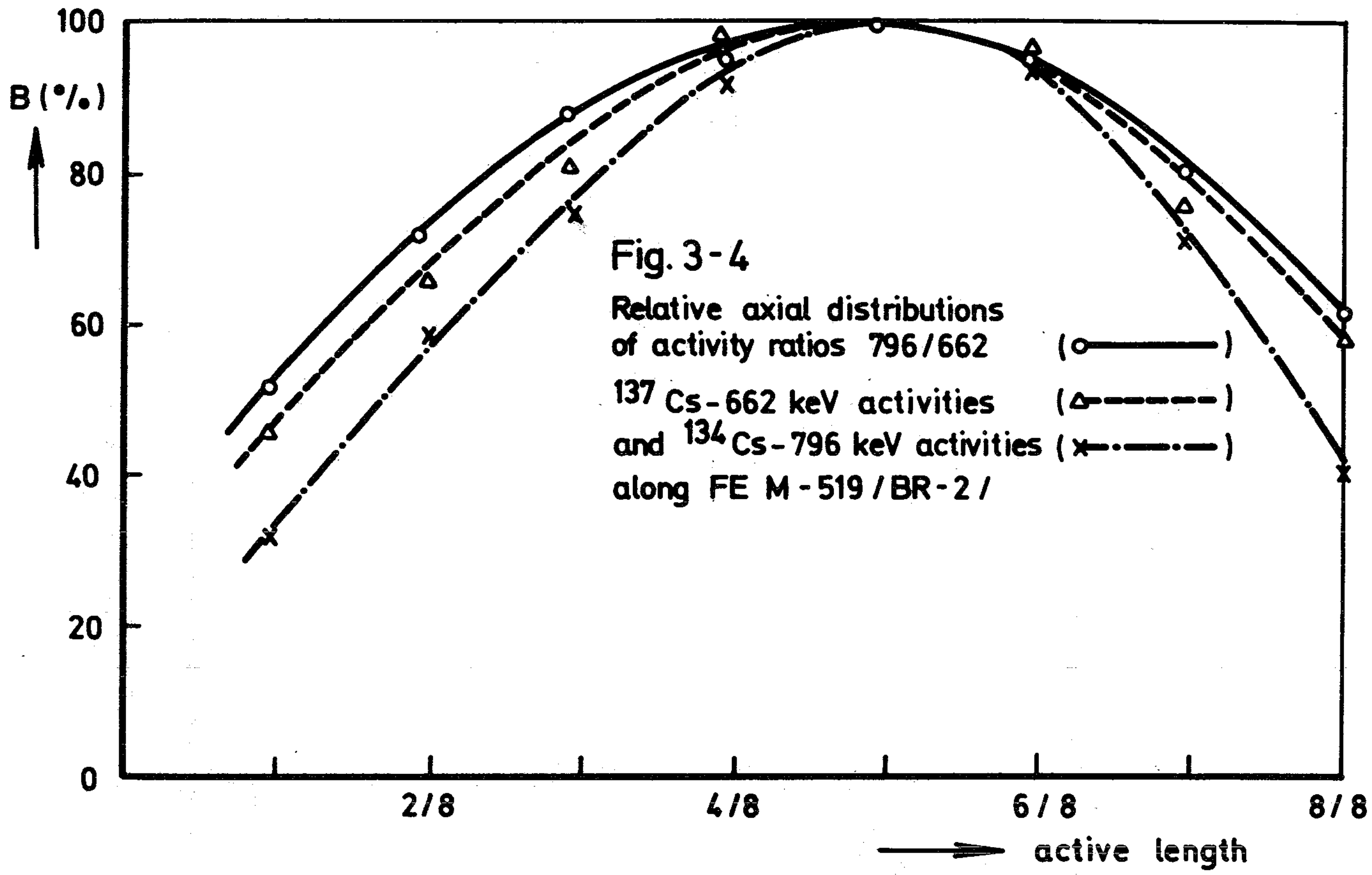


Fig. 3-4

Relative axial distributions
of activity ratios 796/662 (○———)
^{137}Cs-662 keV activities (△– – – –)
and ^{134}Cs-796 keV activities (×–·–·–)
along FE M-519/BR-2/

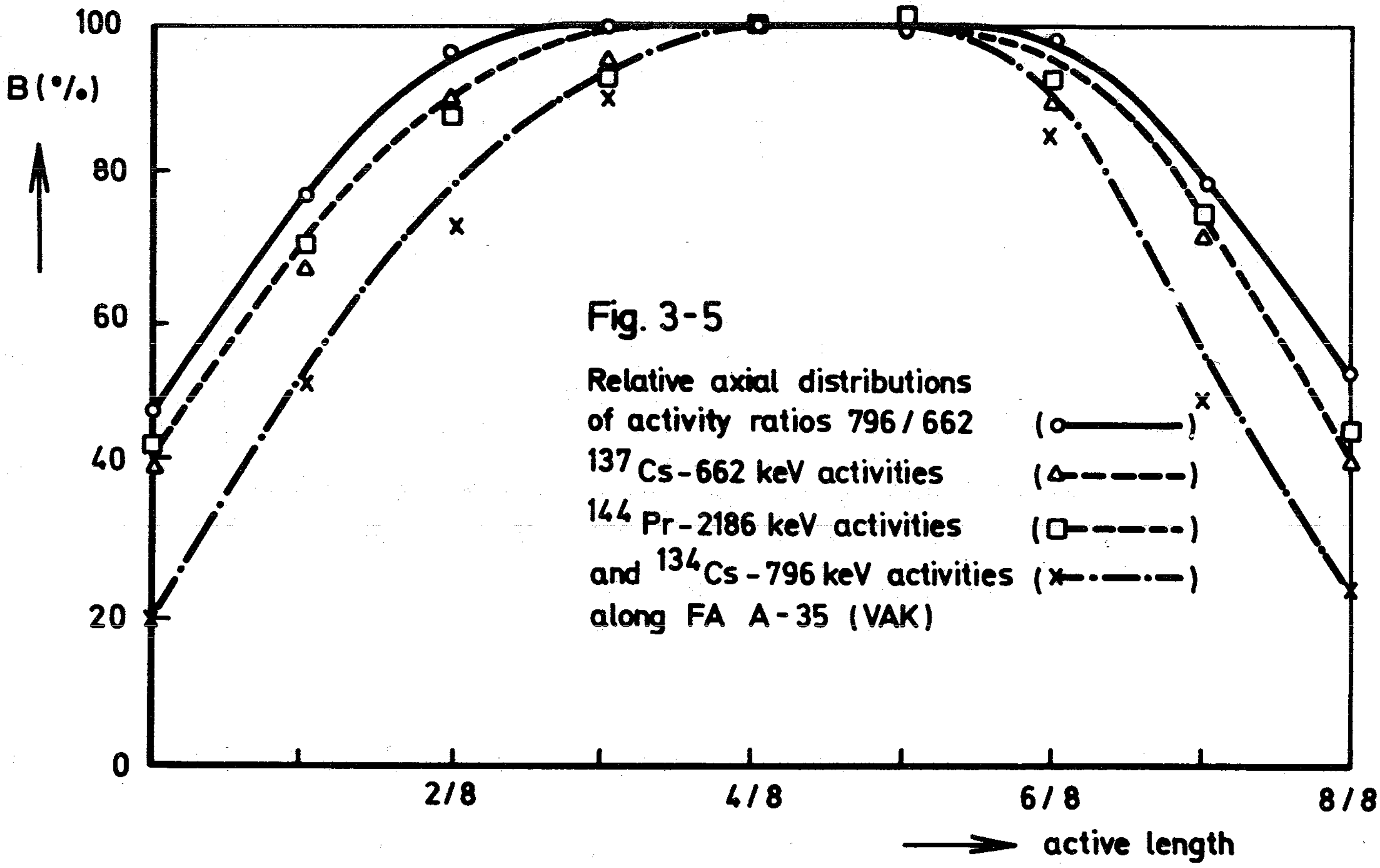


Fig. 3-5

Relative axial distributions
of activity ratios 796/662 (○———)
^{137}Cs-662 keV activities (△– – – –)
^{144}Pr-2186 keV activities (□– – – –)
and ^{134}Cs-796 keV activities (×–·–·–)
along FA A-35 (VAK)

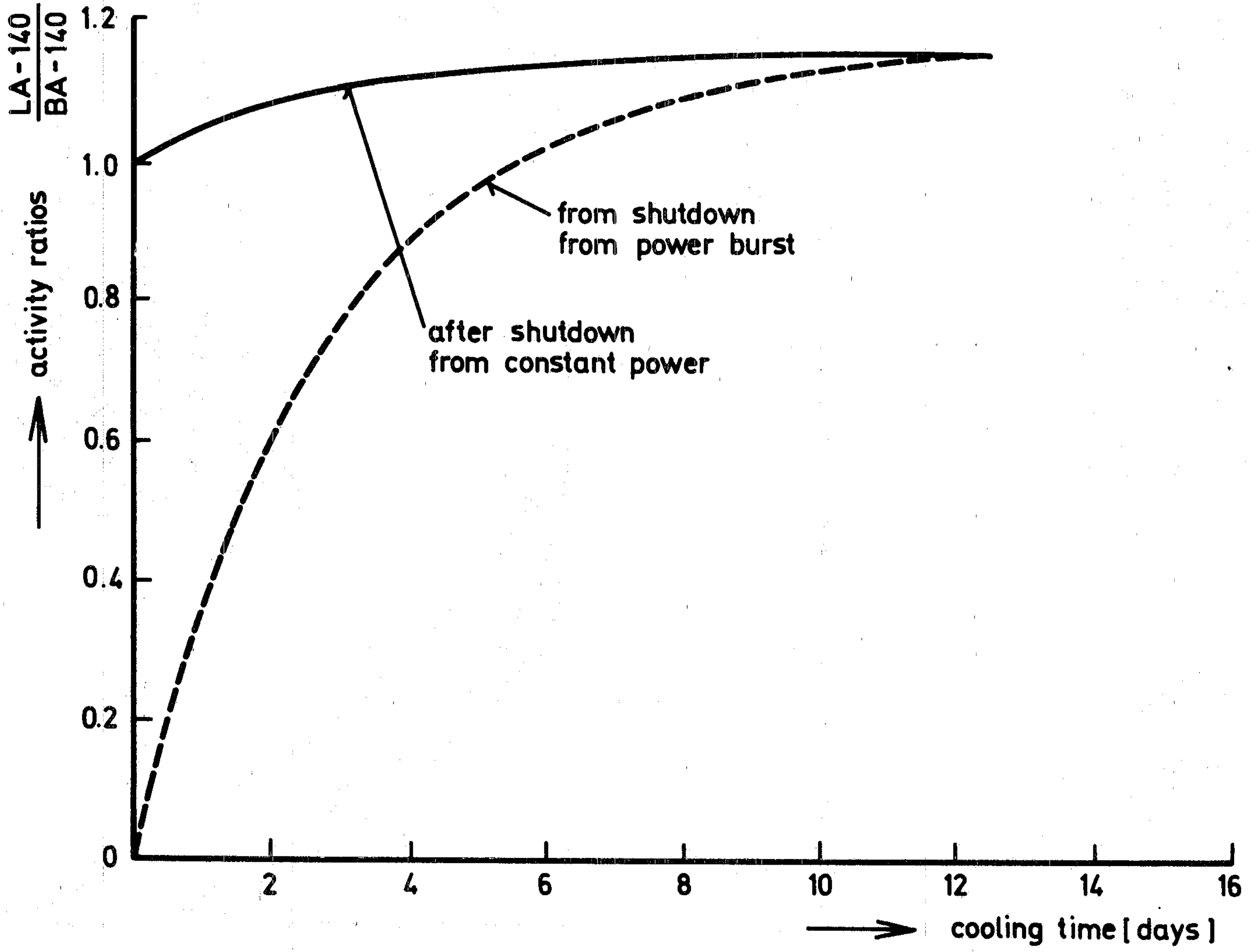


Fig. 3-6 Activity Ratios $\frac{\text{LA-140}}{\text{BA-140}}$

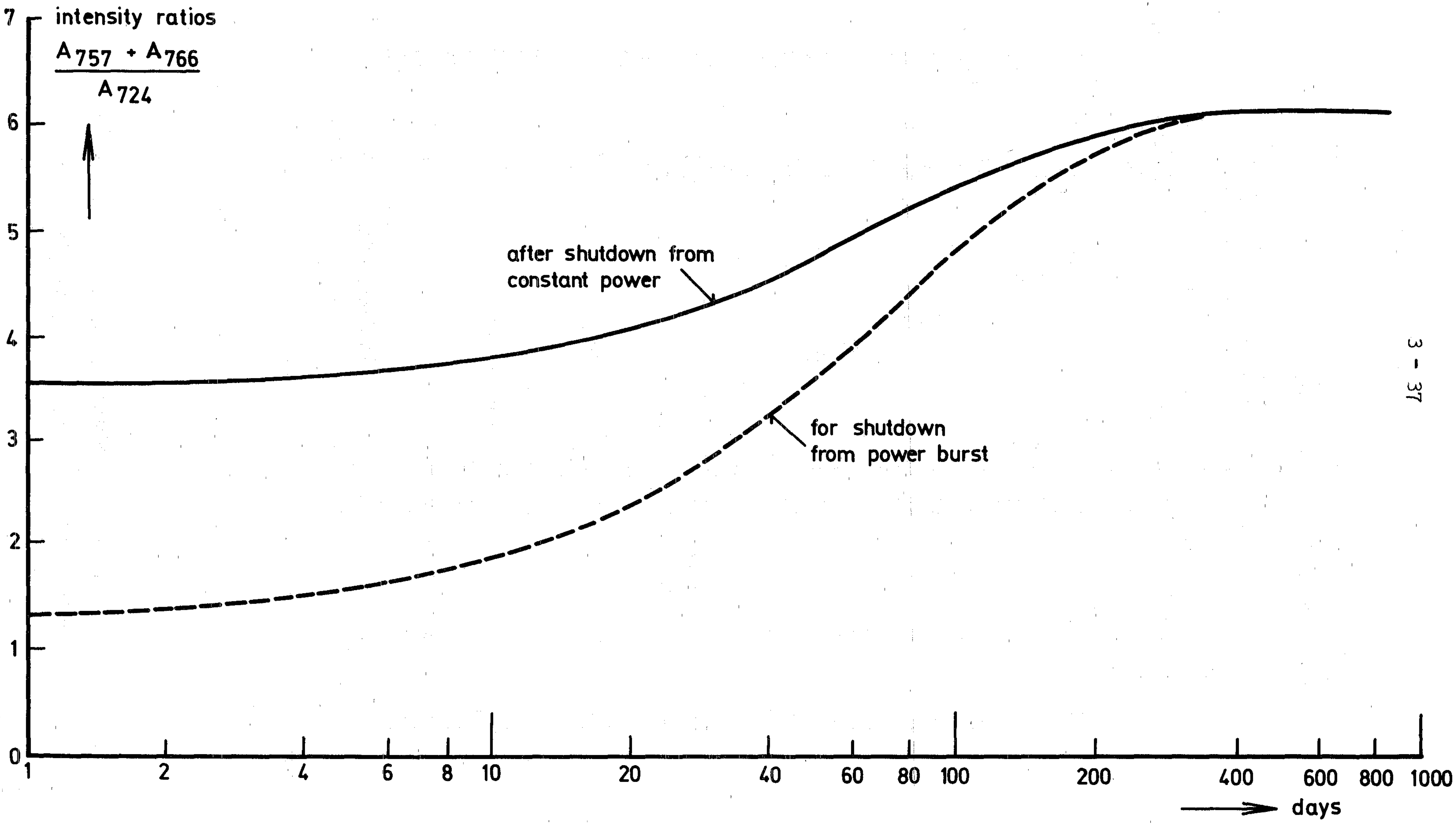


Fig. 3-7 Activity Ratios $\frac{A_{757} + A_{766}}{A_{724}}$

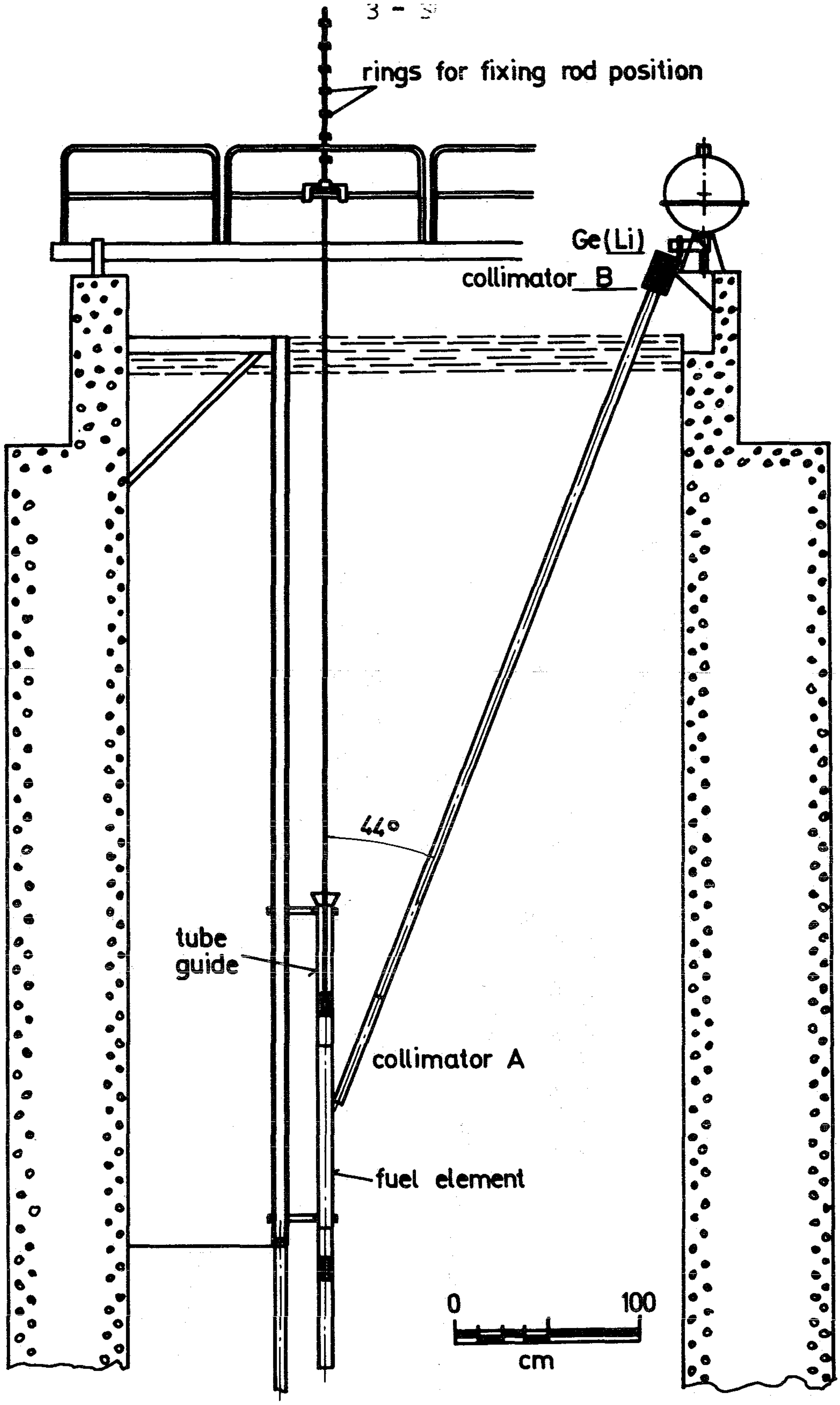


Fig. 3-8 A Sketch of Measurements of Spent Fuel Elements for BR-2 Experiment

PART II

3.10 INTRODUCTION

In connection with the operation of the BR2 reactor, non-destructive tests have been developed for examining highly radioactive materials, [25] such as irradiated fuel elements.

A number of problems arise in common to all these tests: high dose rate, remote control and operation under water.

The industrial television camera is a widely used tool in this field and, because the BR2 reactor and EUROCHEMIC are located near to one another, it was decided to make use of the BR2 equipment to read the identification numbers of the VAK fuel elements in the storage pool of EUROCHEMIC.

3.11 DESCRIPTION OF THE EQUIPMENT

The equipment basically comprises:

a) A waterproof case enclosing the television camera and focusing control. In order to minimize radiation damages, the contents of the case are restricted to those compenents which are essential at that level, namely:

a vidicon tube, 1" in diameter,
deflection coils,
a subminiature-tube preamplifier.

Characteristics of the case:

outer diameter : 76 mm
length : 500 mm
weight : 5 kg

b) An optical head fitting the case and equipped with variable focal length (zoom). The latter yields magnification ratios from 1 to 6 on 20 cm or 36 cm screens with definitions of 0.4 mm and 0.1 mm, respectively.

c) A 48 - conductor connection cable, 25 m long, with double neoprene mantle, flaxen bearing mantle and inner PVC mantle.

d) A central control unit.

e) Two light projectors (500 W iodine bulbs) enclosed in waterproof casings. The resolving power of the equipment is illustrated in figure 3 - 9, the figures have respectively a height of 0.4 cm and 0.7 cm and are viewed at a distance of 2 m.

3.12 EXPERIMENTAL CONDITIONS

The fuel rods were viewed at a depth of roughly 5 m under the water surface and from a distance of 2 m. The figures, which had a height of 1.5 cm, were all read without difficulty, after proper positioning of the projectors. 28 VAK elements were identified in this way, and were subsequently investigated by gamma spectrometry.

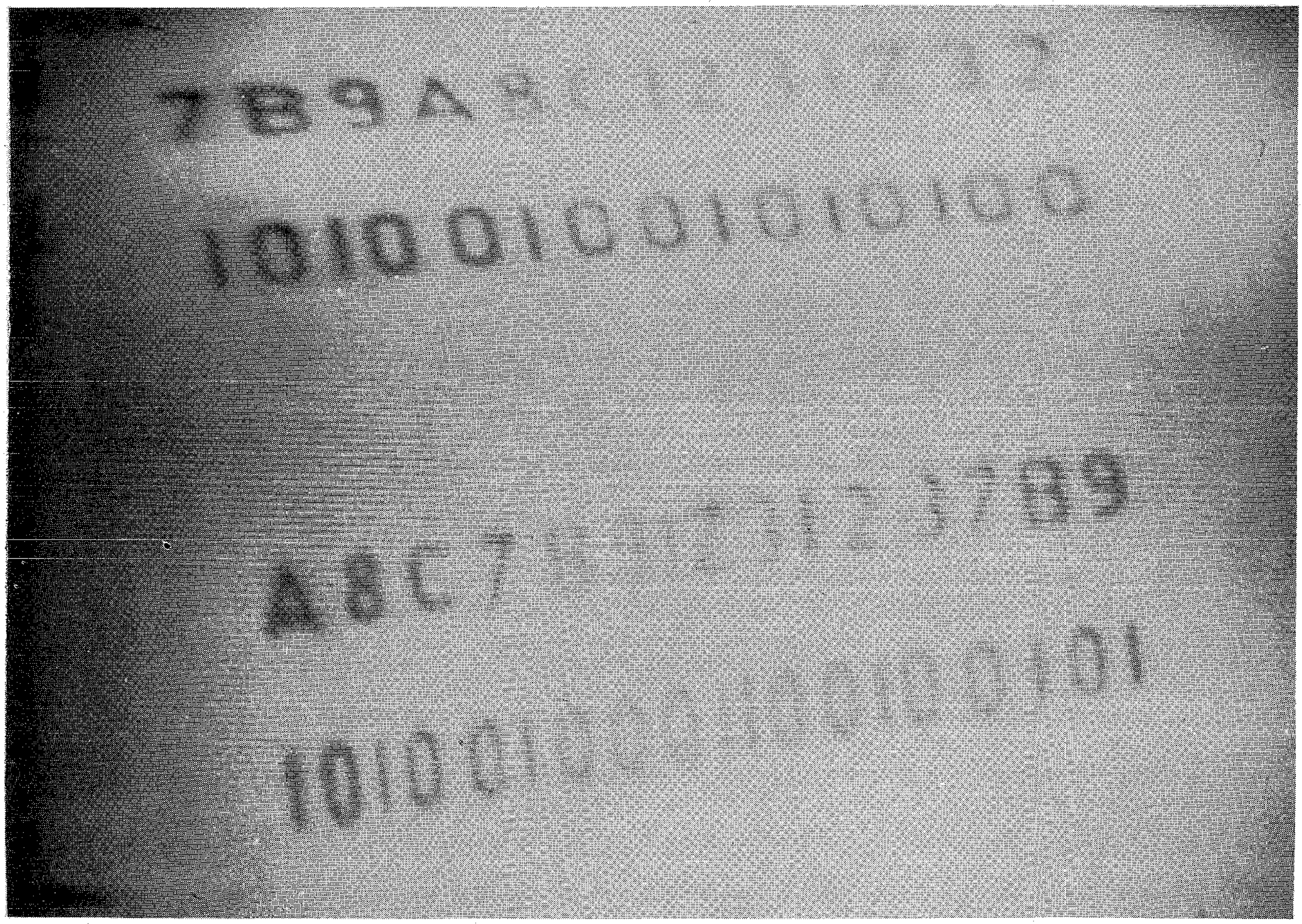
3.13 CONCLUSION

The method has proved satisfactory in this particular case, as a means of identification of fuel rods. It can be introduced with little inconvenience into a sequence or manipluations, e.g. while the rods are being picked out of the pool to be fed into the dissolver. Coupled with the method described in the first part of this paper, it provides a good tool for the verification of the fuel rod identification.

Nevertheless, the problem of the design and implementation of tamper resistant safing systems is a very important one, because these safing systems are both effective and relatively inexpensive [26], [27].

Fig. 3 - 9

RESOLVING POWER OF THE USED TV CAMERA



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Chapter 4

Systems Analysis Studies Performed by Simulation Techniques

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Abstract

The present chapter is composed of two largely independent contributions named parts A and B.

Part A includes paragraphs 4.1 - 4.7 and annexes 4.I and 4.II
Part B includes paragraphs 4.8 and following.

Part A deals mainly with supporting studies for the inventory experiment. The most important results concern statements on the conditions required for a fruitful application of the self-tracering method for the determination of physical inventory in the process area of a reprocessing plant. This new technique correlates the isotopic compositions of subsequent input and product batches in a suitable way. Particular aspects related to the present experiment and remarks of general validity are given.

Part B mainly treats the aspect of the model identification and a special effort is paid in order to reproduce numerically the real reprocessing campaign. The set up of such type of identified model is hoped to be a useful tool for a direct quantitative safeguard utilization.

Some overlap is present in the two parts, because the same technique, numerical simulation, is used in the research. However, the two contributions clearly differ from the point of view of the content.

Due to the different philosophies followed, it appears to be more useful to leave them clearly separated, instead of attempting an integration.

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4. Systems Analysis Studies Performed by Simulation Techniques

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Part A. Critical Analysis of the Self Tracering Technique for Physical Inventory Determination

Summary

During the execution of the integral Mol III experiment different simulation models of the reprocessing process have been established.

In the present chapter some results of this simulation work are given. In the first stage of the simulation work in the framework of the joint experiment it seemed most important to have models which could describe the main features of the actual process and to check the mathematical formulae describing the mixing of different kinds of material during the passage through the plant. This problem could be solved rather soon by two different models. The Mol II campaign was simulated for the Pu and U part and the results looked consistent in a comparison with the real results of the experiment. Also for the Mol III experiment the models could be identified.

After that it has been tried to give some help for an optimal running of the reprocessing campaign. In the end the most important objective of the studies was to test the applicability of the independent method of process inventory determination which profits of the evaluation of the deformation of an isotopic step signal. Under certain limiting conditions which are indicated in the following the method seems to be very useful.

In course of the work two models - for the U- and Pu-cycles of the plant - have been developed. Monte-Carlo-procedures have been used to generate several series of campaigns for statistical studies.

It is one of the great advantages of simulation models that one can do parameter studies by running large numbers of campaigns with special, well known conditions. In the course of these parameter studies the following main topics were investigated:

a) The response function of a "normal operating" system,

b) the influence of the superbatch sizes on the results of the method,

c) the significance of the order of the single batches inside the superbatches,

d) the correlations between input characteristics(as step size and batch-to-batch variation) and the precision of the process inventory determination.

From the results belonging to (b), (c) and (d) conclusions on favorable conditions for inventory experiments can be drawn.

4.1 Introduction

4.1.1 General Remarks

One of the objectives of the Mol III experiment has been the determination of the physical inventory of Pu and U in the process area during the running of the plant. The method chosen for this determination is the self-tracering method which is based on the different isotopic composition of the fuels to be processed. Such different isotopic composition depends essentially on few parameters as: the original isotopic composition of the fresh fuel elements, the type of the reactor in which they have been used and their burn-up.

The outlines of the method and its mathematical formulation may be found in ref. /4-1/; some critical studies on it have been reported by the authors in ref. /4-2/.

At the beginning of the experiment the "simulation group" was entrusted with the task to support the planning of the experiment itself for the physical inventory (PI) determination by formulating recommendations to the operator of the plant in order to minimize the deformation of the isotopic step during its passage through the plant.

During the development of the work however it became clear that the mathematical tools constructed for the original purpose may be profitably utilized for a more important job. The self-tracering technique for the PI determination is quite clear in its theoretical formulation, but the limitations for its application to real cases were not sufficiently known. Some help for the determination of such constraints comes from the results of practical experiments, but in the following it will be shown that the simulation is the tool which can give more rapid, general and cheap answers if it is suitably applied.

4.1.2 The Use of Simulation

With the experience acquired with the development of the present study it is possible, a posteriori, to indicate the correct procedure which should be followed for a profitable use of the simulation techniques.

By doing so one can say for which aims the simulation technique can be applied and what results can be got by it and for which questions simulated results are a better answer than the results of real campaigns and why.

The first step in working on simulation should be to state as clearly as possible the problem or problems which are to be solved.

The second step is the set-up of a model of the considered physical system. The model must be:

a) on the one hand capable to describe the main phenomena of a real experiment, which are interesting with respect to the stated problem, and to give clear results.

b) and on the other hand it must be only detailed enough so far that important features, related to the considered problem (e.g. PI determination) are not neglected.

So, in the application of the technique and in the model studies one has to make a suitable compromise between the items stated in a) and b).

The third step is the "identification" of the model with the real system. This "identification", which means the definition of the model parameters so that model and actual system have the same response function, sometimes may be not completely satisfactory. The researcher must realize what are the possibilities and the limitations of the model in order to estimate correctly the result of the whole procedure.

The last step is the utilization of the constructed tool (the model) to give the answers to the problem questions.

For the reasons of clearness the subject will be ordered according to the steps defined above.

4.2 The Problems

The questions which wait for an answer from simulation have been indicated in the introduction (to the present chapter) and will be briefly resumed here:

1. Study of the deformation of an isotope concentration step function during the passage through a plant working in steady state conditions.
2. Study of the constraints for the application of the self-tracering technique for the determination of the physical inventory. These

constraints can be e.g. the total quantity of fissile material processed in one campaign, the composition of material in "superbatches" with regard to isotopic concentrations, the batch-to-batch variations of isotopic concentration inside one superbatch.

3. The estimation of the precision for the calculated inventory which may be obtained as function of the previously mentioned parameters.

4.3 The Models

Figure 4.1 gives the schematic flowsheet of the EUROCHEMIC plant for U and Pu recovery. It corresponds to fig. 2.1-2 and 2.1-3 of chapter 2. For the construction of the model the different types of elements which compose the plant have been individuated. The approximate behaviour of the fissile material may be easily described by simple mathematical relationships (equations) for most of the plant units. The result of the first examination of the flowsheet led to the conclusion that only few types of equations are necessary for this purpose. Fig. 4.2 gives the types of units together with the analytical relationships. The description becomes quite complicated when pulsed columns or mixer-settler batteries are considered /¯4-3_7. The models used for the simulation of the whole plant have neglected the mixing mechanisms which take place in these continuously operating units. This simplification appears justified, at least in a first approximation, because the mean hold-up and the residence time of the fissile material in these units are small compared with those of the adjacent units.

However, the implications of this simplification are described more precisely in annex I: the possible mixing mechanisms in the mixer-settler batteries have been investigated by a suitable simulation model implemented on an analog computer.

The different units taken into account for composing the EUROCHEMIC plant may be grouped in 4 classes, according to their input - output characteristics (C = continuous, B = batch, i = input, o = output):

$B_i - B_o$

$B_i - C_o$

$C_i - C_o$

$C_i - B_o$

Two types of models, named "space" and "time" model respectively, have been constructed for the plant simulation. They are described in some detail in /4-2/. The "space" model makes use of the transfer function of each single unit to construct a series of output data as function of the series of input data for the considered unit. For input and output these series are ordered historically.

The inter-connection of the subsequent units results in the final response of the model to a given input function.

The "time" model uses a time discretization technique, by which the continuously operating units may be assimilated to the batchwise operating ones. At every time iteration interval the characteristic status of each unit is described as function of the historical series of the input data.

All the results given in this report, except those on the deformation of the step signal illustrated in fig. 4.6 and 4.7, have been obtained by this "time" model.

4.4 Identification of the Models

The proper use of a simulation would require the identification of the model with the real system. Strictly speaking identification means that the model parameters have been adjusted in such a way that both model and real system have the same response function. In the case of a reprocessing plant (at least at present time) such identification is impossible because the normal operation procedures do not allow the definition of a response function: too large are the possibilities of choice left to the operator. At most, a sort of identification can be obtained "a posteriori", when all the operator decisions are known. This kind of comparison is important because it allows to say that the model is able to produce realistic results, that is a series of outputs, related to prescribed inputs, which could be the actual output data of a real plant. From this point of view it is clear that the identification may be considered as reached when the model can produce realistic results.

4.4.1 Pu-Purification-Cycle

Fig. 4.3 illustrates the result of an "a posteriori" identification concerning the model of the Pu-purification cycle of the EUROCHEMIC plant. The careful study of this figure may be illuminating for the performances of a mathematical model in this very special context. The comparison of the "input" and the "real output" curves seems to indicate that:

1. up to a mass of 26.3 kg the Pu units have been mixed very strongly inside the plant, because the concentration of the tracer isotope in the output looks nearly constant compared to the oscillating input,

   however:

2. in the output the concentration step after 26.3 kg is very sharp which is an indication of low mixing, and this step arrives too early with respect to the input (some material seems to be kept back inside the process line),
3. the shape of the output curve after 35.7 kg may be explained by the fact that a lot of internal recycling took place around the second extraction cycle. Such recyclings, not foreseen by the normal operation conditions, proved necessary for operation reasons. (The retained material mentioned under 2. may have been added in this period.)

The "simulated output" is obtained by the model which is made to run according to "normal conditions" up to 35.7 kg. In addition, an attempt to include the abnormal recyclings in the model has been made, but the information available about them was not very precise. It should be noted that the "simulated output" may be more easily explained than the "real" one. In fact:

1. in the zone up to 26.3 kg the output shows some reasonable oscillations in agreement with those of the input,
2. the following zone (up to 35.7 kg) is in a very good agreement with the input because the input step is deformed in a symmetric way - between 26 and 34 kg - without the incomprehensible unmixing which appears in the "real output",
3. an analysis of the real and simulated output curves in comparison with the input signal for the last zone (after 35.7 kg Pu) allows only the explanation of the difference between the actual and simulated output in the region of 25-35 kg and 35-50 kg of Pu by some unforeseen recycling.

According to these conditions a "transfer" function in the sense of an unique definition of the parameters which govern the model utilization could not be found. However, it appears that the available model can describe sufficiently well all possible outputs and may be used for the solution of the stated problems.

4.4.2 U-Purification Cycle

The same comparisons described in the previous section have been carried out also for the U-purification cycle and the related curves are reported in fig. 4.4a, b and c. In the first one the "input" and "real output" tracer concentrations are compared. The mass scale has been adjusted in such a way to take into account, together with the main input, also the contribution of the U^{IV} auxiliary input. The agreement seems to be sufficiently good, apart from the fact that the tracer concentration of the second superbatch is lower at the output and consequently the amount of material of the second superbatch appears to be enlarged due to a mixing with the adjacent batches. It seems that this effect does not come out to the same extent for the simulated output (fig. 4.4b) where the second superbatch has nearly the same size as in the input and the tracer concentration is only slightly decreased. For the following batches real and simulated output have almost the same shape (see fig. 4c).

4.4.3 Corrections for U^{IV} stream

A further proof for the assumption that the mathematical model used for the simulation is correct has been obtained a posteriori in connection with the estimation of the physical inventory of U. In chapter 5 of this report the corrections are indicated which must be made on the input data in order to take into account the auxiliary U^{IV} input to the MBA considered.

Another way to determine the inventory, when an auxiliary input is present, may be to correct the output data so that they can be put in direct connection with the main input as it is (see fig. 4.5). The corrections which must be performed on the output may be obtained by the simulation:

The contribution of the auxiliary input to each output batch is calculated and subtracted from the actual output data.

This type of correction has been applied and the results have been compared with those obtained by correcting the input values. The values for the physical invenotry came out as 1625 and 1620 kg respectively. This indicates that both correction procedures are equivalent.

This very good agreement is a further indication that the used model can reproduce actual results so that it may be considered as "identified".

4.5 Results for the Mol III Campaign

4.5.1 Deformation of the Step Signal

The first problem, which waited for a solution by simulation, was the definition of optimal conditions in the EUROCHEMIC plant conduct. These conditions should allow the best utilization of the self-tracering technique for PI determination on the processing campaign under examination (LEU - 70/1). In other words: an attempt has been made in order to reach experimental results which could be suitably used in the theoretical formula:

$$H = \sum_i M_i \frac{C_i - C_2}{C_1 - C_2}$$

which determines the physical inventory H on the basis of the measured masses M_i and tracer concentrations C_i of the i output batches and of the tracer concentrations, C_1 and C_2 of the input superbatches /‾4-1_7.

In order to give an impression of the deformation of a step signal during its passage through the plant, at the Battelle Institute the form of the signal after its passage through some important units has been plotted. In fig. 4.6 one sees the calculated Pu-242 concentration signal which has been got at three different points of the process line for the input of the Mol III experiment. The numbers of the units are those given in fig. 4.1. Fig. 4.7 gives the same result for the U-235 signal at 4 points. One can see that the sharp input step is spread over about 1500 kg (the calculations were made with a constant flow rate of 15 kg U/h).

It is clear from a simple analysis of the method which can be found in /‾4-2_7, that one of the optimal conditions in question must be the minimum mixing of the materials which belong to different superbatches and the minimization of every necessary recycle.

A more general support to this argument is given by the results of the parametrical studies illustrated in paragraph 4.6.1 below.

The theory treats the tracer concentrations C_1 and C_2 as constants for every batch of a superbatch. In practice this strict condition is not fulfilled, so, in order to approach with physical measures to these theoretical conditions the maximum mixing of the fissile material inside a single superbatch is recommended for the head-end of the plant up to the continuously operating units. The mixing of material of two superbatches inside these units cannot be avoided at the step passage - only an anti-economical and equilibrium disturbing washout could avoid it.

4.5.2 Recommendations to the Operator

As mentioned before it was the result of the first simulation studies that for improving the accuracy of the PI determination by the tracer method the following recommendations should be kept in mind by the operator.

a) The single batches inside the superbatches, which are supposed to give the step function, should differ in their isotopic composition as little as possible, specially for the isotopes which are used for the calculation of the inventory.

b) The step in the concentration of the tracer between the two superbatches should be kept as clear as possible, that means that it should be tried to have low mixing for the two kinds of material during the passage through the plant.

For reaching item (a) two possibilities were discussed with the operators of EUROCHEMIC.

1. It should be tried to mix the dissolution batches of one superbatch in the input accountability tanks (IAT, 221-4 and -6, see fig. 4.1). For doing that it could be useful to make the heels in the IAT bigger than 2 l (normal value).

2. It should be tried to shift the input point of the MBA from the IAT to the intermediate storage tanks (223-6A and -6B, see fig. 4.1) or feed tanks (231-1, 231-11) of the columns. In this case also the mixing inside these tanks could be used to minimize the batch-to-batch variations. (In this connection the question if it is necessary to take additional samples must be solved.)

For reaching item (b) the following possibilities were discussed:

1. It could be advantageous to decrease the heels in certain tanks at the passage of the step.

   It seemed promising to make the feed tanks 231-1, 233-71 and 232-41 (see fig. 4.1)operate on minimum level at the step passage.

2. It should be tried to what extent restrictions on the Pu recycling are necessary and possible.

3. It should be decided if the evaporators 231-7 and 232-4 can be emptied at the step passage.

In a first discussion it came out that no homogenisation would be possible within 223-6A and 223-6B because these tanks serve as feed adjustment units and the solution must not be diluted by additional steam jet transfers. The only possibility for homogenisation would be in 231-1 by increasing the heel volume (this homogenisation effect should be calculated; for 223-6A and 6B process analysis data are available).

After some further discussions with the operators it was possible to mix the last two CANDU-batches 800 and 900 inside the feed tank 231-1.

For the VAK-fuel it was agreed to mix the last two batches instead of the first two ones.

It came out that a lot of recycling was necessary for the Pu part in order to keep the mixer-settler batteries in steady state conditions (for temporary lack of feed from the first purification cycle) and to recover the Pu scraps coming from calcination.

The recycles of U were made in connection with U^{IV} auxiliary input. They are described both in this chapter and in chapter 5 (see paragraph 5.3.2 and fig. 5-7).

4.6 Results concerning the Method of Physical Inventory Determination

4.6.1 Response Function of a "Normal Operating" System

For both the Pu and the U cycles some investigations on the influence of operating conditions on the response function of the system have been made. This is a kind of preliminary study which allows a better interpretation of the results obtained in the following. The "response function" of the plant describes the distribution of the material of a single input batch in the output ones. It is obtained by the simulation model in a campaign in which only one of the series of the input batches is tracered.

For the Pu a series of 6 different campaigns has been studied. The characteristic parameters chosen for these campaigns are reported in table 4-1.

The parameters taken into account were:

a) the heels in the input accountability tanks 221-4 and 221-6 (H = 200 l, L = 2 l)

b) the mixing strategy in the head-end tanks of the plant. (NO means that the input batches have not been mixed with the adjacent ones; LR means that each input batch has been mixed with the preceeding and the following ones; R has the same meaning as LR for all batches exept the traced one which has been mixed with the following batches only)

c) the percentage of the continuous recycling from 2436-1 to 236-4b.

Fig. 4.8 gives as an example the comparison of the "response function" for the cases 1 and 2 of table 4-1. The observation of these shapes of "response functions" and of these related to other trials suggest the following conclusions:

- The use of the mixing strategy at the head-end of the plant leads to a much higher spread of the response.
- With the R-type of mixing (cases 5+6) the spread of the response is a little bit smaller than with the LR-type (case 3+4).
- The influence of a continuous recycling of 5 % seems to be negligible for the investigated cases (3 and 4, or 5 and 6). However it could be hidden for these cases by the influence of the other parameters and could be significant for L heels and NO Mixing.

Similar studies have been made for the U and the results of two campaigns with and without U^{IV}-recycling are given in fig.4.8b. The effect of the mixing strategy and the different heels in the head-end of the plant is of course the same as for Pu campaigns.

For a traced input batch of 1000 kg of U, the response function results spread out over 3200 kg (2000 kg ≙ 98.8 %) and 5200 kg (3200 kg ≙ 98.0 %) respectively without and with 10% U^{IV} recycling.

4.6.2 Requirements on the Superbatch Sizes

As already pointed out in ref. /4-2/, one of the constraints which limit the use of the single tracer method /4-1/ for the P.I. determination is the availability of sufficient quantities of material of different isotopic compositions to construct the two input superbatches. The procedure used for the estimation of the quantities is fully described in /4-2/. The present report merely gives the results of this type of analysis for the two purification lines of the EUROCHEMIC plant, according to the "low enriched uranium" (LEU) flowsheet.

They are resumed in tables 4-2, 4-3, 4-4; Table 4-4, which refers to an U-purification line without any U^{IV} recycling, has been inserted in spite of the fact that such conditions are not fulfilled in the EUROCHEMIC plant, because the Pu reduction can be also performed by other means which do not imply any use of U or Pu. It is interesting to see that, for this case, a recovery of more than 99 % of the inventory can be reached with superbatches 1 and 2 of 4000 and 800 kg respectively, compared to a recovery of only 95 % in the case with U^{IV} recycling. If one wants to have 99 % recovery also for this strategy one needs 6000 and 3200 kg of material for the two superbatches.

4.6.3 Influences of the Batch Order inside the Superbatches

Normally the concentrations C_1 and C_2 are obtained as mean values for a series of batches inside one superbatch. As already pointed out in ref. /4-2/ the order of the single batches inside these superbatches, which give the concentrations step, has an influence on the result which is obtained in determining the process inventory by the tracer method. To indicate this some special cases with very simple ordering of batches have been studied. The studies were made for the Pu-cycle.

Fig. 4.9 gives the input step and the corresponding output for same cases.

For all cases the concentrations C_1 and C_2 were 0.1 and 0.2 respectively, they have been obtained by calculating the mean value of the relative concentrations of the tracer in 5 batches. The maximum concentration difference inside one superbatch is about 10 % of the step size. For all cases the plant inventory I_r at the step input is 16.02 kg of Pu. In the figure the difference between the calculated inventory H and I_r is given with the proper sign. In the first case (ideal case: no variation inside the superbatches) the difference may be attributed to rounding errors in the calculations, it is 0.08 % of the real inventory.

The following group of four cases shows the influence of a monotone variation of the tracer concentration inside one of the two superbatches only. The order inside the second superbatch seems to be more important than that inside the first one. The difference H-I_r becomes negative when the concentrations in the second superbatch decrease and it is positive with an increase. The opposite is true for the variation inside the first superbatch.

The last group shows the influence of combined variation in both superbatches. The biggest difference H-I_r is found for the cases 6 and 9 where the concentration has different slopes in the two superbatches. The results obtained in the cases 6-9 agree with those obtained in the simpler cases 2-5. It should be noticed that the calculated value of H is clearly influenced by the concentration sequence in the input. For the last case the same batches as in the cases 6-9 have been used, but in contrast to the previous cases the individual batches have been arranged in such a way that the straight lines drawn according to linear regression through the concentration values of the individual batches of one superbatch remain horizontal. It is to be noted that the result of H-I_r/I_r = 0.3 % for this case is the lowest of all results for the cases investigated. Therefore it appears that such an arrangement is an optimum. This seems to be plausible as any trend has been eliminated in this case.

In the case of a "going down" step the sign of the variation is reversed (see also the observation following the results of the error analysis in paragraph 5.4.1), but the recommendations about the batch ordering remain the same.

4.6.4 Correlations between Input Characteristics and the Precision of the Physical Inventory Determination

The most important preliminary study that must be performed in actual cases before the utilization of the method of tracer for the PI determination is that which gives the estimate of the precision of the measurement as function of the nuclear material available. In other words, once stated that a sufficient quantity of material is available to construct two superbatches (see 4.6.2) the knowledge of the probable variation of the tracer concentrations in single batches of each superbatch and of the mean step size indicate limits which one has to expect for the precision of the determination.

A first approach to the solution of this problem can be found in [4-1] where an analytical formula is proposed. In the present study the problem has been solved by Monte Carlo technique, which allows also to take into account the correlations among the different variables of the formula giving the PI.

The results have been obtained using a model which for one special set of parameters refers to the actual Pu - and U-lines of EUROCHEMIC, but in general, may reproduce a whole series of different reprocessing strategies.

Table 4-5 gives a summary of the investigated strategies. For every type of strategy the standard error of the difference between measured (H) and book inventory (A) relative to the mean book inventory, i.e. $\sigma_{H-A}/\bar{A}$, is given as function of r, the ratio between the batch-to-batch variation of the tracer concentrations inside one superbatch and the step size $^{+)}$. As a quantifiable measure of this variation the standard deviation of the distribution has been chosen. The relationship $\sigma_{H-A}/\bar{A} = f(r)$ has been obtained by an interpolation among some points. Every point is, in turn, the result of a statistical analysis of 50 (for U) or 100 (for Pu) campaigns. For each of these campaigns the tracer concentrations of each input batch have been randomly chosen from two normal distributions (one for each superbatch) of prescribed mean value and standard deviation (see Appendix II). The difference between the mean values is the step size. The standard deviation is a measure of the batch-to-batch variation; this means that we assumed the possible concentration of the tracer for a batch inside one superbatch as normally distributed. In the actual calculations both standard deviations have been assumed equal.

Fig. 4.10a and b give a summary of this parametrical study. The full lines which appear in the figures are not the best fit through the calculated points, but represent the graphical interpretation of the relationship indicated here. A general conclusion may be drawn both from Pu and U results: within the considered interval of r (0.02 ÷ 0.4) relations of the following type hold:

$$\ln \frac{\sigma_{H-A}}{A} = a \cdot \ln r + \ln \text{const.}$$

and since a is ≈1

$$\frac{\sigma_{H-A}}{A} = r \cdot \text{const.}$$

+) This definition for r differs slightly from that given in chapter 5.

Moreover, the value of this constant comes out to be independent of the strategies summarized in table 4-5, except for the cases in which the feed of each superbatch is mixed up in the head-end of the plant.

Note that in these studies no restrictions on the material available for the construction of the superbatches have been made. As an additional result of the simulation one finds out that the more precise results for the mixing cases (curves 2 and 8) require a larger amount (~10%) of material.

4.7 Conclusive Remarks

In connection with the Mol III experiment the simulation technique has been mainly used to test the applicability of the tracer method for physical inventory determination. The step signal which is taken for the evaluation of the physical inventory is the inherent isotopic composition of the heavy material itself and no artificial tracer is required. This method of isotopic analysis for the PI calculation can be successfully applied in normal practice only when some conditions are fulfilled.

The most important conditions concern

a) the total quantity of fissile material inside the superbatches which define the step - for the Mol reprocessing plant a recovery of more than 99 % can be reached with superbatcnes of 19.8 and 8.5 kg Pu before and after the step signal. For U the corresponding numbers are 4000 and 800 kg for campaigns without recycling, with recycles one needs 6000 and 3200 kg for the two superbatches,

b) the isotopic characteristics of the processed material - see below, and

c) the possibility of ordering the single input batches inside a superbatch in a suitable way - it came out that the best results for the inventory determination can be found if the batches are ordered in such a way that the straight lines drawn through the single concentration values according to linear regression remain horizontal.

When these conditions are fulfilled the hold-up of the plant can be calculated with a precision of a few percent.

The results of the method may depend on the way in which the plant is operated. In the simulated experiments described above the assumption of a regular operation procedure was made. It follows that, with the restrictions mentioned at the beginning of this chapter, the method can give reliable results if the operator follows the prescription of a regular running of the plant.

In order to get an estimate of the precision of measurement as function of the nuclear material available, for the U- and Pu-case several series of campaigns were run. In these cases it was taken for granted that enough material was available.

For every type of the different strategies of the plant under study the relative standard error $\sigma_{H-A}/\bar{A}$ of the difference between measured and book inventory was given as a function of r, the ratio between the batch-to-batch variation of the tracer concentrations inside the superbatches and the step size.

As a general conclusion we found that for both the Pu- and U-cases a relation of the following type holds:

$$\frac{\sigma_{H-A}}{\bar{A}} = r \cdot \text{const.}$$

The values of this constant come out to be independent of the different investigated strategies except for the cases in which the feed of each superbatch is mixed up in the head-end of the plant.

PART B. Simulation Studies of Campaigns at the Eurochemic Fuel Reprocessing Plant

4.8 Introduction

Earlier work at the Nuclear Fuel Services plant at West Valley, New York had established the feasibility of simulating the operation of a fuel reprocessing plant with a mathematical model. Although the NFS flow sheet for the plutonium cycle was relatively simple and straightforward, with only a modest number of compartments, the results of the FT-62 field test were not conclusive since it was not possible to control operations in the desired fashion. A subsequent similar experiment was proposed at the Eurochemic fuel reporcessing plant at Mol, Belgium where the possibility existed of specifying plant operations approximating those desired for the experiment.

The objectives of this investigation of simulation were to examine different simulation models in order to evaluate their limitations, and to determine the influence of process parameters on the models. Comparison of predicted results with the actual data, quite important in validating models, was one of the main tasks.

Principal responsibility for the simulation studies rested with the Institut für Angewandte Reaktorphysik (IAR) which was charged with the overall management of the JEX-70 experiment. Battelle-Columbus, in its capacity of subcontractor to the United States Arms Control and Disarmament Agency, participated in the simulation studies in a supporting role.

During the planning phase of the experiment, simplified models of the Eurochemic plutonium and uranium cycles were constructed and programmed for the Battelle-Columbus CDC-6400 digital computer. These models were based on the provisional flow sheet and upon the process data supplied by the Eurochemic staff for vessel sizes, routine heels, normal mode of operation, ect.. The uranium cycle model was not further investigated during JEX-70; attention was concentrated on the plutonium model (PUEURO).

The supplementary Battelle-Columbus efforts were addressed primarily to the experimental aspects of the Mol III campaign and towards the practical problem of determining what operating constraints are necessary for an in-contains some plutonium. However, since this acid is analyzed, amounts are known and input totals are corrected appropriately. Based on postcampaign information obtained at Eurochemic, the total plutonium so recycled was only 730 g for the whole campaign, an insignificant part (1.2%) of the total plutonium product.

Plutonium lost to the mother liquor from the continuous precipitator is also routinely returned to the process, but evidently in a fairly random fashion. Data have been recently obtained from Eurochemic on the quantities of plutonium so recycled but no data are available on the isotopic composition of this material or on the details of its recycle. so that no way exists to make this correction. Total amount recycled was about 1835 g, or approximately 3 % of total product. Compared to other uncertainties in the campaign, this too is regarded as relatively insignificant.

In addition to these two minor plutonium recycles, however, there was a third very major one, whose existence and magnitude was not known until after the conclusion of the experiment. This is the recycle of entire batches of product from the specification analysis tank (2416-1) back to buffer tank 236-1a or to the feed adjustment tank 236-4b preceding the mixer-settlers. There are two possible causes for this recycle. Occasionally, a product batch will be out of specifications on impurities and will need re-extraction for additional purification. More generally, however, this recycling is a technique to place the mixer-settlers on total reflux while more fresh feed is being processed. (The capacity of this section of the plant is greater than that of the head-end so that it tends to run out of feed).

Since information on this recycle from 2416-1, the magnitude of which was so great as to approach the total product quantity, was unavailable until after the simulation work was completed, it has not been taken into account in the simulations. Also, to do so would have necessitated a major revision in the Battelle-Columbus Eurochemic simulation model which, in its present form, is unable to handle such a recycle satisfactorily. Fortunately, the evidence suggests that this recycling of the product from 2416-1 was on a total reflux basis, so that the original processing order of the batches was generally reasonably well maintained. Where there are significant divergences between model and experiment, as described in the following sections, it appears that they result primarily from this recycling of product.

4.10 Simulation of Mol III Campaign

The Mol III campaign (plutonium cycle) was simulated using the PUEURO model. Plant operating data and analyses were drawn primarily from the various JEX reports. Plutonium input and output data from Eurochemic are shown in Tables 4-8 and 4-9. The data for CANDU, VAK, TRINO, and CdN were obtained from interim experimental reports and from R. Kraemer /¯4-5_7. The quantity and analysis of the plutonium in inventory was obtained from E. Drosselmeyer /¯4-6_7. Although this plutonium presumably entered the process at the mixer-settlers, for the sake of simplicity it was assumed to consist of 4 batches entering at the intermediate feed tanks. Recovery of total plutonium based on the masses given, was calculated to be 95.5 %. Recoveries of the individual isotopes are shown in Table 4-8. As usual, the greatest divergence is shown by plutonium-238, the smallest constituent; the other isotopes were in fair agreement.

Aliquot samples of the input batches were also analyzed at Oak Ridge National Laboratory by mass spectrometry. Plutonium-238 is analyzed for by α-spectrometry because of possible uranium-238 contamination. Since it was not possible to do this on these samples, no plutonium-238 values were given in the ORNL analyses. In order to place the ORNL analyses on a comparable basis with the Eurochemic analyses, the Eurochemic values for plutonium-238 were assumed, and the other isotopic concentrations appropriately adjusted. The adjusted ORNL analyses, including the Eurochemic plutonium-238 values, are shown in Table 4-8. The two sets of analyses were in fairly good general agreement, and comparable simulation results were obtained with either set.

Attempts to define the mixing strategies used during the campaign from the JEX reports were not too successful. These strategies seemed to vary, and it was not always possible for the operator to execute the planned strategies due to operational difficulties in the plant. Also, as simulation results were compared to actual results it became apparent that more internal mixing was occurring than was provided by the assumed simulation parameters. In the absence of the actual operational data, it was decided to arbitrarily select a mixing strategy which would provide the observed mixing. Some of the mixing may have resulted from the mixer-settlers, where mixing was ignored in the present simplified model, and some may have resulted from assuming too-small heels in process vessels. Actually, for the present simplified model, it does not matter particularly where the mixing occurs, as long as it is accounted for.

A number of simulations of the Mol III campaign were performed with varying parameters, primarily the size of the heels in the intermediate feed tanks 223-6a/b (R_2). The plans for JEX-70 were to achieve maximum mixing for a given reactor fuel in order to approach a uniform "superbatch" as nearly as possible. Also, as noted earlier, comparison of predicted and actual results indicated that substantial mixing was occurring beyond the intermediate feed tanks. Thus, not surprisingly, best agreement with actual output analyses was obtained when large R_2 heels were assumed.

Results of a typical simulation with Eurochemic input analyses are shown in Table 4-10 and 4-11 (Similar results, differing only in degree, were obtained when the ORNL input analyses were used). Predicted vs actual output concentrations are shown graphically for plutonium-241 in Figure 4.12. Over the first 25,000 g of product it is obvious from the uniformity of the experimental plutonium-241 concentrations that there was considerably more mixing than was assumed for the simulation. Nevertheless, up to approximately 36,000 g, the simulation agrees reasonably well with the eyperimental results. While part of the subsequent divergences might be eyplained by analytical discrepancies, a more likely explanation is the excessive recycling of plutonium nearly 20,000 g, which began at about this point and continued over a period of about 10 days before product was again collected.

Other conclusions are suggested by the data. The high (6.05 %) plutonium-241 content of the first output batch is similar to that of the last material processed during the preceding Mol II campaign on TRINO fuel (see Table 4-20) and suggests that residual Mol II product was displaced from the plutonium dryer and calciner upon commencement of the new campaign.

The slight lag in arrival of the first step function suggest that the holdup in the system is greater than that assumed, by an amount in the 1-2 kg range. Presence of a couple heels of 500 g or so above those assumed for the model would eliminate much of this apparent lag and also would provide the greater than predicted mixing which was observed.

Plutonium product is first collected in Tank 2416-1, designated the specification analysis tank, where it is checked for purity specifications, and either returned for recycle or sent ahead to the precipitator and calciner as final product. During JEX-70 acceptable product batches from 2416-1 (designated as 2 BP product) were also analyzed for isotopic composition.

Masses and isotopic analyses of 2 BP product batches are shown in Table 4-12, which also shows the approximate quantities of plutonium returned as recycle; the extent of recycling is apparent. A comparison of simulated and experimental results for 2 BP product is shown in Table 4-14. Input basis differs from that in Table 4-10 in that ORNL isotopic analyses were used, and larger heels were assumed in Tanks 223-6a/6b and 231-8. The results for plutonium-241 are plotted in Figure 4.13. It is apparent that the agreement between model and plant is better at the 2 BP stage. For example, the 6 % plutonium-241 found in the first PuO_2 product is absent, additional evidence for the supposition that this was residual material in the drver and calciner.

4.11 Evaluation of the Physical Inventory

In chapter 5 the inprocess physical inventory at the moment VAK feed was introduced into the system was calculated using the actual input and output data. The output batches were considered in three categories:

(a) Clean CANDU material
(b) 2-component mixture of CANDU and VAK material, and
(c) 3-component mixture of CANDU, VAK, and TRINO material.

Several assumptions were necessary in order to make the calculations. Change from clean CANDU product to CANDU + VAK material was fairly evident from the sharp jump in plutonium-241 content from the CANDU composition plateau, beginning with batch 133. Change from a 2-camponent to a 3-component mixture was less certain but could be defined as reasonably including product batches 145-148 or 145-149. Unfortunately, due to the lack of well-mixed superbatches of each type of feed, the calculated average plutonium concentrations necessarily used for the calculations were not truly representative of the variations in the individual feed batches. Thus, the input concentrations were constantly changing over each input batch. The precision of the method of determinants suffers when feed concentrations are nonuniform. In addition, the method is based on the premise that the mixture being solved is comprised of the specified constituents, and only these. When there is a high percentage of recycling, as in the Mol III campaign, additional components can be introduced into the mixture, leading to calculation errors, unless their identity is known.

For purposes of comparison with the actual results a simulation was performed, in which these parameters were idealized. Theoretical "superbatches" of the average composition of the CANDU, VAK, and TRINO feeds were constructed; for better uniformity, the CANDU was assumed to be divided into two slightly different types. Except for this averaging, all other parameters were maintained the same as before, as shown in Table 4-15. Results of this simulation are shown in Table 4-16. Change from clean CANDU-A to a mixture of A and B in the product was evident, beginning with batch 8. Product batches of A + B were readily solved as 2-component mixtures, with the results shown in Table 4-17. CANDU-B fuel, first evident in batch 8, reached a maximum in batch 16, at which time CANDU-A fuel was essentially exhausted. VAK fuel made its first appearance in batch 16. The percentage of CANDU fuel (A+B) in the output decreased steadily from batch 16 onward; by batch 23 it had decreased to 3.0 %. Plutonium-241 reached its maximum concentration (7.800%) in batch 23; decrease to 7.684 % in batch 24 signalled the advent of a new feed component (TRINO) in the mixture. Subsequent batches were 3-component mixtures. Calculations of CANDU fractions were possible in only the next two output batches, by which time the percentage had decreased to 1.4 % (∿23 g Pu).

The steady and consistent decrease in the fractions of CANDU fuel present in the output batches after the introduction of VAK fuel into the process is evident in the plot in Figure 4-14. The comparable fractions calculated (in chapter 5) for the actual Mol data are also plotted. The agreement seems quite good; supporting evidence that the model represents what is actually occurring in the plant.

It is quite apparent from calculations based on the actual Mol III data that by the 23rd batch (142) the percentage of CANDU material in a product batch has decreased to about 6.6 %, and can be expected to continue to decrease similarly, as additional different feed materials enter the plant. Therefore, if the batches are maintaining their normal processing order, an upper limit of 6.6 % may be set for CANDU material in subsequent output batches. Thus, it is surprising that the solution reported in chapter 5 for the 3-component mixtures in batches 145-148 (149) indicated that the amount of CANDU material present was as great as 1141 g. This is a much greater percentage of these product batches than that expected with the exponential decrease predicted by the model in the absence of recycling. One possibility is that a significant quantity of CANDU material was delayed and was returned to the process during this time span. However, the available operating records do not indicate conclusively whether this occured or not.

In-process inventory at the moment of introduction of VAK fuel, calculated for the simulated superbatch run, was as follows:

		gm Pu
Batches 12-15	Clean CANDU material	6,300
Batches 16-23	CANDU-VAK mixture	5,342
Batches 24-25	CANDU-VAK-TRINO mixture	54
	Total	11,696

Interestingly, the 11,642 g total for clean CANDU and the CANDU-VAK mixture is in good agreement with the 12,599 g total calculated for these same two portions of the actual Mol III campaign.

4.12 Mol II Campaign

An examination of the earlier controlled experiment at the Eurochemic plant (Mol II) furnishes additional information on the requirements and capabilities of a simulation model. Less information was available on the conduct of the Mol II experiment, but the following summarizes the data on which the simulation was based. These data were obtained principally from /‾4-7_7 and from E. Drosselmeyer /‾4-6_7, with additional background information from /‾4-8_7.

Considering only the plutonium, differences in the isotopic composition of the input batches of fuel were not great. The fuel appeared to consist of two fairly similar types, which differed principally in Pu-240 content; differences in the other isotopes were insufficient for a useable step function. Presumably, there was also recycle of dissolution acid containing uranium and plutonium during Mol II although there are no data on this. Since no data were available on vessel heels, mixing stratgies, etc., for purposes of the simulation the same basic assumptions used in the Mol III simulation were employed. It was known that approximately 11.8 kg of off-specification plutonium nitrate solution remained in the plant at the conclusion of the Mol II campaign, although it was not known during which period of the campaign this material was accumulated.

Plutonium input data are tabulated in Table 4-18 which also shows computer program parameters. Calculated plutonium concentrations in output batches are presented in Table 4-19; actual assays are shown in Table 4-20.

Isotopic analyses of input batches were performed at Eurochemic; output analyses were performed at GfK, except that the composition reported for the 11.8 kg residual inventory (batch 116) was obtained from Eurochemic. There appeared to be a slight bias between the two laboratories, so that agreement of input and output masses for the individual isotopes showed more variation than would have been expected had all analyses been performed at one laboratory.

Calculated and actual plutonium concentrations are compared in Figure 4.15a. The general shapes of the two plots are comparable, except for a lateral displacement, which is discussed in the following paragraph. The consistent minor differences in magnitude between predicted and actual values of the plutonium-240 concentration are believed to be due primarily to the analytical differences mentioned above.

However, the major lateral displacement of the two plots is of particular significance. It is illustrative, in a qualitative fashion, of one application of simulation models to safeguards. The abrupt change in plutonium-240 concentration should not have occurred when it did if the input batches had been processed according to the reported schedule. If the model is truly representative of the plant response, then one could conclude that there was possibly a substantial diversion of plutonium from the product stream, on the order of 10 kg, commencing after output batch 87, or that there had been some deviation from the announced input sequence. A more quantitative statement than this is unwarranted at this time, in view of the oversimplification of the simulation model and the lack of more detailed information on the actual plant operations. Conceivably, at a later stage of development, a more positive statement could be made by a safeguards inspector viewing these data. As an example of what may have occurred, the effect on isotopic composition of the output of assuming that the 5th and 6th input batches were delayed, and then released at the end of the campaign was simulated, with the results shown in Figure 4.15 b.

4.13 Other Simulation Models

Another mathematical model for fuel reprocessing plants which is currently under development is a "mass-flow" model. This model will not only provide plutonium concentrations, as in the present models, but will also compute the relative fractions of the input batches present in each output batch. Such a model will be useful for in-process inventory studies, and may offer a means of getting around some of the problems associated with the calculation of in-process inventory by schemes based on the method of determinants.

Such a model could be applied as an indirect method of surveillance, much as the present concentration model can, but would furnish additional corroborative information. With the present model agreement of predicted and actual plutonium isotopic concentrations is evidence that plant operations are as stated, so that the material in each input batch is accounted for. The mass-flow model will go one step further and detail how each input batch is distributed in the product, corroborating the agreement of predicted and actual concentrations.

The model is being developed to fit the NFS plant, it being a simpler case than the Eurochemic plant in terms of number of compartments and alternative pathways. Once the model is debugged and operable, it should not be difficult to adapt it to the Eurochemic plant.

4.14 Discussion

The Eurochemic plant is a small multi-purpose fuel reprocessing plant possessing many of the characteristics of a large pilot plant. Nominal capacity for low-enrichment fuels is 130 T/yr, only about 70 tons were processed in the first three years of operation. The processing section is very flexible, and has numerous buffer and in-process storage tanks, many more than are to be found in larger reprocessing plants. These conditions are not ideal for the validation of simulation models. Also disadvantageous for modeling can be the recycle of plutonium in the recovered nitric and in the mother liquor from the continuous plutonium precipitator.

Additionally, with the rather complex process flow sheet, the plant operator has many operating strategies available to him, and in any given campaign is likely to be forced to adopt one or more variations of these by processing exigencies. Thus, the Mol plant is a difficult plant to model.

Since the Battelle-Columbus efforts were restriced wholly to consideration of the plutonium fuel cycle, the conclusions drawn apply necessarily to plutonium, they may or may not be applicable to the uranium side of the plant. The conclusions are also based only on the data and process information which was available in the U.S. Most of this was derived from the various interim reports.

Qualitatively, comparisons of predicted results with actual results indicate that the model is approximately representative of the plant. It does not seem feasible, at least on the basis of the data used in these studies, to attempt to draw too many quantitative conclusions. More detailed data on such matters as important heels, mixing of input batches, the reprocessing of the initial plutonium inventory and actual reprocessing strategies would have been beneficial. Nevertheless, in spite of the lack of some information and with the numerous arbitrary selections of model parameters which were necessary, the general agreement between model and plant confirms the basic validity of the model. By using a combination of actual operating data and plutonium concentrations predicted by the model for mathematically averaged "superbatches", determination of in-process inventory was also simulated, with interesting results.

A number of limitations associated with mathematical modeling of fuel reprocessing plants in general, and with the Eurochemic plant in particular, were identified during the simulation studies. One of the most fundamental is that developing (and especially testing) of a simulation model requires full, complete, and accurate data. While a considerable body of information was available for the Mol III campaign, there were some deficiencies, so that a rigorous comparison of predicted and actual results was not possible.

High on the list of accurate data needs are the isotopic plutonium analyses. In addition, differences in isotopic composition between fuels are generally not great, which accentuates the need for accurate analyses. While the results of input and output analyses from a given laboratory will normally be internally consistent, the problem of bias between laboratories may well be a problem. This can pose problems in research investigations, and even worse ones for safeguards surveillance.

The relative sizes of input batches, output batches, and plant can impose limitations on in-process inventory determination. Rather large superbatches, possibly larger than the average reactor batch processed at Mol, are needed to insure that a step function clears the plant. If this does not happen, passage of subsequent input batches so increases the number of constituents in an output batch that they cannot be satisfactorily resolved.

Refinement of a model, or more strictly speaking, validation of the fact that changes made in a model are really refinements, ultimately requires feedback from the real plant being modeled; and the better the data fed back, the better can be the comparison. Since it was fairly obvious that th JEX-70 data were not sufficiently detailed to evaluate the effects of other than the major variables, no attempts were made to incorporate minor variables, such as mixing in extraction columns and mixer-settlers, into the Mol III model.

4.15 Conclusions and Recommendations

(1) While qualitative agreement of the mathematical model with the actual results of the JEX-70 experiment verifies the feasibility and identity of the model, quantitative conclusions relative to the closeness of fit appear unwarranted. The deviations from steady-state conditions and the numerous unrecorded variations from planned operating strategies preclude quantitative identification of the model with the plant.

(2) A more flexible model than the PUEURO model is desirable for greater compatibility with fuel reprocessing plant strategies; such a model should be time-independent, so that recycle streams can be incorporated into it.

(3) Construction of a more powerful mathematical model which can calculate not only concentrations in a vessel, but also the batch fractions present will be very useful in further inventory determination studies and its development should be pursued.

(4) Accurate isotopic analyses are critical to both simulation studies and to in-process inventory determinations by isotopic-tracer techniques and efforts to generally improve levels of accuracy should be continued.

(5) Additional plant experiments should be conducted, preferably in high throughput fuel reprocessing plants; in any such experiments provision of acceptable "superbatch" sizes and adequate step-function sizes should be stressed. Such a test, if successful, may show that a reasonably precise in-process inventory can be calculated with relatively simple mathematical techniques.

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Table 4-1: Review on the parameter for studies on the "response function for Pu.

No.	Computer Ref.	Heels H	Heels L	Mixing No	Mixing LR	Mixing R	Recycling 0%	Recycling 5%	Kg.of total Pu output to recover x% of the traced input batch.		
1	130/2		+	+			+		8.5 (91%)	11.3 (98.4%)	17.0 (100%)
2	130/1		+		+		+		19.8 (93%)	25.5 (97.6%)	>29. (100%)
3	129/1	+			+		+		19.7 (92,4%)	28.2 (98.4%)	>30. (100%)
4	128/1	+			+			+	19.1 (90.7%)	30.1 (99.3%)	>33. (100%)
5	129/2	+				+	+		16.9 (92.7%)	22.6 (97.6%)	>25. (100%)
6	128/2	+				+		+	15.3 (90.7%)	23.7 (98.3%)	>26. (100%)

Table 4-2: Minimum size of the two superbatches

No. of output batches considered.	Percentage of the inventory measured.	superbatch size (kg of Pu) 1.	2.
4	70.6	11.32	0
5	86.9	14.15	2.83
6	96.9	16.98	5.66
7	99.44	19.82	8.50
8	99.90	22.65	11.34
9	99.98	25.47	14.15
10	100.	28.30	16.98

Table 4-3: Minimum size of the two superbatches for U (with U^{IV} recycling).

No. of output batches considered.	% of the inventory measured.	Superbatch size /¯kg_7 1	2
8	80.6	3200	0
9	92.2	3600	400
10	95.3	4000	800
11	96.5	4400	1600
12	97.4	4800	2000
13	98.1	5200	2400
14	98.7	5600	2800
15	99.11	6000	3200
16	99.41	6400	3600
17	99.70	6800	4000
18	99.85	7200	4400
19	100.	7600	4800

From the calculated numbers 1000 kg were subtracted because the IAT does not belong to the MBA.

Table 4-4: Minimum size of the two superbatches For U in case of no recyclings.

No. of output batches considered	% of the inventory measured	Superbatch size [kg] 1.	2.
8	82.8	3200	0
9	96.1	3600	400
10	99.24	4000	800
11	99.69	4400	1600
12	99.84	4800	2000
13	100.00	5200	2400

Table 4-5: Different strategies for parametersstudies.

		Heels IAT	Mixing	Re-cycling [%]	No. of campaigns
1	Pu-1	L	NO	0	2300
2	Pu-2	L	YES	0	400
3	Pu-3	H	NO	0	400
4	U 4-5-6	L	NO	0	150
5	U 1-2-3	L	NO	10	150
6	U 7-8-9	L	NO	16	150
7	U 10-11-12	H	NO	10	150
8	U 13-14-15	L	YES	10	150

$\Sigma = \underline{\underline{3850}}$

Table 4-6: PLUTONIUM OPERATING PARAMETERS

Flowsheet Point	Vessel Number	Vessel Description	Mode of Flow In	Mode of Flow Out	Mode of Flow Schematic	Conc. g/l	Flow g/hr	Volume Soln., l Max	Volume Soln., l Normal	Volume Soln., l Min	Pu, gms Normal Range Full	Pu, gms Normal Range Empty	Pu, gms Min. Heel	Remarks
	226-1/2	Dissolver	Batch	Batch	⎍⎍⎍⎍	1-1.5	--	?	2500	0	3000	0	0	400 gU/l - 1 ton batch (3 kg Pu/t)
C_1	221-4	Accountability Tank	Batch	Batch	⎍⎍⎍⎍	1-1.5	--	3000	2400	<2	2400	~ 0	0	221-4 receives most of batch
	221-6	Accountability Tank	Batch	Batch	⎍⎍⎍⎍	1-1.5	--	2000	<1600	<2	600	~ 0	0	221-6 receives excess
C_2	223-6a	Intermed. Feed Tank	Batch	Batch	⎍⎍⎍⎍	1-1.5	--	4000	3000	30	3000	25-50	~ 0	Used alternately?
	223-6b	Intermed. Feed Tank	Batch	Batch	⎍⎍⎍⎍	1-1.5	--	4000	3000	40	3000	25-50	~ 0	
C_3	231-1	Column Feed Tank	Batch	Cont.	◸◸◸	1-1.5	50-80	4000	3500	20	3000	50	20	Transfer made when heel down to 20 l
C_4	231-2	Extraction Col.	Cont.	Cont.	———	0.5-1	50-80	375	375	375	100	100	--	
C_5	231-3	Scrub Col.	Cont.	Cont.	———	0.5-1	50-80	165	165	165	50	50	--	
C_6	231-4	Partition Col.	Cont.	Cont.	———	2-3	50-80	165	165	165	50	50	--	
C_7	231-5	Strip Col.	Cont.	Cont.	———	2-3	50-80	25	25	25	20	20	--	
C_8	231-58	Product Receiver	Cont.	Cont.	———	2-3	50-80	120	90	--	200	200	--	
C_9	236-2c	Evaporator	Cont.	Batch	◿◿◿	40	50-80	10	10	<1	400	<40	~ 0	Equiv. to a batch of ~ 2800 g which will evidently pass through Pu cycle as a batch
	236-1b	Evap. Reboiler	Cont.	Batch		40	50-80	80	60	<1	2400	<40	~ 0	
C_{10}	236-4a	Buffer Tank	Batch	Batch	⎍⎍⎍⎍	40	--	90	70	<1	~ 2800	<40	~ 0	
C_{11}	236-1a	Buffer Tank	Batch	Batch	⎍⎍⎍⎍	40	--	80	70	<1	~ 2800	<40	~ 0	
C_{12}	236-4b	Feed Adjust Tank	Batch	Batch	⎍⎍⎍⎍	40	--	100	70	<1	~ 2800	<40	~ 0	
C_{13}	237-1	Buffer Tank	Batch	Batch	⎍⎍⎍⎍	40	--	50	<40	<1	1200	<40	~ 0	237-1 overflows to 237-2
C_{14}	237-2	Extraction Feed Tank	Batch	Cont.	◸◸◸	40	200	50	40	2	1600	100	40	
C_{15}	237-3	Mixer-Settler	Cont.	Cont.	———	20	200	40	40	40	150	150	150	
C_{16}	237-4	Mixer-Settler	Cont.	Cont.	———	12	200	40	40	40	200	200	200	
	237-9	Buffer Tank	Cont.	Batch	◿◿◿	12	200	50	<40	<1	<500	<40	~ 0	Temporary catch tank for 2416-1
C_{17}	236-2a/b	Evaporator	Cont.	Batch	◿◿◿	40	200	5	5	--	200	~ 0	~ 0	
	2416-1	Specific. Anal. Tank	Cont.	Batch		40	200	100	70	<1	2800	<40	~ 0	
C_{18}	2436-1	Product Receiver	Batch	Batch	⎍⎍⎍⎍	40	--	250	<150	<1	2800	<40	~ 0	
C_{19}	238-1	Buffer Tank	Batch	Batch	⎍⎍⎍⎍	40	--	250	80	<1	2800	<40	~ 0	No particular function
C_{20}	238-2	Feed Adjust Tank	Batch	Batch	⎍⎍⎍⎍	30	120	250	90	<1	2800	<40	~ 0	
C_{21}	238-3	Pptor. Feed Tank	Batch	Cont.	◸◸◸	30	120	--	90	<1	2800	60	20	
C_{22}		Cont. Pptor.	Cont.	Cont.	———	--	120	--	4	4	200	100	100	
C_{23}		Ppt. Settler	Cont.	Cont.	———	--	120	--	10	10	200	100	100	
C_{24}		Dryer - Calciner	Cont.	Cont.	———	--	120	--	--	--	500	200	200	
C_{25}		Product Can	Cont.	Batch	◿◿◿	--	--	--	--	--	2000	1500	--	
		M.L. Collection Tank	Cont.	Batch	◿◿◿	<0.3	--							Pu should be <0.05 g/l

Table 4-7: STATEMENTS DESCRIBING PLUTONIUM OPERATION SIMPLIFIED PLUTONIUM CYCLE - EUROCHEMIC PLANT

$M_1;\ C_1$

$$k_2 = k;\ C_2^n = \frac{M_1C_1^n + R_2C_2^{n-1}}{M_1 + R_2}$$

$$k_3 = k;\ C_3^n = \frac{M_2C_2^n + R_3C_3^{n-1}}{M_2 + R_3}$$

$$k_4 = k_5 = k_6 = k_7 = k;\ C_4^n \sim C_5^n \sim C_6^n \sim C_7^n \sim C_3^n$$

$$k_8 = k;\ C_8 = \frac{dC_8}{dt} = \frac{k_8}{R_8}(C_7 - C_8)$$

$$k_9 = k;\ C_9 = \frac{k\int_{to}^{to+T} C_8dt + R_9C_9^{n-1}}{kT + R_9}$$

$$k_{10} = k_{11};\ C_{10} \sim C_{11} \sim C_9$$

$$k_{12} = k;\ C_{12}^n = \frac{M_{11}C_{11}^n + R_{12}C_{12}^{n-1}}{M_{11} + R_{12}}$$

$$k_{13} = k;\ C_{13}^n = \frac{M_{12}C_{12}^n + R_{13}C_{13}^{n-1}}{M_{12} + R_{13}}$$

$$k_{14} = k;\ C_{14}^n = \frac{M_{13}C_{13}^n + R_{14}C_{14}^{n-1}}{M_{13} + R_{14}}$$

$$k_{15} = k;\ C_{15} = \frac{dC_{15}}{dt} = \frac{k_{15}}{R_{15}}(C_{14} - C_{15})$$

$$k_{16} = k;\ C_{16}^n = \frac{dC_{16}}{dt} + \frac{k_{16}}{R_{16}}(C_{15} - C_{16})$$

$$k_{17} = k;\ C_{17}^n = k\,\frac{\int_{to}^{to+T} C_{16}dt + R_{17}C_{17}^{n-1}}{kT + R_{17}}$$

$$k_{18} = k;\ C_{18}^n = \frac{M_{17}C_{17}^{\,n} + R_{18}C_{18}^{\,n-1}}{M_{17} + R_{18}}$$

$$k_{19} = k;\ C_{19}^n = \frac{M_{18}C_{18}^n + R_{19}C_{19}^{n-1}}{M_{18} + R_{19}}$$

$$k_{20} = k;\ C_{20}^n = \frac{M_{19}C_{19}^n + R_{20}C_{20}^{n-1}}{M_{19} + R_{20}}$$

$$k_{21} = k;\ C_{21}^n = \frac{M_{20}C_{20}^n + R_{21}C_{21}^{n-1}}{M_{20} + R_{21}}$$

$$k_{22} = k;\ C_{22} = \frac{dC_{22}}{dt} = \frac{k_{22}}{R_{22}}(C_{21} - C_{22})$$

$$k_{23} = k;\ C_{23} = \frac{dC_{23}}{dt} = \frac{k_{23}}{R_{23}}(C_{22} - C_{23})$$

$$k_{24} = k;\ C_{24} = \frac{dC_{24}}{dt}\ \frac{k_{24}}{R_{24}}(C_{23} - C_{24})$$

$$k_{25} = k;\ C_{25} = \frac{k\int_{to}^{to+T} C_{24}dt}{kT}$$

Nomenclature

M_1 = mass of plutonium input
C_i = weight fraction of plutonium isotope x in total plutonium in stream at point i
R_i = mass of residual plutonium in vessel
k_i = total plutonium mass flow rate, mass/unit time
T = filling time
n = batch number

Table 4-8: PLUTONIUM INPUT DATA--MOL III CAMPAIGN

Batch No.	Date	Pu Mass, g	Σ Pu Mass, g	Eurochemic Analyses					ORNL Analyses				
				-238	-239	-240	-241	-242	-238[a]	-239	-240	-241	-242
						CANDU							
1	2-10	3543	3,543	0.14	71.72	23.32	3.74	1.07	0.14	71.792	23.389	3,637	1.042
2	2-13	3500	7,043	0.14	71.55	23.29	3.92	1.09	0.14	71,627	23.372	3,804	1,055
3	2-15	3510	10,553	0.74	70.55	24.08	4.04	1.18	0.74	70,191	24.060	3.864	1.133
4	3-03	2889	13,442	0.77	76.00	20.38	2.82	0.694	0.77	75.517	20,275	3.736	0.679
5	3-06	3177	16,617	0.12	74.27	21.63	3.15	0.840	0.12	74.312	21.690	3.066	0.810
6	3-10	3373	19,992	0.13	71.63	23.44	3.72	1.09	0.13	71.677	23.487	3.610	1.082
7	3-20	3337	23,329	0.13	71.24	23.71	3.81	1.11	0.13	71.466	23.628	3.694	1.080
8	3-23	3177	26,506	0.13	71.71	23.43	3.67	1.05	0.13	71.722	23.513	3.583	1.050
9	3-26	3397	29,903	0.12	73.05	22.43	3.41	0.989	0.12	73.555	22.202	3.214	0.899
						VAK							
10	3-31	2981	32,884	0.577	67.78	22.13	7.53	1.97	0.577	67.778	22.186	7.475	1.982
11	4-06	2942	35,026	0.629	66.03	22.96	8.08	2.30	0.629	66.528	22.926	7.719	2.196
12	4-12	4067	39,093	0.742	65.35	23.31	8.18	2.42	0.742	64.507	23.687	8.356	2.705
13(b)	4-16	741	39,834	0.528	68.31	21.64	7.74	1.78					
						TRINO							
14	4-24	3559	43,393	0.44	75.46	15.74	7.18	1.29	0.44	76.040	15.065	6.809	1.106
15	4-26	3139	46,532	0.36	78.73	14.07	5.94	0.90	0.36	79.080	13.973	5.724	0.853
						CdN							
16	4-30	315	46,847	0.070	86.22	11.46	1.37	1.76	0.070	86.995	11.446	1.318	0.171
17	5-01	238	47,085	0.081	85.33	12.81	1.52	2.10	0.081	85.587	12.655	1.466	0.205
18	5-03	358	47,443	0.085	86.63	11.82	1.33	1.48	0.085	86.546	11.888	1.325	0.155
19	5-04	289	47,732	0.069	87.32	11.23	1.19	1.31	0.069	87.471	11.194	1.140	0.126
20(c)	5-06	19	47,751	0.069	87.32	11.23	1.19	1.31	0.069	87.669	10.976	1.148	0.137
						Inventory(b)							
21		2950	50,701	0.30	78.65	14.64	5.55	0.86					
22		2950	53,651	0.30	78.65	14.64	5.55	0.86					
23		2950	56,601	0.30	78.65	14.64	5.55	0.86					
24		2950	59,551	0.30	78.65	14.64	5.55	0.86					
Pu recovery fraction			0.955	0.797	0.955	0.957	0.947	0.958	0.799	0.955	0.958	0.966	0.969

(a) Plutonium-238 analyses were not made by ORNL; Eurochemic values

(b) Not analyzed by ORNL

(c) No analyses available for batch 20; taken as same as batch 19.

Table 4-9: PLUTONIUM OUTPUT DATA FOR MOL III

				Plutonium concentration, percent					
	BATCH	PU-GM	SUM PU-GM	-238	239	240	-241	-242	DATE
1	118	1671.	1671.	00.427	69.320	22.570	6.050	1.630	3-11
2	143	1396.	3067.	00.135	72.130	23.020	3.690	1.020	3-12
3	121	1164.	4231.	00.144	72.350	22.870	3.630	1.010	3-13
4	122	1923.	6154.	00.137	72.680	22.560	3.630	00.995	3-18
5	124	1624.	7778.	00.134	72.920	22.410	3.570	00.967	3-21
6	123	1602.	9380.	00.139	73.100	22.220	3.590	00.953	3-23
7	126	1664.	11044.	00.129	73.030	22.330	3.550	00.962	3-24
8	125	1592.	12636.	00.118	72.920	22.450	3.550	00.967	3-28
9	131	1486.	14122.	00.128	72.550	22.730	3.590	1.010	3-29
10	132	1668.	15790.	00.130	72.660	22.680	3.550	00.990	3-30
11	134	1810.	17600.	00.134	72.530	22.750	3.590	00.996	4-02
12	135	1613.	19213.	00.130	72.480	22.800	3.590	00.999	4-04
13	136	1550.	20763.	00.126	72.120	23.030	3.670	1.050	4-05
14	127	1562.	22325.	00.129	72.470	22.810	3.550	1.040	4-06
15	128	1586.	23911.	00.124	72.570	22.770	3.540	00.996	4-10
16	129	1549.	25460.	00.123	72.730	22.670	3.480	00.987	4-11
17	130	895.	26355.	00.127	72.660	22.730	3.500	00.989	4-16
18	133	1704.	28059.	00.345	70.440	22.540	5.260	1.420	4-18
19	138	1440.	29499.	00.432	69.320	22.540	6.070	1.640	4-26
20	139	1321.	30820.	00.540	67.750	22.760	6.940	2.010	4-26
21	140	1554.	32374.	00.620	66.780	23.050	7.350	2.200	4-27
22	141	1653.	34027.	00.620	66.380	23.080	7.620	2.310	4-28
23	142	1703.	35730.	00.700	66.280	23.060	7.650	2.310	4-30
24	145	1723.	37453.	00.470	74.490	17.140	6.560	1.340	5-11
25	146	1624.	39077.	00.420	75.720	16.420	6.240	1.200	5-12
26	147	1268.	40345.	00.470	74.610	16.980	6.650	1.290	5-13
27	148	1379.	41724.	00.420	75.500	16.380	6.470	1.230	5-14
28	149	1810.	43534.	00.390	76.970	15.630	5.940	1.080	5-16
29	155	1370.	44904.	00.330	78.110	15.160	5.500	00.998	6-07
30	156	1481.	46385.	00.300	78.600	14.820	5.400	00.886	6-07
31	157	1385.	47770.	00.320	78.540	14.860	5.390	00.885	6-08
32	150	1569.	49339.	00.270	77.140	16.810	4.890	00.889	6-08
33	158	1493.	50832.	00.310	78.620	14.780	5.390	00.891	6-10
34	159	1090.	51922.	00.320	78.550	14.860	5.410	00.867	6-13
35	160	1125.	53047.	00.330	78.590	14.780	5.410	00.885	6-14
36	162	921.	53969.	00.290	78.890	15.040	4.930	00.859	6-21
37	161	1032.	55001.	00.300	78.620	15.350	4.840	00.884	6-23
38	163	562.	55563.	00.290	78.590	15.420	4.830	00.875	
39	164	1336.	56899.	00.330	75.310	18.110	5.370	00.886	
	TOTAL GMS			165.3	41769.0	11471.0	2820.7	672.6	

Table 4-10: PLUTONIUM INPUT DATA FOR MOL III SIMULATION - EUROCHEMIC ANALYSES

```
INPUT DATA                  EUROCHEMIC PLANT MODEL-MOL-3 CANDU-VAK-TRINO-CDN-INVENTORY

FLOW RATE= 1.800E+03  GM/DAY

TIME STEP= 5.000E-02  DAY

MAX. TIME= 4.000E+01  DAY

RECOVERY FACTOR= 00.955

                                                     CONCENTRATIONS-PER CENT

 BATCH          MASS     MASS SUM        PU238          PU239          PU240          PU241          PU242       DATE

   1           3543.0     3543.0      1.400E-01      7.172E+01      2.332E+01      3.740E+00      1.070E+00     2-10
   2           3500.0     7043.0      1.400E-01      7.155E+01      2.329E+01      3.920E+00      1.090E+00     2-13
   3           3510.0    10553.0      7.400E-01      7.055E+01      2.408E+01      4.040E+00      1.180E+00     2-15
   4           2889.0    13442.0      7.700E-01      7.600E+01      2.038E+01      2.820E+00      6.940E-01     3-03
   5   CANDU   3177.0    16619.0      1.200E-01      7.427E+01      2.163E+01      3.150E+00      8.400E-01     3-06
   6           3373.0    19992.0      1.300E-01      7.163E+01      2.344E+01      3.720E+00      1.090E+00     3-10
   7           3337.0    23329.0      1.300E-01      7.124E+01      2.371E+01      3.810E+00      1.110E+00     3-20
   8           3177.0    26506.0      1.300E-01      7.171E+01      2.343E+01      3.670E+00      1.050E+00     3-23
   9           3397.0    29903.0      1.200E-01      7.305E+01      2.243E+01      3.410E+00      9.890E-01     3-26
  10           2981.0    32884.0      5.970E-01      6.778E+01      2.213E+01      7.530E+00      1.970E+00     3-31
  11           2142.0    35026.0      6.290E-01      6.603E+01      2.296E+01      8.080E+00      2.300E+00     4-06
  12   VAK     4067.0    39093.0      7.420E-01      6.535E+01      2.331E+01      8.180E+00      2.420E+00     4-12
  13            741.0    39834.0      5.280E-01      6.831E+01      2.164E+01      7.740E+00      1.780E+00     4-16
  14           3559.0    43393.0      4.400E-01      7.546E+01      1.574E+01      7.180E+00      1.290E+00     4-24
  15   TRINO   3139.0    46532.0      3.600E-01      7.873E+01      1.407E+01      5.940E+00      9.000E-01     4-26
  16            315.0    46847.0      7.000E-02      8.622E+01      1.146E+01      1.370E+00      1.760E-01     4-30
  17            238.0    47085.0      8.100E-02      8.533E+01      1.281E+01      1.520E+00      2.100E-01     5-01
  18            358.0    47443.0      8.500E-02      8.663E+01      1.182E+01      1.330E+00      1.480E-01     5-03
  19   CdN      289.0    47732.0      6.900E-02      8.732E+01      1.123E+01      1.190E+00      1.310E-01     5-04
  20             19.0    47751.0      6.900E-02      8.732E+01      1.123E+01      1.190E+00      1.310E-01     5-06
  21           2950.0    50701.0      3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01
  22           2950.0    53651.0      3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01
  23   INV.    2950.0    56601.0      3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01
  24           2950.0    59551.0      3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01

TOTAL GMS                            207.50        43720.10       11983.40        2978.90         702.20

                              VESSEL     RMIN          RMAX        VESSEL     RMIN          RMAX

                                1        0.000      3466.000        14      100.000      2800.000
                                2       -2.000      4000.000        15       50.000       150.000
                                3       50.000      4000.000        16       50.000       200.000
                                4      100.000       100.000        17       50.000      2850.000
                                5       50.000        50.000        18       50.000      2850.000
                                6       50.000        50.000        19       50.000      2850.000
                                7       20.000        20.000        20       50.000      2850.000
                                8      200.000       200.000        21       60.000        60.000
                                9       50.000      2850.000        22      100.000       100.000
                               10       50.000      2850.000        23      100.000       100.000
                               11       50.000      2800.000        24      100.000       200.000
                               12       50.000      2800.000        25        0.000      2000.000
                               13       50.000      2800.000

                              IF ANY OF THE ABOVE RMIN-S ARE EQUAL TO (-2) THEN THAT RMIN WILL
                              HAVE A DIFFERENT HEEL FOR EACH INPUT BATCH DESCRIBED BELOW

   BATCH     1      2      3      4      5      6      7      8      9     10     11     12     13     14     15     16
     GMS  2250.  2250.  2250.  2250.  2250.  2250.  2250.  2250.   270.  2700.  2700.  2700.   180.  2700.   900.  2250.

   BATCH    17     18     19     20     21     22     23     24
     GMS  2250.  2250.  2250.   900.  2250.  2250.  2250.     0.
```

Table 4-11: CALCULATED MOL III PLUTONIUM OUTPUT CONCENTRATIONS[a]

OUTPUT BATCHES - C-25

BATCH	MASS	MASS SUM	PU238	PU239	PU240	PU241	PU242	TIME
1	1710.0	1710.0	1.436E-01	7.166E+01	2.331E+01	3.802E+00	1.077E+00	4.5
2	1440.0	3150.0	1.687E-01	7.161E+01	2.334E+01	3.819E+00	1.082E+00	5.3
3	1170.0	4320.0	2.407E-01	7.146E+01	2.343E+01	3.867E+00	1.096E+00	5.9
4	1890.0	6210.0	3.150E-01	7.143E+01	2.345E+01	3.870E+00	1.099E+00	7.0
5	1620.0	7830.0	4.626E-01	7.139E+01	2.349E+01	3.874E+00	1.104E+00	7.9
6	1620.0	9450.0	5.402E-01	7.263E+01	2.266E+01	3.586E+00	9.933E-01	8.8
7	1620.0	11070.0	5.753E-01	7.329E+01	2.222E+01	3.433E+00	9.349E-01	9.7
8	1620.0	12690.0	4.077E-01	7.381E+01	2.190E+01	3.290E+00	8.861E-01	10.6
9	1530.0	14220.0	3.650E-01	7.368E+01	2.199E+01	3.311E+00	8.981E-01	11.4
10	1710.0	15930.0	2.529E-01	7.291E+01	2.254E+01	3.461E+00	9.697E-01	12.4
11	1800.0	17730.0	2.159E-01	7.247E+01	2.285E+01	3.552E+00	1.008E+00	13.4
12	1620.0	19350.0	1.867E-01	7.211E+01	2.310E+01	3.627E+00	1.038E+00	14.3
13	1530.0	20880.0	1.616E-01	7.187E+01	2.328E+01	3.665E+00	1.052E+00	15.1
14	1530.0	22410.0	1.561E-01	7.187E+01	2.329E+01	3.664E+00	1.053E+00	16.0
15	1620.0	24030.0	1.410E-01	7.212E+01	2.311E+01	3.604E+00	1.037E+00	16.9
16	1530.0	25560.0	1.404E-01	7.220E+01	2.303E+01	3.604E+00	1.037E+00	17.7
17	900.0	26460.0	1.407E-01	7.235E+01	2.287E+01	3.610E+00	1.039E+00	18.2
18	1710.0	28170.0	1.808E-01	7.191E+01	2.283E+01	3.961E+00	1.129E+00	19.2
19	1440.0	29610.0	3.762E-01	6.975E+01	2.264E+01	5.673E+00	1.567E+00	20.0
20	1350.0	30960.0	4.290E-01	6.913E+01	2.267E+01	6.085E+00	1.690E+00	20.7
21	1530.0	32490.0	6.049E-01	6.703E+01	2.282E+01	7.443E+00	2.101E+00	21.6
22	1620.0	34110.0	6.280E-01	6.677E+01	2.283E+01	7.621E+00	2.151E+00	22.5
23	1710.0	35820.0	6.582E-01	6.644E+01	2.284E+01	7.855E+00	2.215E+00	23.4
24	1710.0	37530.0	6.263E-01	6.764E+01	2.189E+01	7.781E+00	2.079E+00	24.4
25	1620.0	39150.0	5.999E-01	6.870E+01	2.109E+01	7.673E+00	1.965E+00	25.3
26	1260.0	40410.0	4.570E-01	7.469E+01	1.667E+01	6.887E+00	1.345E+00	26.0
27	1350.0	41760.0	4.469E-01	7.510E+01	1.637E+01	6.825E+00	1.302E+00	26.7
28	1800.0	43560.0	3.946E-01	7.707E+01	1.513E+01	6.339E+00	1.097E+00	27.7
29	1350.0	44910.0	3.682E-01	7.783E+01	1.481E+01	5.990E+00	1.017E+00	28.5
30	1440.0	46350.0	2.889E-01	7.996E+01	1.403E+01	4.876E+00	7.907E-01	29.3
31	1350.0	47700.0	2.875E-01	7.986E+01	1.409E+01	4.927E+00	7.919E-01	30.0
32	1530.0	49230.0	2.895E-01	7.930E+01	1.436E+01	5.214E+00	8.166E-01	30.9
33	1530.0	50760.0	2.916E-01	7.915E+01	1.443E+01	5.291E+00	8.261E-01	31.7
34	1080.0	51840.0	2.955E-01	7.890E+01	1.453E+01	5.421E+00	8.425E-01	32.3
35	1170.0	53010.0	2.957E-01	7.888E+01	1.454E+01	5.427E+00	8.434E-01	33.0
36	900.0	53910.0	2.978E-01	7.877E+01	1.459E+01	5.487E+00	8.514E-01	33.5
37	990.0	54900.0	2.980E-01	7.876E+01	1.460E+01	5.495E+00	8.525E-01	34.0
38	540.0	55440.0	2.980E-01	7.876E+01	1.460E+01	5.495E+00	8.525E-01	34.3
39	1350.0	56790.0	2.985E-01	7.873E+01	1.461E+01	5.509E+00	8.544E-01	35.1
40	1080.0	57870.0	2.987E-01	7.872E+01	1.461E+01	5.514E+00	8.551E-01	35.7

[a] Based on Eurochemic input analyses.

Table 4-12: PLUTONIUM BATTERY-PRODUCT BATCHES (SPECIFICATION ANALYSIS TANK 2416-1)

2 BP Batch Number	Transfer from 2416-1 to Tank No. Date	(Recycle)	(Product)	Mass Pu g	Σg Product	Isotopic Composition, w/o -238	-239	-240	-241	-242	Remarks
- 100	3-5	236-1a		~1740							(a)
- 200	3-8	236-1a		~ 700							(a)
- 300	3-8		238-1	2196	2,196	0.136	71.982	23.103	3.742	1.037	
- 400	3-11		238-1	2175	4,371	0.132	72.501	22.747	3.629	0.991	
- 500	3-12	236-1a		~2320							(a)
- 600	3-13	236-1a		~2640							(a)
- 700	3-14	236-1a		~2640							(a)
- 800	3-15	236-1a		~2180							(a)
- 900	3-17		238-1	3539	7,910	0.129	73.038	22.375	3.510	0.948	
-1000	3-18	236-4b		~1120							(a)
-1100	3-21		238-1	2283	10,193	0.125	73.233	22.263	3.458	0.921	
-1200	3-23		238-1	2205	12,398	--	--	--	--	--	(b)
-1300	3-27		238-1	2816	15,214	0.126	72.491	22.781	3.599	1.003	
-1400	3-28		238-1	1964	17,178	0.124	72.372	22.835	3.648	1.021	
-1500	3-30		238-1	2276	19,454	0.126	72.523	22.743	3.597	1.011	
-1600	4-5		238-1	4337	23,791	0.121	72.485	22.887	3.509	0.999	
-1700	4-9		238-1	3465	27,256	0.121	72.477	22.920	3.493	0.989	
-1800	4-15		238-1	2881	30,137	0.379	69.969	22.522	5.596	1.532	
-1900	4-16		238-1	2351	35,488	0.497	68.699	22.488	6.519	1.797	
-2000	4-22		238-1	2657	35,145	0.653	66.681	22.987	7.472	2.207	
-2100	4-27		238-1	3786	38,930	0.701	66.146	23.146	7.667	2.340	
-2200	4-29	236-1a		~1440							(a)
-2300	4-30	236-4b		~1580							(a)
-2400	5-1	236-4b		~2320							(a)
-2500	5-2	236-4b		~2580							(a)
-2600	5-3	236-4b		~1120							(a)
-2700	5-4	236-4b		~2640							(a)
-2800	5-5	236-4b		~1880							(a)
-2900	5-7	236-4b		~2640							(a)
-3000	5-7	236-4b		~2040							(a)
-3100	5-10		238-1	5416	44,346	0.460	75.098	16.617	6.575	1.250	
-3200	5-13		238-1	3028	47,374	0.372	77.863	15.167	5.622	0.976	
-3300	5-13	236-4b		~2340							(a)
-3400	5-22	236-4a		~2040							(a)
-3500	5-22	236-4b		~2640							(a)
-3600	6-1	236-4b		~2850							(a)
-3700	6-2	236-4a		~3000							(a)
-3800	6-4	236-1a		~2640							(a)
-3900	6-6		238-1	2955	50,329	0.329	78.473	14.892	5.429	0.877	
-4000	6-7		238-1	3428	53,757	0.328	78.468	14.936	5.380	0.888	
-4100	6-8		238-1	3718	57,475	0.329	78.454	14.931	5.405	0.881	
--	6-8 6-12	236-1a 236-4b		--							(a) (a) } Four recycle batches
-4200	6-15	236-1a		~2920							(a)
-4300	6-18	236-4b		~1400							(a)
-4400	6-20		238-1	1289	58,764	0.296	78.884	15.295	4.676	0.849	
-4500	6-22		238-1	730	59,494	--	--	--	--	--	(b)
-4600	6-22		238-1	41	59,535	0.298	78.636	15.443	4.757	0.866	
-4700	6-23		238-1	227	59,762	--	--	--	--	--	(b) } Dilute flush-out product
-4800				113	59,875	--	--	--	--	--	(b)
-4900				12	59,887	--	--	--	--	--	(b)
-5000				20	59,907	--	--	--	--	--	(b)
-5100	6-24			2	59,909	--	--	--	--	--	(b)

(a) Recycle material; approximate masses; not analyzed.

(b) No isotopic analyses available.

Table 4-13: Plutonium Input Data for Mol III Simulation - ORNL Analyses

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INPUT DATA                EUROCHEMIC PLANT MODEL-MOL-3 CANDU-VAK-TRINO-CDN-INVENTORY

FLOW RATE= 1.800E+03  GM/DAY

TIME STEP= 5.000E-02  DAY

MAX. TIME= 4.000E+01  DAY

RECOVERY FACTOR= 00.955

                                                    CONCENTRATIONS-PER CENT

 BATCH      MASS     MASS SUM       PU238          PU239          PU240          PU241          PU242      DATE

    1      3543.0     3543.0     1.400E-01      7.179E+01      2.339E+01      3.637E+00      1.042E+00   2-10
    2      3500.0     7043.0     1.400E-01      7.163E+01      2.337E+01      3.804E+00      1.055E+00   2-13
    3      3510.0    10553.0     7.400E-01      7.019E+01      2.406E+01      3.864E+00      1.133E+00   2-15
    4      2887.0    13442.0     7.700E-01      7.552E+01      2.030E+01      2.736E+00      6.790E-01   3-03
    5      3177.0    16617.0     1.200E-01      7.431E+01      2.169E+01      3.066E+00      8.100E-01   3-06
    6      3373.0    19992.0     1.300E-01      7.168E+01      2.349E+01      3.610E+00      1.082E+00   3-10
    7      3337.0    23329.0     1.300E-01      7.147E+01      2.363E+01      3.694E+00      1.080E+00   3-20
    8      3177.0    26506.0     1.300E-01      7.172E+01      2.351E+01      3.583E+00      1.050E+00   3-23
    9      3397.0    29903.0     1.200E-01      7.355E+01      2.220E+01      3.214E+00      8.990E-01   3-26
   10      2981.0    32884.0     5.770E-01      6.778E+01      2.219E+01      7.475E+00      1.982E+00   3-31
   11      2142.0    35026.0     6.290E-01      6.653E+01      2.293E+01      7.719E+00      2.196E+00   4-06
   12      4067.0    39093.0     7.420E-01      6.451E+01      2.369E+01      8.356E+00      2.705E+00   4-12
   13       741.0    39834.0     5.280E-01      6.831E+01      2.164E+01      7.740E+00      1.780E+00   4-16
   14      3559.0    43393.0     4.400E-01      7.604E+01      1.506E+01      6.809E+00      1.106E+00   4-24
   15      3139.0    46532.0     3.600E-01      7.908E+01      1.397E+01      5.724E+00      8.530E-01   4-26
   16       315.0    46847.0     7.000E-02      8.699E+01      1.145E+01      1.318E+00      1.710E-01   4-30
   17       238.0    47085.0     8.100E-02      8.559E+01      1.265E+01      1.466E+00      2.050E-01   5-01
   18       358.0    47443.0     8.500E-02      8.655E+01      1.189E+01      1.325E+00      1.550E-01   5-03
   19       289.0    47732.0     6.900E-02      8.747E+01      1.119E+01      1.140E+00      1.260E-01   5-04
   20        19.0    47751.0     6.900E-02      8.767E+01      1.098E+01      1.148E+00      1.370E-01   5-06
   21      2950.0    50701.0     3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01
   22      2950.0    53651.0     3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01
   23      2950.0    56601.0     3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01
   24      2950.0    59551.0     3.000E-01      7.865E+01      1.464E+01      5.550E+00      8.600E-01

TOTAL GMS                           207.50       43720.10       11983.40        2978.90         702.20

                            VESSEL     RMIN          RMAX       VESSEL     RMIN          RMAX


                               1       0.000      3466.000       14      100.000      2800.000
                               2      -2.000      4000.000       15       50.000       150.000
                               3     300.000      4000.000       16       50.000       200.000
                               4     100.000       100.000       17       50.000      2850.000
                               5      50.000        50.000       18       50.000      2850.000
                               6      50.000        50.000       19       50.000      2850.000
                               7      20.000        20.000       20       50.000      2850.000
                               8     200.000       200.000       21       60.000        60.000
                               9      50.000      2850.000       22      100.000       100.000
                              10      50.000      2850.000       23      100.000       100.000
                              11      50.000      2800.000       24      100.000       200.000
                              12      50.000      2800.000       25        0.000      2000.000
                              13      50.000      2800.000

                               IF ANY OF THE ABOVE RMIN-S ARE EQUAL TO (-2) THEN THAT RMIN WILL
                               HAVE A DIFFERENT HEEL FOR EACH INPUT BATCH DESCRIBED BELOW

 24 BATCH     1      2      3      4      5      6      7      8      9     10     11     12     13     14     15     16
       GMS 2700.  2700.  2700.  2700.  2700.  2700.  2700.  2700.  2700.  2700.  2700.  2700.  1800.  2700.  1800.  2700.

 24 BATCH    17     18     19     20     21     22     23     24
       GMS 2700.  2700.  2700.  1800.  2250.  2250.  2250.     0.
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Table 4-14: Comparison of Predicted and Experimental Plutonium Isotopic Concentrations in 2 BP Product

OUTPUT BATCHES - C-17

Calculated Plutonium Concentrations, w/o

BATCH	MASS	MASS SUM	PU238	PU239	PU240	PU241	PU242	TIME
1	2160.0	2160.0	1.400E-01	7.172E+01	2.338E+01	3.706E+00	1.047E+00	3.0
2	2160.0	4320.0	2.565E-01	7.142E+01	2.351E+01	3.745E+00	1.065E+00	4.2
3	3510.0	7830.0	4.214E-01	7.152E+01	2.333E+01	3.680E+00	1.044E+00	6.1
4	2250.0	10080.0	5.125E-01	7.277E+01	2.241E+01	3.377E+00	9.288E-01	7.4
5	2250.0	12330.0	4.362E-01	7.328E+01	2.212E+01	3.264E+00	8.894E-01	8.6
6	2790.0	15120.0	3.125E-01	7.314E+01	2.233E+01	3.299E+00	9.159E-01	10.2
7	1980.0	17100.0	2.372E-01	7.261E+01	2.275E+01	3.416E+00	9.738E-01	11.3
8	2250.0	19350.0	1.892E-01	7.213E+01	2.312E+01	3.531E+00	1.020E+00	12.5
9	4320.0	23670.0	1.548E-01	7.211E+01	2.319E+01	3.523E+00	1.021E+00	14.9
10	3510.0	27180.0	2.104E-01	7.183E+01	2.274E+01	4.077E+00	1.142E+00	16.9
11	2880.0	30060.0	3.658E-01	7.005E+01	2.259E+01	5.480E+00	1.511E+00	18.5
12	2340.0	32400.0	5.355E-01	6.765E+01	2.296E+01	6.831E+00	2.017E+00	19.8
13	2700.0	35100.0	6.029E-01	6.668E+01	2.310E+01	7.388E+00	2.221E+00	21.3
14	3780.0	38880.0	5.564E-01	6.968E+01	2.042E+01	7.301E+00	1.867E+00	23.4
15	5400.0	44280.0	3.993E-01	7.667E+01	1.574E+01	5.910E+00	1.109E+00	26.4
16	3060.0	47340.0	3.043E-01	7.923E+01	1.451E+01	5.047E+00	8.376E-01	28.1
17	2970.0	50310.0	2.993E-01	7.897E+01	1.456E+01	5.309E+00	8.435E-01	29.7
18	3420.0	53730.0	2.997E-01	7.877E+01	1.461E+01	5.456E+00	8.536E-01	31.6
19	3690.0	57420.0	2.999E-01	7.871E+01	1.463E+01	5.507E+00	8.571E-01	33.7
20	360.0	57780.0	2.999E-01	7.870E+01	1.463E+01	5.511E+00	8.573E-01	33.9

PLANT OUTPUT DATA

BATCH	PU-GM	SUM PU-GM	-238	239	240	-241	-242	DATE
300	2196.	2196.	00.136	71.982	23.103	3.742	1.037	3-08
400	2175.	4371.	00.132	72.501	22.747	3.629	0.991	3-11
900	3539.	7910.	00.129	73.038	22.375	3.510	0.948	3-17
1100	2283.	10193.	00.125	73.233	22.263	3.458	0.921	3-21
1200	2205.	12398.	-0.000	-0.000	-0.000	-0.000	0.000	3-23
1300	2816.	15214.	00.126	72.491	22.781	3.599	1.003	3-27
1400	1964.	17178.	00.124	72.372	22.835	3.648	1.021	3-28
1500	2276.	19454.	00.126	72.523	22.743	3.597	1.011	3-30
1600	4337.	23791.	00.121	72.485	22.887	3.509	0.999	4-05
1700	3465.	27256.	00.121	72.477	22.920	3.493	0.989	4-09
1800	2881.	30137.	00.379	69.969	22.522	5.596	1.532	4-15
1900	2351.	32488.	00.497	68.699	22.488	6.519	1.797	4-16
2000	2657.	35145.	00.653	66.681	22.987	7.472	2.207	4-22
2100	3786.	38930.	00.701	66.146	23.146	7.667	2.340	4-27
3100	5416.	44346.	00.460	75.098	16.617	6.575	1.250	5-10
3200	3028.	47374.	00.372	77.863	15.167	5.622	0.976	5-13
3900	2955.	50329.	00.329	78.473	14.892	5.492	0.877	6-06
4000	3428.	53757.	00.328	78.468	14.936	5.380	0.888	6-07
4100	3718.	57475.	00.329	78.454	14.931	5.405	0.881	6-08
4400	1289.	58764.	00.296	78.884	15.295	4.676	0.849	6-20
4500	730.	59494.	-0.000	-0.000	-0.000	-0.000	-0.000	6-22
4600	41.	59535.	00.298	78.636	15.443	4.757	0.866	6-22
4700	374.	59909.	-0.000	-0.000	-0.000	-0.000	-0.000	6-23

Table 4-15: PLUTONIUM INPUT DATA FOR MOL III SIMULATION WITH SUPERBATCHES

FLOW RATE= 1.800E+03 GM/DAY

TIME STEP= 5.000E-02 DAY

MAX. TIME= 4.000E+01 DAY

RECOVERY FACTOR= 00.955

BATCH		MASS	MASS SUM	PU238	PU239	PU240	PU241	PU242	DATE
				CONCENTRATIONS-PER CENT					
1	CANDU-A	3543.0	3543.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	2-10
2		3500.0	7043.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	2-13
3		3510.0	10553.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	2-15
4		2887.0	13442.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	3-03
5		3177.0	16617.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	3-06
6	CANDU-B	3373.0	19992.0	1.270E-01	7.191E+01	2.325E+01	3.651E+00	1.060E+00	3-10
7		3337.0	23329.0	1.270E-01	7.191E+01	2.325E+01	3.651E+00	1.060E+00	3-20
8		3177.0	26506.0	1.270E-01	7.191E+01	2.325E+01	3.651E+00	1.060E+00	3-23
9		3397.0	29903.0	1.270E-01	7.191E+01	2.325E+01	3.651E+00	1.060E+00	3-26
10	VAK	2981.0	32884.0	6.580E-01	6.645E+01	2.275E+01	7.930E+00	2.211E+00	3-31
11		2142.0	35026.0	6.580E-01	6.645E+01	2.275E+01	7.930E+00	2.211E+00	4-06
12		4067.0	39093.0	6.580E-01	6.645E+01	2.275E+01	7.930E+00	2.211E+00	4-12
13		741.0	39834.0	6.580E-01	6.645E+01	2.275E+01	7.930E+00	2.211E+00	4-16
14	TRINO	3559.0	43393.0	4.030E-01	7.695E+01	1.495E+01	6.596E+00	1.106E+00	4-24
15		3139.0	46532.0	4.030E-01	7.695E+01	1.495E+01	6.596E+00	1.106E+00	4-26
16	CdN	315.0	46847.0	7.600E-02	8.662E+01	1.180E+01	1.345E+00	1.630E-01	4-30
17		238.0	47085.0	7.600E-02	8.662E+01	1.180E+01	1.345E+00	1.630E-01	5-01
18		358.0	47443.0	7.600E-02	8.662E+01	1.180E+01	1.345E+00	1.630E-01	5-03
19		289.0	47732.0	7.600E-02	8.662E+01	1.180E+01	1.345E+00	1.630E-01	5-04
20		19.0	47751.0	7.600E-02	8.662E+01	1.180E+01	1.345E+00	1.630E-01	5-06
21	Inv.	2950.0	50701.0	3.000E-01	7.865E+01	1.464E+01	5.550E+00	8.600E-01	
22		2950.0	53651.0	3.000E-01	7.865E+01	1.464E+01	5.550E+00	8.600E-01	
23		2950.0	56601.0	3.000E-01	7.865E+01	1.464E+01	5.550E+00	8.600E-01	
24		2950.0	59551.0	3.000E-01	7.865E+01	1.464E+01	5.550E+00	8.600E-01	
TOTAL GMS				207.50	43720.10	11983.40	2978.90	702.20	

VESSEL	RMIN	RMAX	VESSEL	RMIN	RMAX
1	0.000	3466.000	14	100.000	2800.000
2	-2.000	4000.000	15	50.000	150.000
3	50.000	4000.000	16	50.000	200.000
4	100.000	100.000	17	50.000	2850.000
5	50.000	50.000	18	50.000	2850.000
6	50.000	50.000	19	50.000	2850.000
7	20.000	20.000	20	50.000	2850.000
8	200.000	200.000	21	60.000	60.000
9	50.000	2850.000	22	100.000	100.000
10	50.000	2850.000	23	100.000	100.000
11	50.000	2800.000	24	100.000	200.000
12	50.000	2800.000	25	0.000	2000.000
13	50.000	2800.000			

IF ANY OF THE ABOVE RMIN-S ARE EQUAL TO (-2) THEN THAT RMIN WILL HAVE A DIFFERENT HEEL FOR EACH INPUT BATCH DESCRIBED BELOW

BATCH	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
GMS	2250.	2250.	2250.	2250.	180.	2250.	2250.	2250.	270.	2700.	2700.	2700.	180.	2700.	900.	2250.

BATCH	17	18	19	20	21	22	23	24
GMS	2250.	2250.	2250.	900.	2250.	2250.	2250.	0.

Table 4-16: CALCULATED MOL III PLUTONIUM OUTPUT CONCENTRATIONS WITH SUPERBATCHES

OUTPUT BATCHES - C-25

BATCH	MASS	MASS SUM	PU238	PU239	PU240	PU241	PU242	TIME
1	1710.0	1710.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	4.5
2	1440.0	3150.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	5.3
3	1170.0	4320.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	5.9
4	1890.0	6210.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	7.0
5	1620.0	7830.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	7.9
6	1620.0	9450.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	8.8
7	1620.0	11070.0	3.710E-01	7.250E+01	2.259E+01	3.560E+00	9.860E-01	9.7
8	1620.0	12690.0	3.695E-01	7.249E+01	2.259E+01	3.561E+00	9.865E-01	10.6
9	1530.0	14220.0	3.598E-01	7.247E+01	2.262E+01	3.564E+00	9.894E-01	11.4
10	1710.0	15930.0	3.189E-01	7.237E+01	2.273E+01	3.579E+00	1.002E+00	12.4
11	1800.0	17730.0	2.373E-01	7.218E+01	2.295E+01	3.610E+00	1.027E+00	13.4
12	1620.0	19350.0	1.695E-01	7.202E+01	2.313E+01	3.635E+00	1.047E+00	14.3
13	1530.0	20880.0	1.396E-01	7.194E+01	2.321E+01	3.646E+00	1.056E+00	15.1
14	1530.0	22410.0	1.344E-01	7.193E+01	2.323E+01	3.648E+00	1.058E+00	16.0
15	1620.0	24030.0	1.295E-01	7.192E+01	2.324E+01	3.650E+00	1.059E+00	16.9
16	1530.0	25560.0	1.317E-01	7.189E+01	2.324E+01	3.673E+00	1.065E+00	17.7
17	900.0	26460.0	1.374E-01	7.182E+01	2.324E+01	3.726E+00	1.080E+00	18.2
18	1710.0	28170.0	1.819E-01	7.136E+01	2.319E+01	4.085E+00	1.177E+00	19.2
19	1440.0	29610.0	3.984E-01	6.913E+01	2.299E+01	5.834E+00	1.647E+00	20.0
20	1350.0	30960.0	4.455E-01	6.864E+01	2.295E+01	6.214E+00	1.749E+00	20.7
21	1530.0	32490.0	5.988E-01	6.706E+01	2.281E+01	7.452E+00	2.082E+00	21.6
22	1620.0	34110.0	6.174E-01	6.688E+01	2.278E+01	7.604E+00	2.122E+00	22.5
23	1710.0	35820.0	6.414E-01	6.666E+01	2.273E+01	7.800E+00	2.172E+00	23.4
24	1710.0	37530.0	6.162E-01	6.787E+01	2.178E+01	7.684E+00	2.051E+00	24.4
25	1620.0	39150.0	5.929E-01	6.890E+01	2.099E+01	7.568E+00	1.945E+00	25.3
26	1260.0	40410.0	4.562E-01	7.469E+01	1.665E+01	6.863E+00	1.342E+00	26.0
27	1350.0	41760.0	4.466E-01	7.509E+01	1.636E+01	6.808E+00	1.300E+00	26.7
28	1800.0	43560.0	3.985E-01	7.690E+01	1.520E+01	6.387E+00	1.113E+00	27.7
29	1350.0	44910.0	3.722E-01	7.767E+01	1.488E+01	6.040E+00	1.033E+00	28.5
30	1440.0	46350.0	2.919E-01	7.988E+01	1.411E+01	4.913E+00	8.024E-01	29.3
31	1350.0	47700.0	2.900E-01	7.980E+01	1.415E+01	4.959E+00	8.018E-01	30.0
32	1530.0	49230.0	2.904E-01	7.928E+01	1.439E+01	5.226E+00	8.203E-01	30.9
33	1530.0	50760.0	2.923E-01	7.913E+01	1.445E+01	5.300E+00	8.288E-01	31.7
34	1080.0	51840.0	2.958E-01	7.889E+01	1.454E+01	5.425E+00	8.437E-01	32.3
35	1170.0	53010.0	2.960E-01	7.888E+01	1.455E+01	5.431E+00	8.445E-01	33.0
36	900.0	53910.0	2.979E-01	7.877E+01	1.459E+01	5.489E+00	8.520E-01	33.5
37	990.0	54900.0	2.982E-01	7.875E+01	1.460E+01	5.497E+00	8.530E-01	34.0
38	540.0	55440.0	2.982E-01	7.875E+01	1.460E+01	5.497E+00	8.530E-01	34.3
39	1350.0	56790.0	2.986E-01	7.873E+01	1.461E+01	5.510E+00	8.548E-01	35.1
40	1080.0	57870.0	2.988E-01	7.872E+01	1.461E+01	5.516E+00	8.555E-01	35.7

Table 4-17: CALCULATED DISTRIBUTION OF CANDU, VAK, AND TRINO FUEL IN PLUTONIUM OUTPUT BATCHES WITH SUPERBATCHING

Calc. Output Batch	Corresp. Actual Batch	Pu-241, w/o (x)	X-Cn[a]	% in Product Batch					Pu, gms					
				Candu A C_1	Candu B C_2	Candu, total	VAK C_3	TRINO C_4	C_1	C_2	C_3	C_4	Batch	Σ gm
1	118	3.560	0.0	100.0		100.0			1710				1710	1710
2	143	3.560	0.0	100.0		100.0			1440				1440	3150
3	121	3.560	0.0	100.0		100.0			1170				1170	4320
4	122	3.560	0.0	100.0		100.0			1890				1890	6210
5	124	3.560	0.0	100.0		100.0			1620				1620	7830
6	123	3.560	0.0	100.0		100.0			1620				1620	9450
7	126	3.560	0.0	100.0		100.0			1620				1620	11070
8	125	3.561	0.001	98.9	1.1	100.0			1602	18			1620	12690
9	131	3.564	0.003	96.7	3.3	100.0			1480	50			1530	14220
10	132	3.579	0.019	79.1	20.9	100.0			1352	358			1710	15930
11	134	3.610	0.050	45.0	55.0	100.0			810	990			1800	17730
12	135	3.635	0.075	17.6	82.4	100.0			282	1338			1620	19350
13	136	3.646	0.086	5.5	94.5	100.0			84	1446			1530	20880
14	127	3.648	0.088	3.3	96.7	100.0			50	1480			1530	22410
15	128	3.650	0.090	1.1	98.9	100.0			18	1602			1620	24030
16	129	3.673	0.022	~0.0	99.5	99.5	0.5			1520	10		1530	25560
17	130	3.726	0.075		98.2	98.2	1.8			873	17		900	26460
18	133	4.085	0.434		79.8	79.8	20.2			1365	345		1710	28170
19	138	5.834	2.183		49.0	49.0	51.0			705	735		1440	29610
20	139	6.214	2.563		40.0	40.0	60.0			540	810		1350	30960
21	140	7.452	3.801		11.0	11.0	89.0			168	1362		1530	37490
22	141	7.604	3.953		7.5	7.5	92.5			120	1500		1620	34110
23	142	7.800	4.149		3.0	3.0	97.0			51	1659		1710	35820
24	145	7.684	3 component		1.8	1.8	85.6	12.6		31	1464	215	1710	37530
25	146	7.568			1.4	1.4	76.0	22.6		23	1231	366	1620	39150
26	147	6.863			-		21.6	78.4			269	981	1260	40410

Notes:

(a) $C_1 - C_2 = 0.091$; $C_2 - C_3 = 4.277$

Table 4-18: PLUTONIUM INPUT DATA FOR MOL II SIMULATION

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INPUT DATAEUROCHEMIC PLANT MODEL - MOL II

FLOW RATE= 1.800E+03  GM/DAY

TIME STEP= 5.000E-02  DAY

MAX. TIME= 4.500E+01  DAY

RECOVERY FACTOR=  1.017

                                                        CONCENTRATIONS-PER CENT

  BATCH        MASS       MASS SUM          PU238            PU239            PU240            PU241            PU242

  100         5637.0       5637.0         4.630E-01        7.493E+01        1.587E+01        7.555E+00        1.185E+00
  200         5572.0      11209.0         4.050E-01        7.515E+01        1.582E+01        7.443E+00        1.175E+00
  300         5560.0      16769.0         4.370E-01        7.508E+01        1.577E+01        7.508E+00        1.201E+00
  500         5675.0      22444.0         3.920E-01        7.506E+01        1.586E+01        7.487E+00        1.191E+00
  400         5664.0      28108.0         4.530E-01        7.542E+01        1.564E+01        7.339E+00        1.145E+00
  600         5900.0      34008.0         3.740E-01        7.526E+01        1.589E+01        7.323E+00        1.149E+00
  700         5400.0      39408.0         4.350E-01        7.726E+01        1.453E+01        6.820E+00        9.500E-01
  800         5426.0      44834.0         3.590E-01        7.712E+01        1.463E+01        6.924E+00        9.690E-01
  900         3688.0      48522.0         4.200E-01        7.667E+01        1.483E+01        7.049E+00        1.024E+00
 1000         5070.0      53592.0         3.600E-01        7.761E+01        1.454E+01        6.540E+00        9.440E-01
 1100         4771.0      58363.0         3.700E-01        7.768E+01        1.446E+01        6.530E+00        9.610E-01
 1200         5509.0      63872.0         3.660E-01        7.550E+01        1.570E+01        7.290E+00        1.145E+00
 1300         5482.0      69354.0         3.970E-01        7.523E+01        1.581E+01        7.406E+00        1.162E+00
 1400         3743.0      73097.0         4.380E-01        7.506E+01        1.588E+01        7.460E+00        1.162E+00

 TOTAL GMS                                  207.50         43720.10         11983.40          2978.90           702.20


                              VESSEL    RMIN         RMAX       VESSEL    RMIN          RMAX

                                 1       0.000     3466.000       14     100.000      2800.000
                                 2      -2.000     4000.000       15      50.000       150.000
                                 3      50.000     4000.000       16      50.000       200.000
                                 4     100.000      100.000       17      50.000      2850.000
                                 5      50.000       50.000       18      50.000      2850.000
                                 6      50.000       50.000       19      50.000      2850.000
                                 7      20.000       20.000       20      50.000      2850.000
                                 8     200.000      200.000       21      60.000        60.000
                                 9      50.000     2850.000       22     100.000       100.000
                                10      50.000     2850.000       23     100.000       100.000
                                11      50.000     2800.000       24     100.000       200.000
                                12      50.000     2800.000       25       0.000      2000.000
                                13      50.000     2800.000

                                 IF ANY OF THE ABOVE RMIN-S ARE EQUAL TO (-2) THEN THAT RMIN WILL
                                 HAVE A DIFFERENT HEEL FOR EACH INPUT BATCH DESCRIBED BELOW

BATCH      1      2      3      4      5      6      7      8      9     10     11     12     13     14
  GMS  2250.  2250.  2250.  2250.  2250.   900.  2250.  2250.  2250.  2250.   900.  2250.  2250.     0.
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Table 4-19: CALCULATED MOL.II PLUTONIUM OUTPUT CONCENTRATIONS

OUTPUT BATCHES - C-25

BATCH	MASS	MASS SUM	PU238	PU239	PU240	PU241	PU242	TIME
1	1350.0	1350.0	4.621E-01	7.494E+01	1.587E+01	7.553E+00	1.185E+00	4.3
2	1710.0	3060.0	4.582E-01	7.495E+01	1.586E+01	7.546E+00	1.184E+00	5.2
3	1620.0	4680.0	4.391E-01	7.502E+01	1.585E+01	7.509E+00	1.181E+00	6.1
4	1530.0	6210.0	4.331E-01	7.505E+01	1.584E+01	7.497E+00	1.180E+00	7.0
5	1710.0	7920.0	4.249E-01	7.508E+01	1.584E+01	7.481E+00	1.179E+00	7.9
6	1530.0	9450.0	4.272E-01	7.508E+01	1.582E+01	7.487E+00	1.185E+00	8.8
7	1530.0	10980.0	4.282E-01	7.508E+01	1.581E+01	7.489E+00	1.187E+00	9.6
8	1620.0	12600.0	4.308E-01	7.508E+01	1.579E+01	7.496E+00	1.192E+00	10.5
9	1440.0	14040.0	4.298E-01	7.508E+01	1.579E+01	7.496E+00	1.193E+00	11.3
10	1350.0	15390.0	4.175E-01	7.507E+01	1.582E+01	7.494E+00	1.193E+00	12.1
11	1350.0	16740.0	4.162E-01	7.507E+01	1.582E+01	7.494E+00	1.193E+00	12.8
12	1350.0	18090.0	4.072E-01	7.507E+01	1.583E+01	7.490E+00	1.192E+00	13.6
13	1620.0	19710.0	4.082E-01	7.509E+01	1.583E+01	7.483E+00	1.190E+00	14.5
14	1710.0	21420.0	4.198E-01	7.518E+01	1.578E+01	7.441E+00	1.177E+00	15.4
15	1530.0	22950.0	4.261E-01	7.523E+01	1.575E+01	7.421E+00	1.170E+00	16.3
16	1620.0	24570.0	4.348E-01	7.529E+01	1.571E+01	7.392E+00	1.162E+00	17.2
17	1530.0	26100.0	4.255E-01	7.530E+01	1.574E+01	7.376E+00	1.158E+00	18.0
18	1890.0	27990.0	4.185E-01	7.530E+01	1.576E+01	7.365E+00	1.156E+00	19.1
19	1980.0	29970.0	3.980E-01	7.528E+01	1.582E+01	7.345E+00	1.152E+00	20.2
20	1530.0	31500.0	3.953E-01	7.530E+01	1.581E+01	7.337E+00	1.150E+00	21.0
21	1710.0	33210.0	3.935E-01	7.532E+01	1.581E+01	7.330E+00	1.148E+00	22.0
22	1350.0	34560.0	4.113E-01	7.618E+01	1.525E+01	7.105E+00	1.060E+00	22.7
23	1710.0	36270.0	4.158E-01	7.643E+01	1.508E+01	7.040E+00	1.035E+00	23.7
24	1710.0	37980.0	4.139E-01	7.688E+01	1.479E+01	6.932E+00	9.898E-01	24.6
25	1980.0	39960.0	4.015E-01	7.697E+01	1.472E+01	6.921E+00	9.812E-01	25.7
26	1530.0	41490.0	3.865E-01	7.705E+01	1.467E+01	6.916E+00	9.742E-01	26.6
27	1710.0	43200.0	3.868E-01	7.702E+01	1.468E+01	6.932E+00	9.791E-01	27.5
28	1800.0	45000.0	3.894E-01	7.698E+01	1.470E+01	6.945E+00	9.841E-01	28.5
29	1170.0	46170.0	4.000E-01	7.688E+01	1.474E+01	6.977E+00	9.982E-01	29.2
30	1260.0	47430.0	3.989E-01	7.690E+01	1.474E+01	6.963E+00	9.967E-01	29.9
31	1620.0	49050.0	3.818E-01	7.723E+01	1.465E+01	6.767E+00	9.734E-01	30.8
32	1440.0	50490.0	3.794E-01	7.727E+01	1.464E+01	6.740E+00	9.703E-01	31.6
33	1350.0	51840.0	3.746E-01	7.737E+01	1.461E+01	6.694E+00	9.640E-01	32.3
34	1530.0	53370.0	3.739E-01	7.741E+01	1.459E+01	6.662E+00	9.633E-01	33.2
35	1350.0	54720.0	3.718E-01	7.754E+01	1.453E+01	6.599E+00	9.618E-01	33.9
36	1440.0	56160.0	3.716E-01	7.754E+01	1.453E+01	6.597E+00	9.627E-01	34.7
37	1170.0	57330.0	3.711E-01	7.753E+01	1.453E+01	6.595E+00	9.652E-01	35.4
38	1170.0	58500.0	3.710E-01	7.749E+01	1.456E+01	6.609E+00	9.688E-01	36.0
39	990.0	59490.0	3.687E-01	7.652E+01	1.511E+01	6.942E+00	1.055E+00	36.6
40	990.0	60480.0	3.683E-01	7.635E+01	1.521E+01	6.998E+00	1.070E+00	37.1
41	1170.0	61650.0	3.693E-01	7.621E+01	1.529E+01	7.047E+00	1.082E+00	37.8
42	900.0	62550.0	3.724E-01	7.580E+01	1.552E+01	7.192E+00	1.117E+00	38.3
43	11520.0	74070.0	3.977E-01	7.538E+01	1.573E+01	7.345E+00	1.147E+00	44.7

Table 4-20: PLUTONIUM OUTPUT DATA FOR MOL II

				Plutonium concentrations, percent					
	BATCH	PU-GM	SUM PU-GM	-238	239	240	-241	-242	A
1	76	1335.	1335.	00.408	75.865	15.679	6.956	1.092	
2	77	1685.	3020.	00.435	75.580	15.809	7.039	1.137	
3	78	1645.	4665.	00.435	75.501	15.828	7.092	1.145	
4	79	1522.	6187.	00.439	75.496	15.826	7.089	1.150	
5	73	1743.	7930.	00.421	75.661	15.726	7.068	1.124	
6	74	1502.	9432.	00.425	75.638	15.764	7.034	1.139	
7	75	1486.	10918.	00.406	75.712	15.715	7.035	1.132	
8	80	1581.	12499.	00.419	75.552	15.773	7.128	1.128	
9	81	1465.	13964.	00.410	75.761	15.696	6.943	1.190	
10	82	1392.	15356.	00.412	75.714	15.763	6.995	1.116	
11	83	1313.	16669.	00.414	75.740	15.645	7.078	1.123	
12	84	1385.	18054.	00.420	75.828	15.690	6.955	1.107	
13	85	1649.	19703.	00.420	75.825	15.705	6.940	1.110	
14	86	1668.	21371.	00.411	75.758	15.676	7.058	1.097	
15	87	1548.	22919.	00.404	75.924	15.697	6.884	1.091	
16	88	1605.	24524.	00.410	76.380	15.334	6.841	1.030	
17	89	1543.	26067.	00.405	76.809	15.023	6.782	00.981	
18	90	1904.	27971.	00.404	77.022	15.013	6.581	00.980	
19	92	2016.	29987.	00.399	77.107	14.941	6.579	00.974	
20	93	1551.	31538.	00.403	77.004	15.006	6.597	00.990	
21	94	1721.	33259.	00.395	77.065	14.959	6.609	00.972	
22	95	1362.	34621.	00.407	77.029	14.955	6.642	00.967	
23	96	1667.	36298.	00.404	77.075	14.959	6.590	00.973	
24	97	1665.	37953.	00.402	77.213	14.863	6.555	00.967	
25	98	1991.	39944.	00.396	77.276	14.831	6.514	00.983	
26	99	1503.	41447.	00.396	77.314	14.809	6.504	00.977	
27	100	1703.	43150.	00.391	77.352	14.780	6.491	00.986	
28	101	1775.	44925.	00.394	77.282	14.859	6.504	00.961	
29	102	1141.	46066.	00.392	77.159	14.912	6.548	00.989	
30	103	1245.	47311.	00.393	77.190	14.908	6.524	00.985	
31	104	1657.	48968.	00.386	77.043	14.897	6.704	00.970	
32	105	1421.	50389.	00.409	76.399	15.329	6.805	1.058	
33	106	1368.	51757.	00.412	76.133	15.424	6.948	1.083	
34	107	1520.	53277.	00.421	76.173	15.419	6.905	1.082	
35	108	1380.	54657.	00.419	76.068	15.491	6.937	1.085	
36	109	1435.	56092.	00.420	75.920	15.521	7.044	1.095	
37	110	1158.	57250.	00.421	75.878	15.583	7.008	1.110	
38	111	1176.	58426.	00.420	75.925	15.565	6.986	1.104	
39	112	1014.	59440.	00.426	75.819	15.586	7.055	1.114	
40	113	971.	60411.	00.422	75.888	15.572	7.009	1.109	
41	114	1206.	61617.	00.426	75.876	15.593	7.025	1.104	
42	115	898.	62515.	00.420	76.117	15.471	6.909	1.083	
43	116	11800.	74315.	00.300	78.650	14.640	5.550	00.862	
	TOTAL GMS			165.3	41769.0	11471.0	2820.7	672.6	

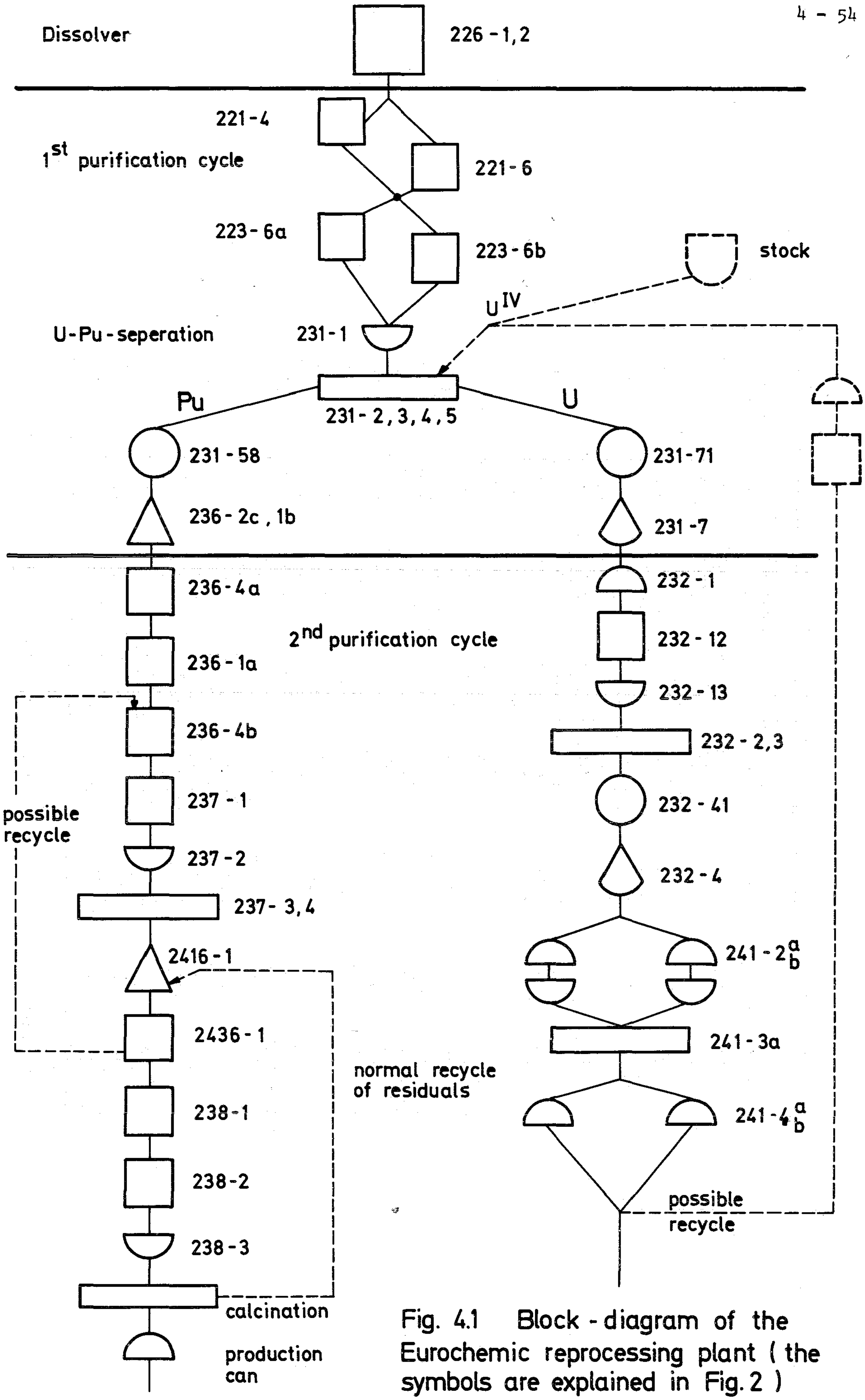
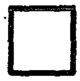
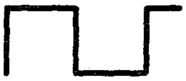
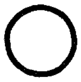
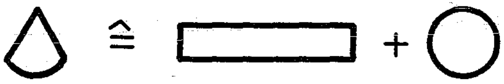


Fig. 4.1 Block - diagram of the Eurochemic reprocessing plant (the symbols are explained in Fig. 2)

symbol	equation type	flow characteristic	name
	$c_i^n = \frac{M_{i-1} c_{i-1}^n + R_i c_i^{n-1}}{M_{i-1} + R_i}$		tank
			alimentation tank
	$\frac{dc_i}{dt} = \frac{k}{R_i} (c_{i-1} - c_i)$		buffer tank
	$c_i^n = \frac{k \int c_{i-1}^n dt + R_i c_i^{n-1}}{k T_i + R_i}$		discontinuous evaporator
			receiving tank
	$c_i = c_{i-1} \cdot a$		columns and mixer - settlers
			continuous evaporator

Nomenclature for the equations:

c_i^n = Relative concentration of the tracer isotope in batch n at the output of unit i

M_{i-1} = Mass of Pu - or U - input into unit i

R_i = Residual mass in unit i

t = Time

k = Mean flow rate [mass / unit time]

T_i = Filling time of unit i

a = Constant concentration ratio

Fig. 4.2 Description of the main units of the Eurochemic reprocessing plant

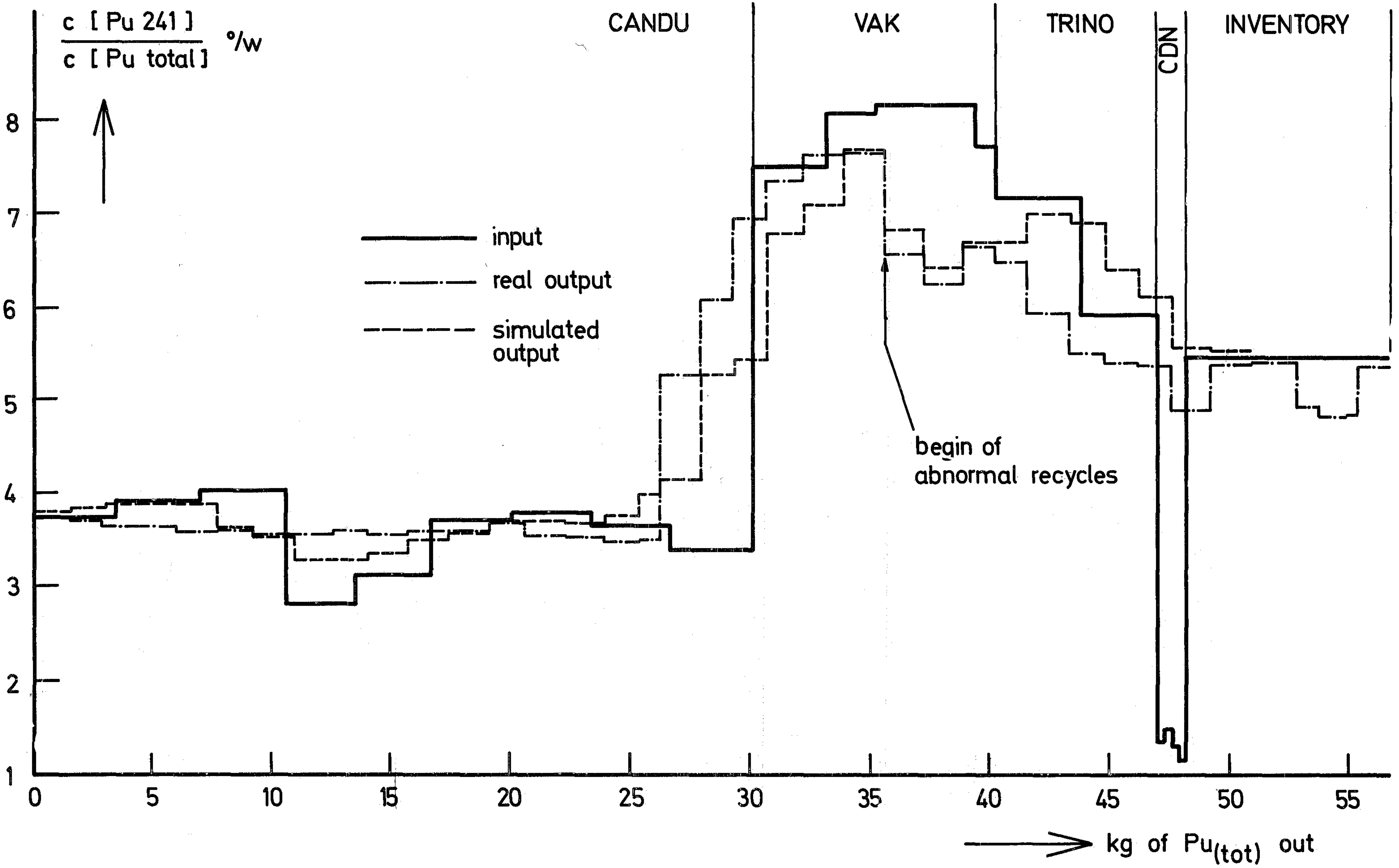


Fig. 4.3 Comparison between Experimental (Mol III) and Simulation Results for Pu

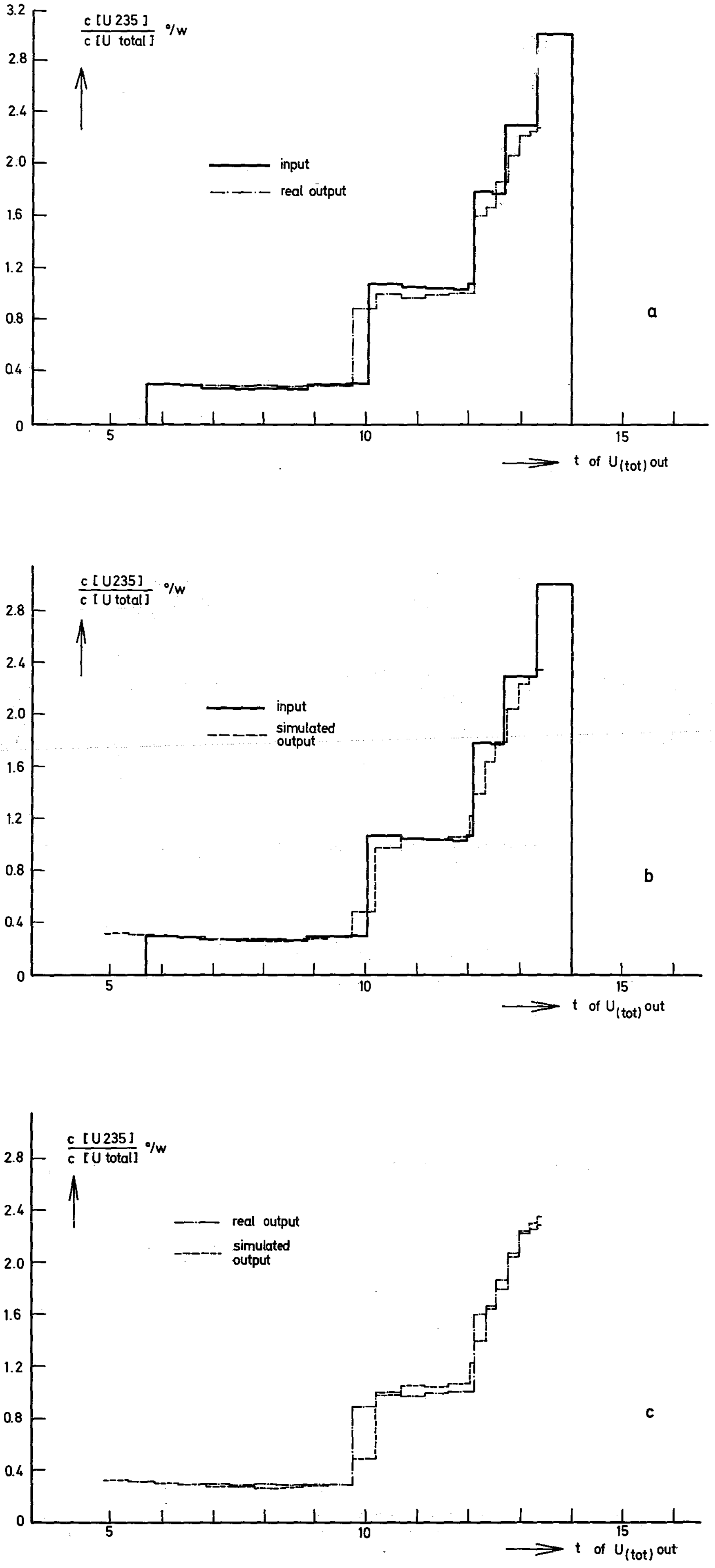


Fig. 4.4 Comparison between Experimental (Mol III) and Simulated Results for U

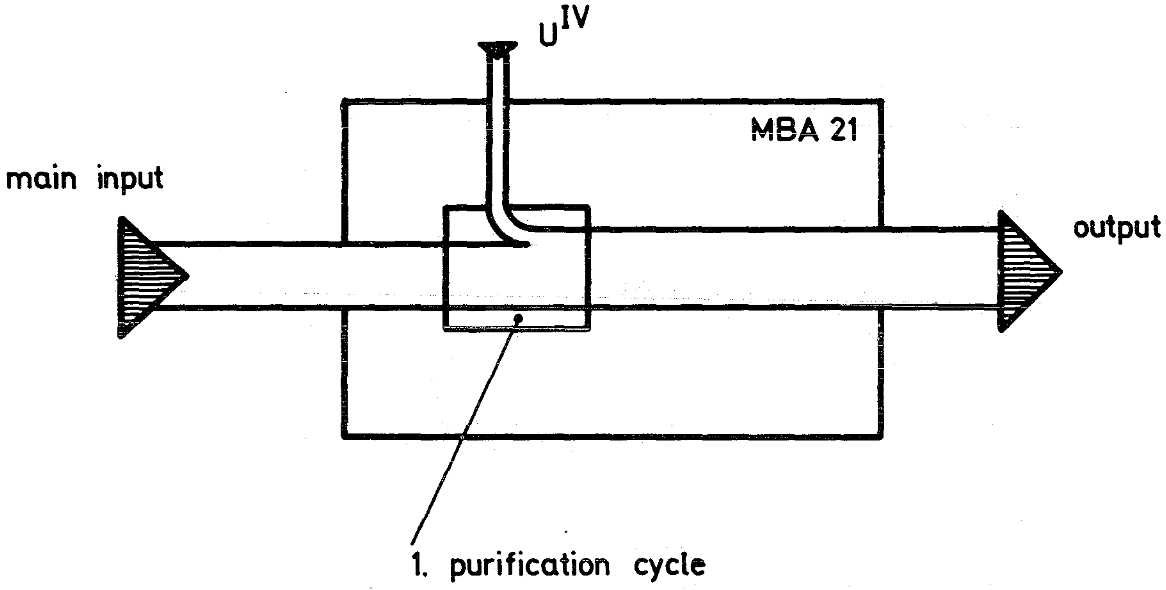


Fig. 4.5 Main U streams

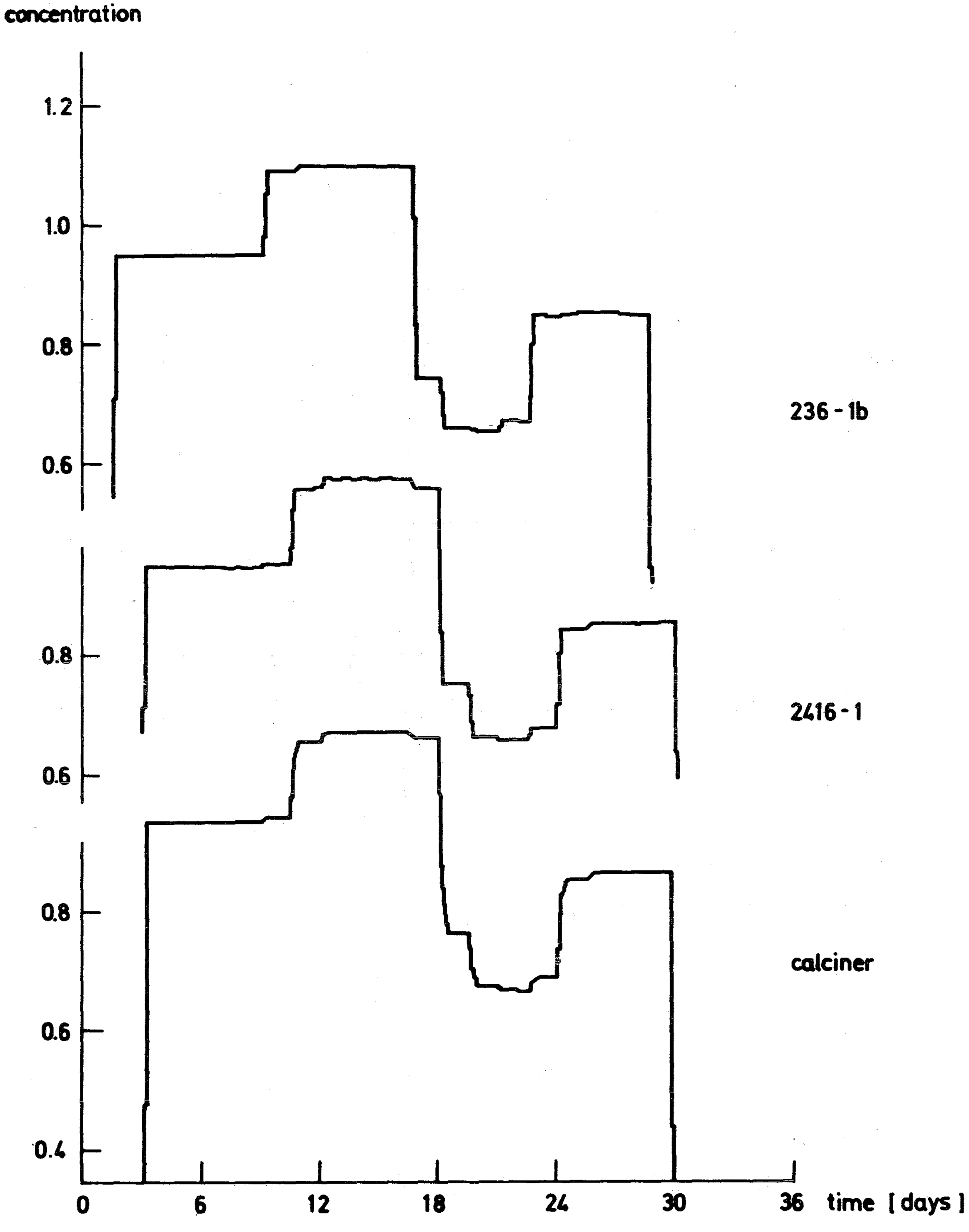


Fig. 4.6 Calculated Pu - 242 concentrations at various process points - simulated Mol III campaign

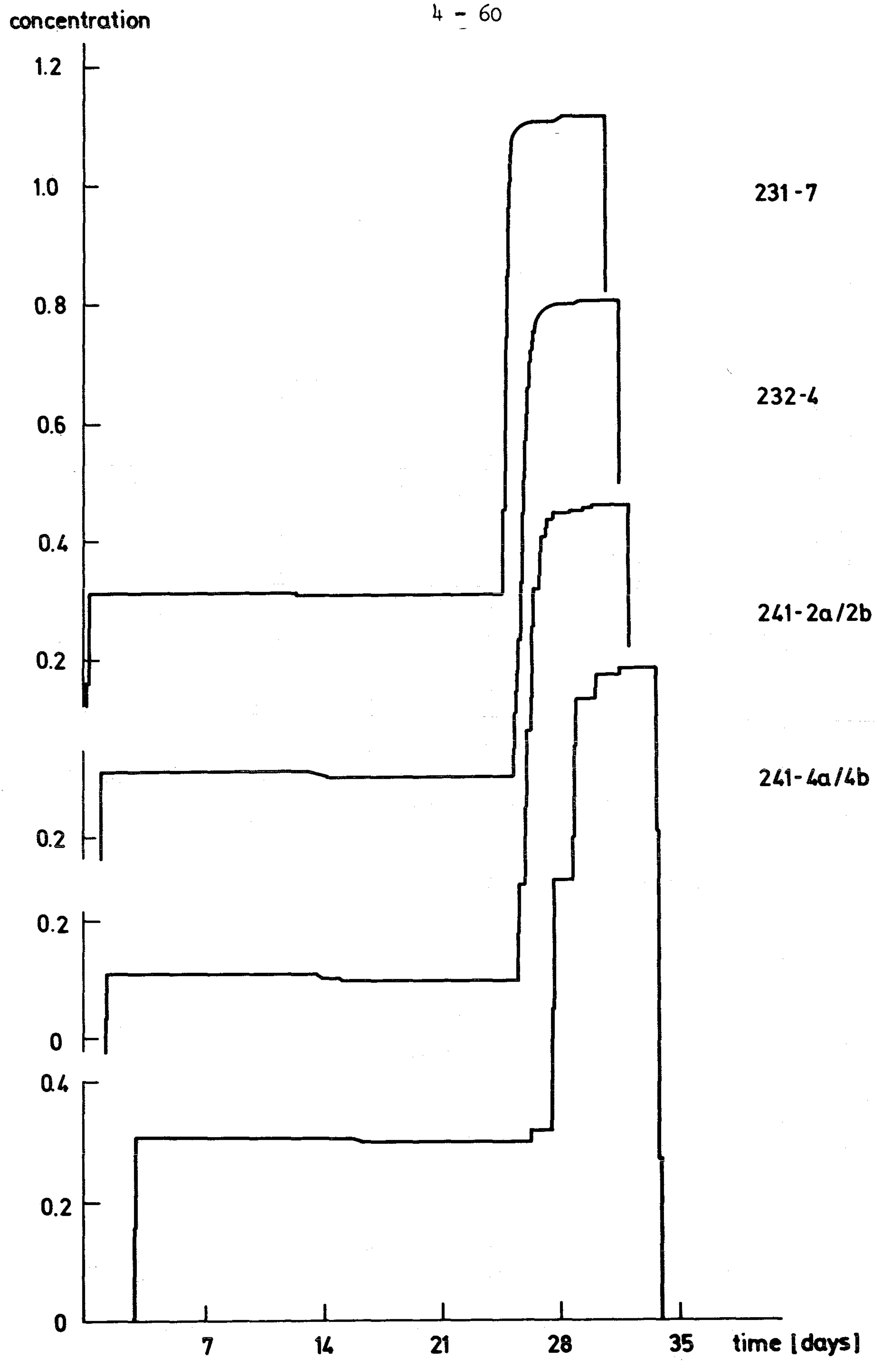


Fig. 4.7 Calculated U 235 concentrations at various process points - simulated Mol III campaign

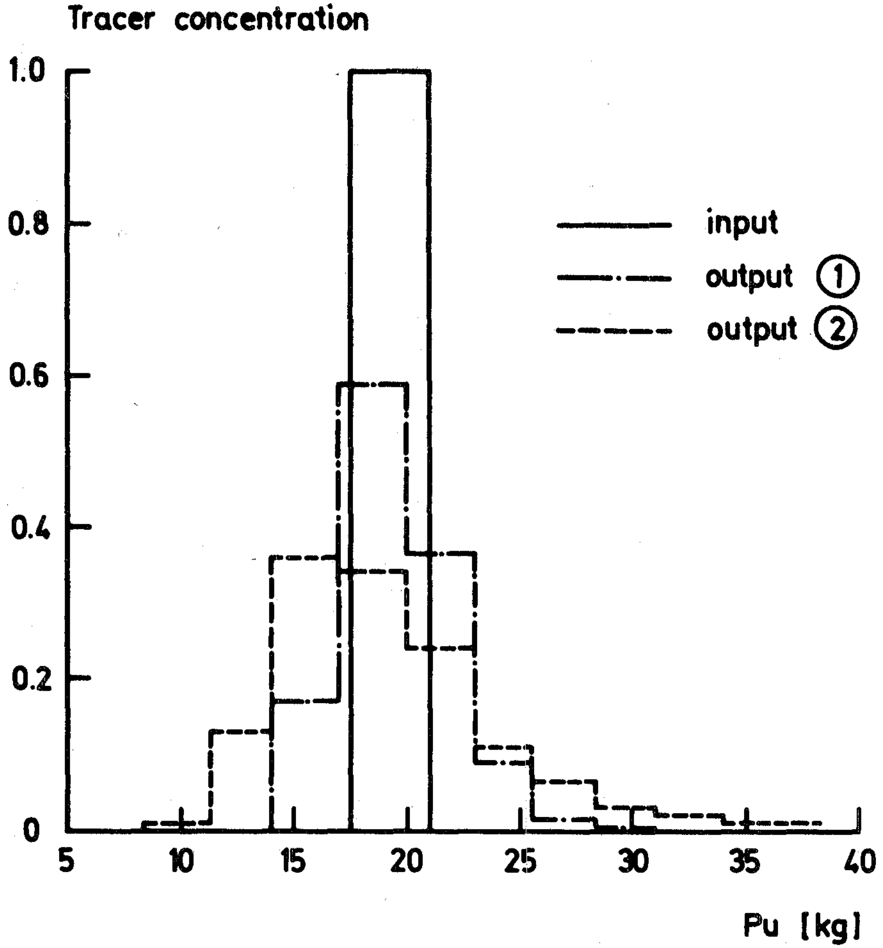


Fig. 4.8a Pu response function

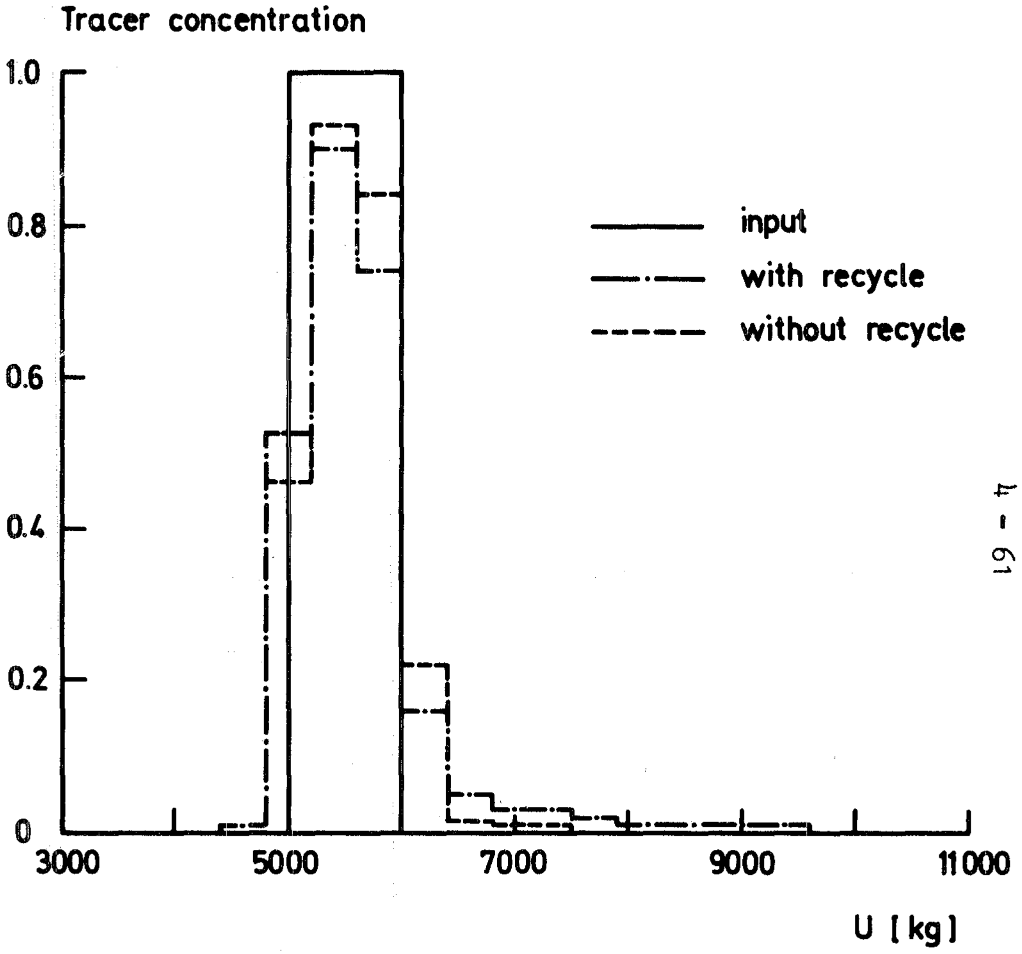


Fig. 4.8b U response function

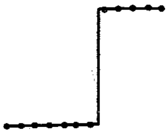
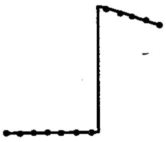
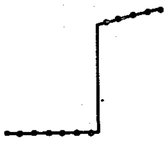
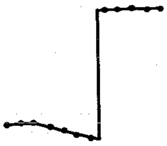
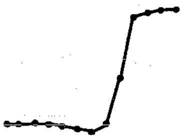
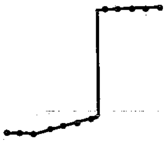
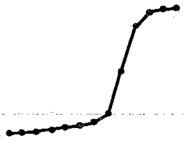
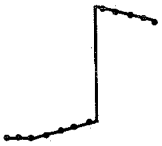
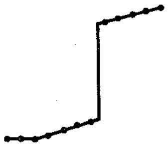
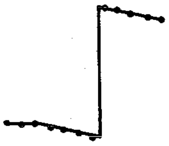
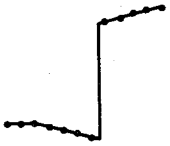
Case	Input	Output	$H-I_r$ (g)	$(H-I_r)/I_r$ (%)
1			-11	-0.08
2			-200	-1.25
3			+251	+1.57
4			+95	+0.60
5			-135	-0.84
6			-318	-1.98
7			-144	-0.90
8			+127	+0.79
9			+375	+2.35
10			+42	+0.30

Fig. 4.9 Dependence of $H-I_r$ on the variation of the input concentration and deformation of the step

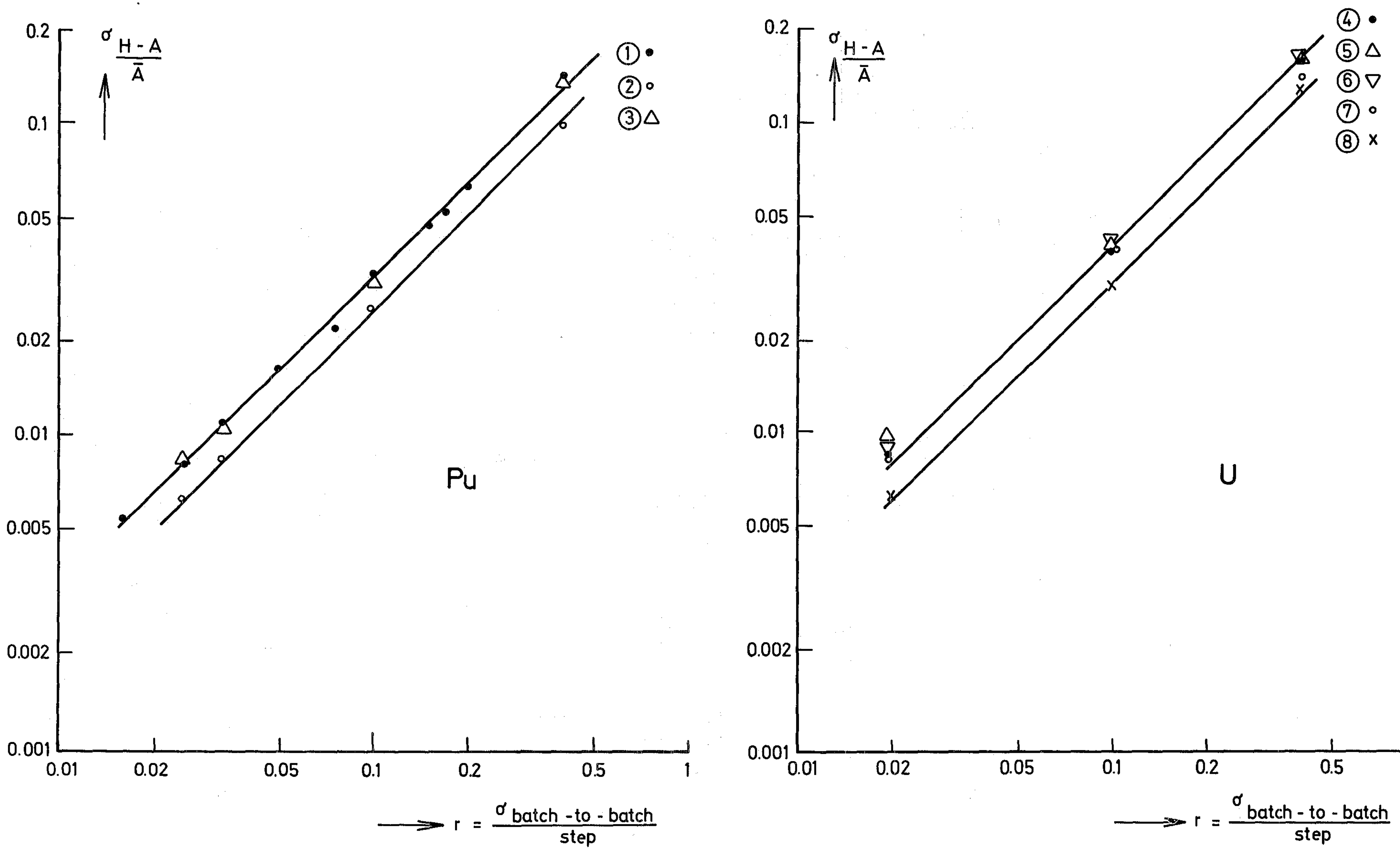


Fig. 4.10 Correlations between input characteristics and the precision of the PI determination for Pu and U (parameters in table 4-5)

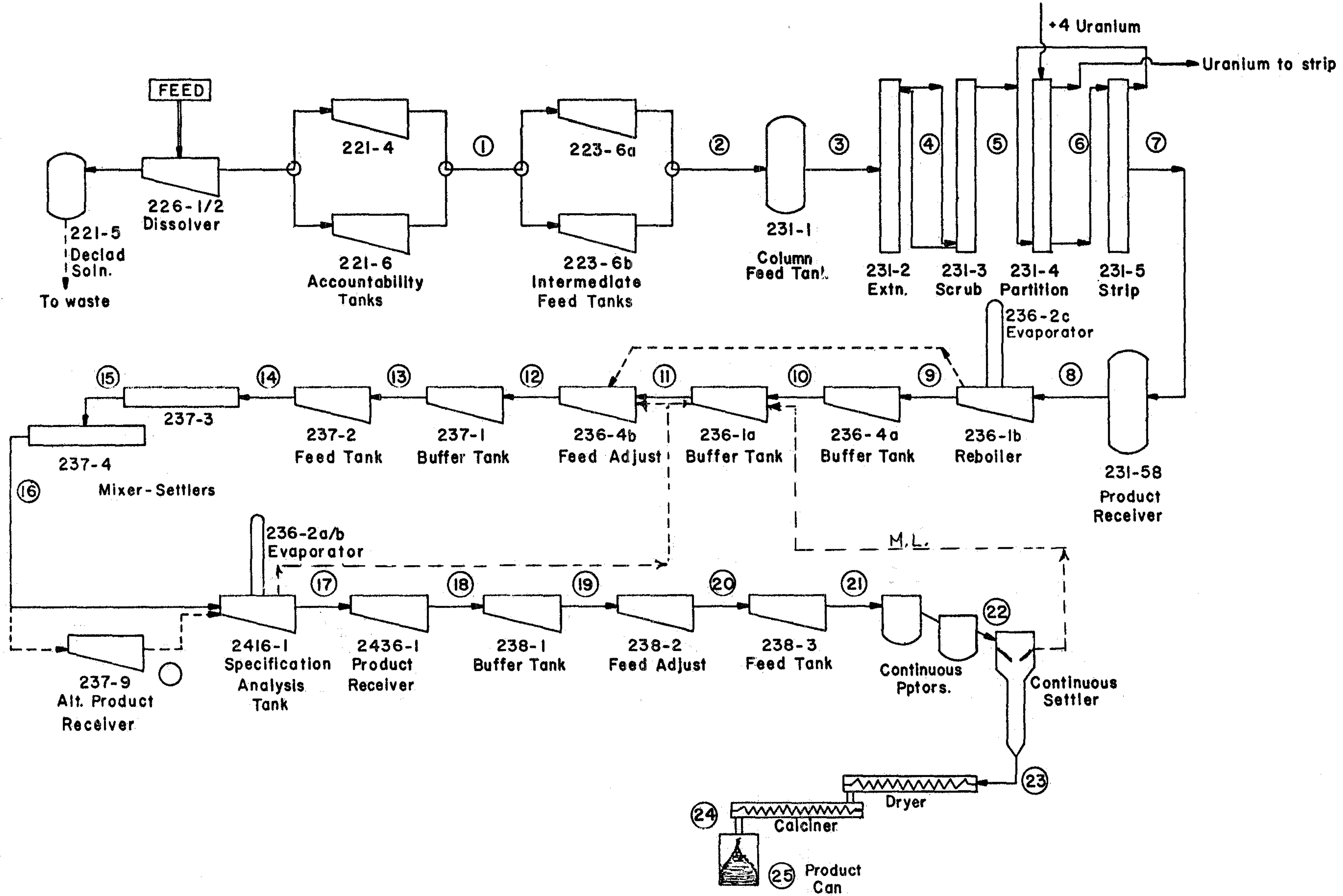


FIG. 4.11 SCHEMATIC FLOWSHEET EUROCHEMIC PLANT - Pu Cycle

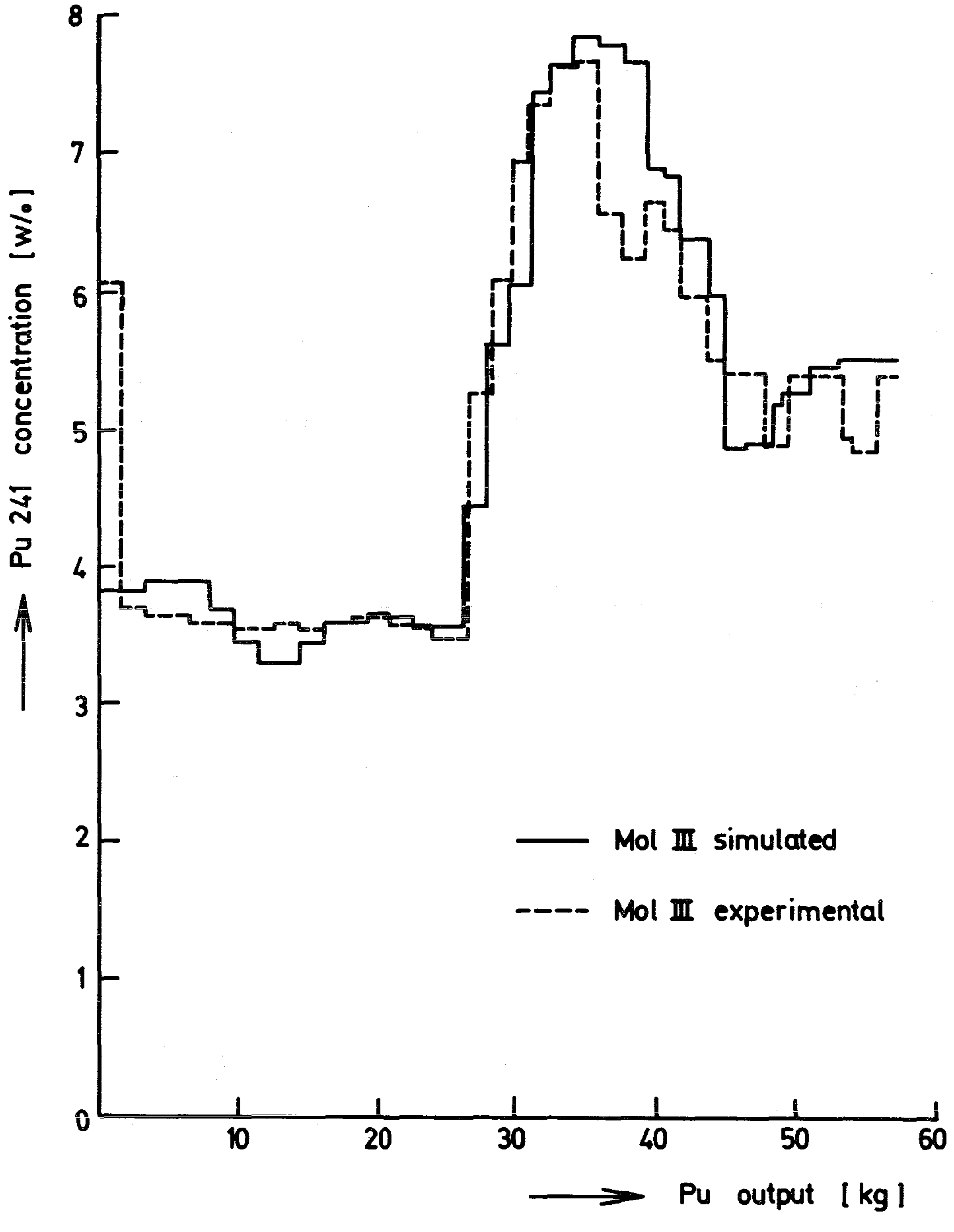


Fig. 4.12 Comparison of Predicted and Experimental Plutonium 241 Concentrations for Mol III Campaign

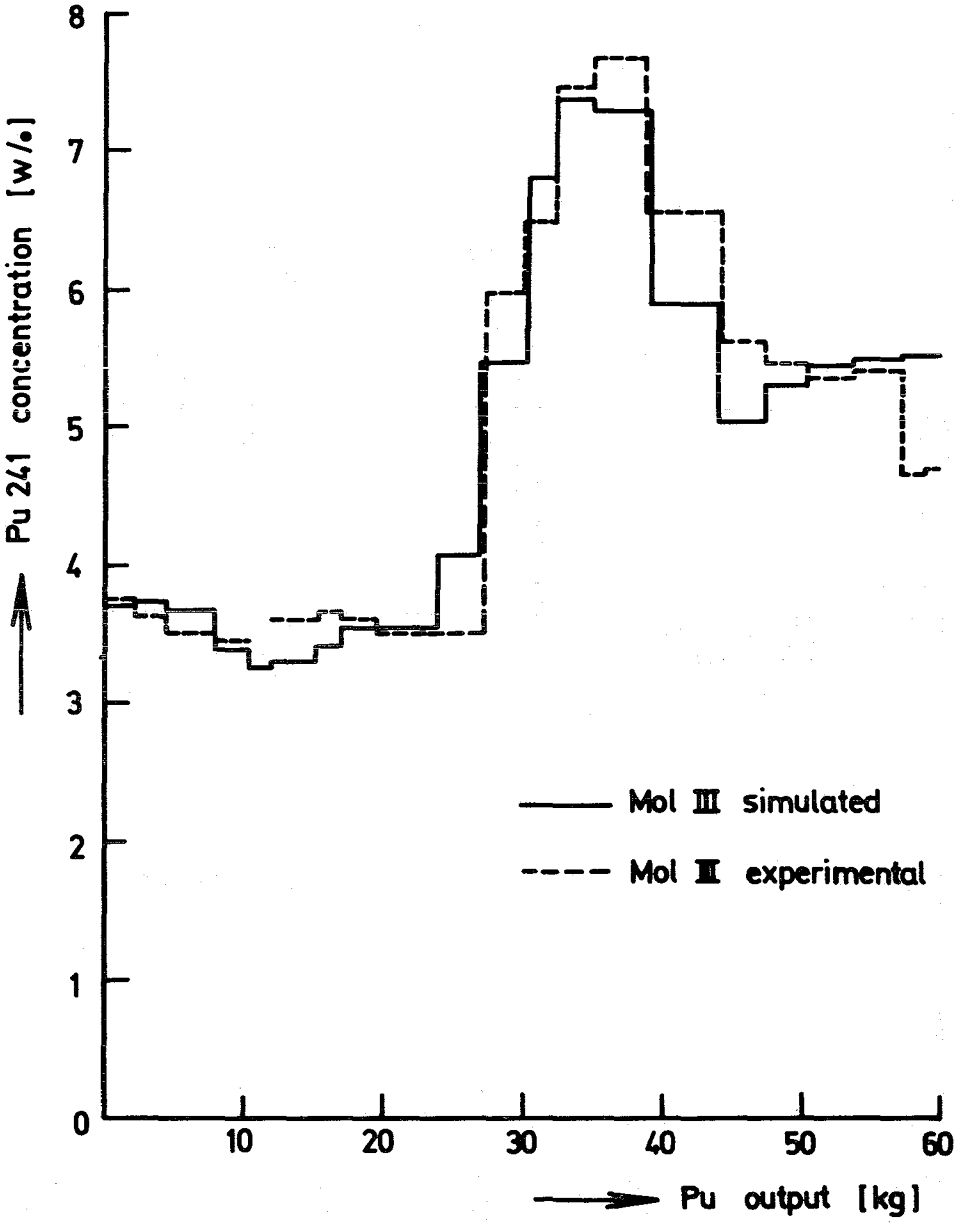


Fig. 4.13 Comparison of Predicted and Experimental Plutonium 241 Concentration in 2BP Product for Mol II Campaign

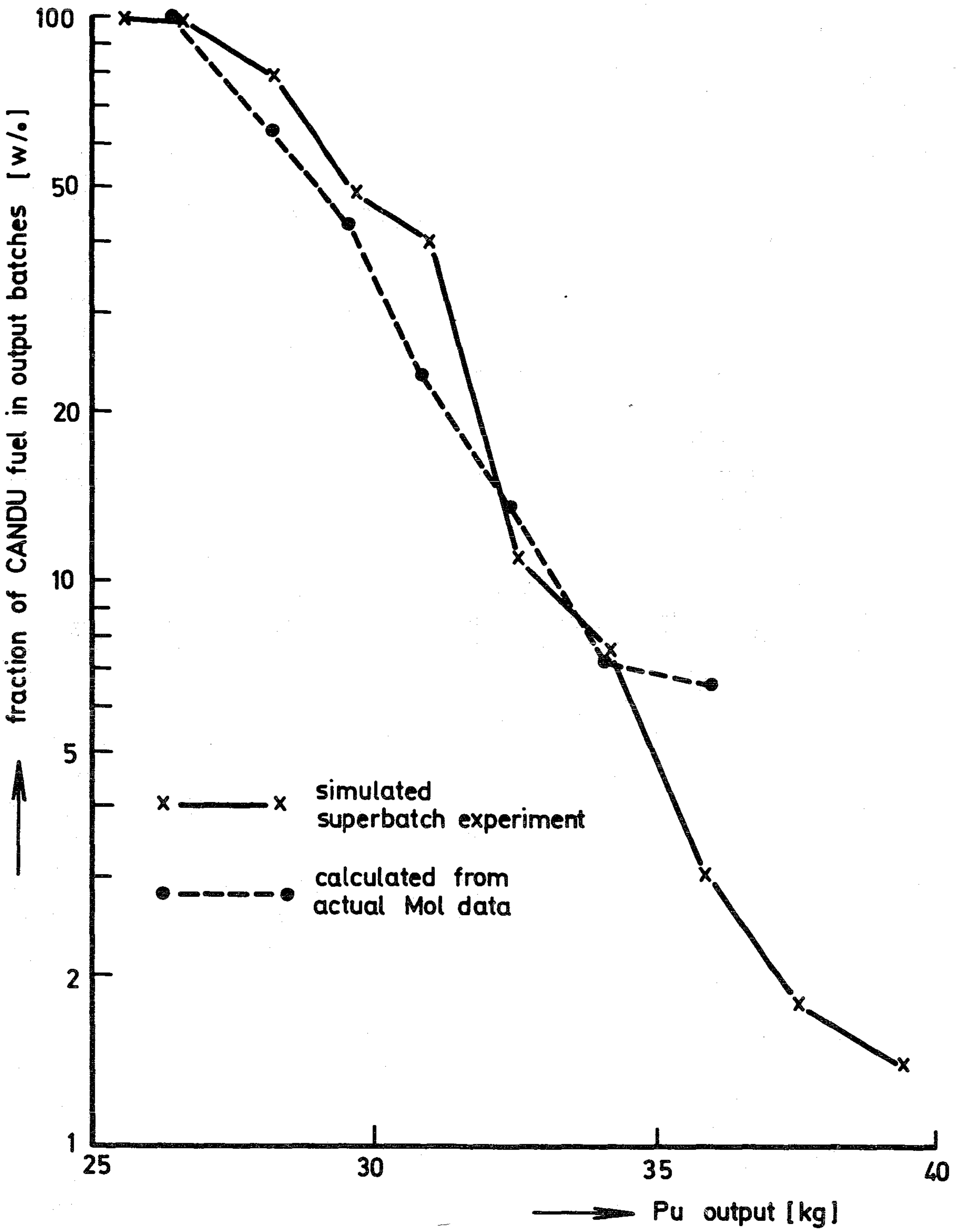


Fig. 4.14 Decrease of CANDU Fraction in Product after Entrance of the VAK Step-Function

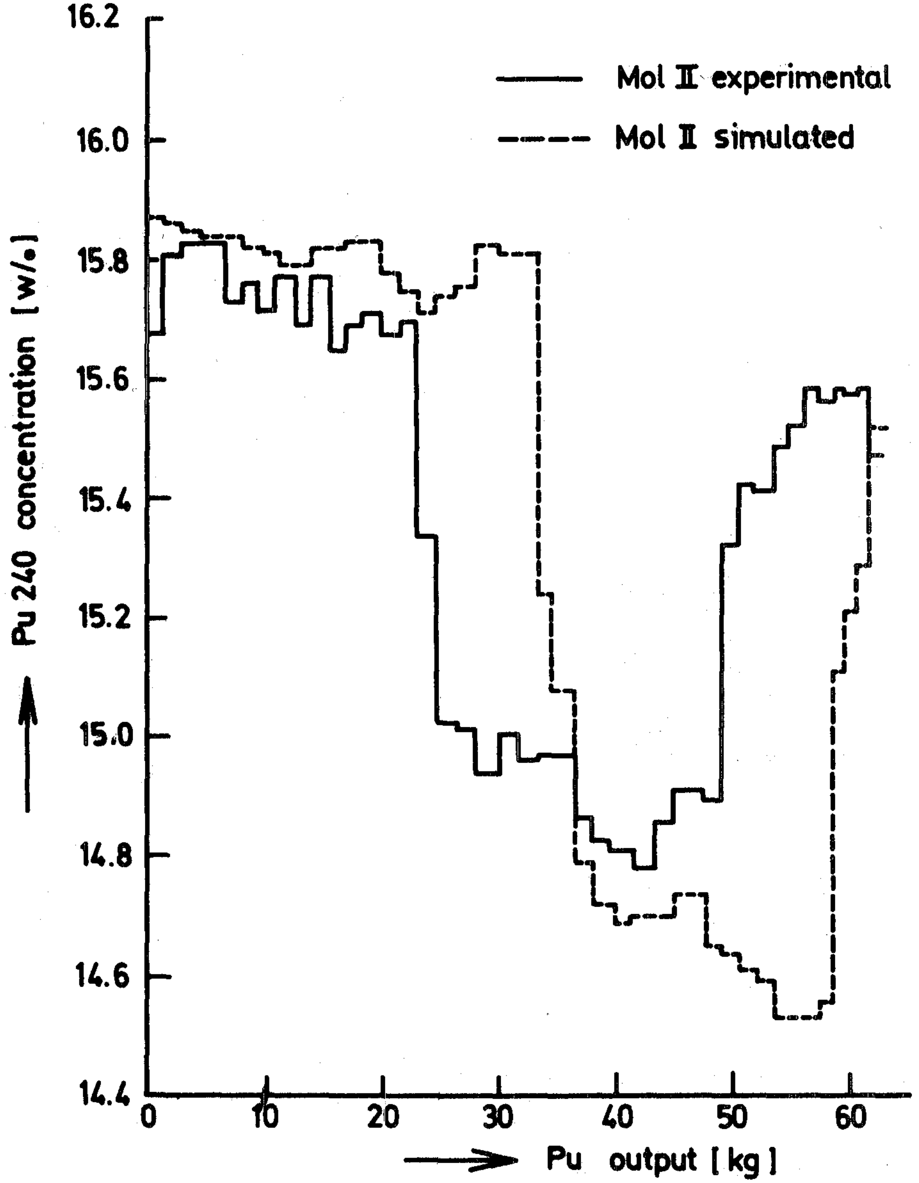


Fig. 4.15a Comparison of Predicted and Experimental Plutonium 240 Concentrations for Mol II Campaign

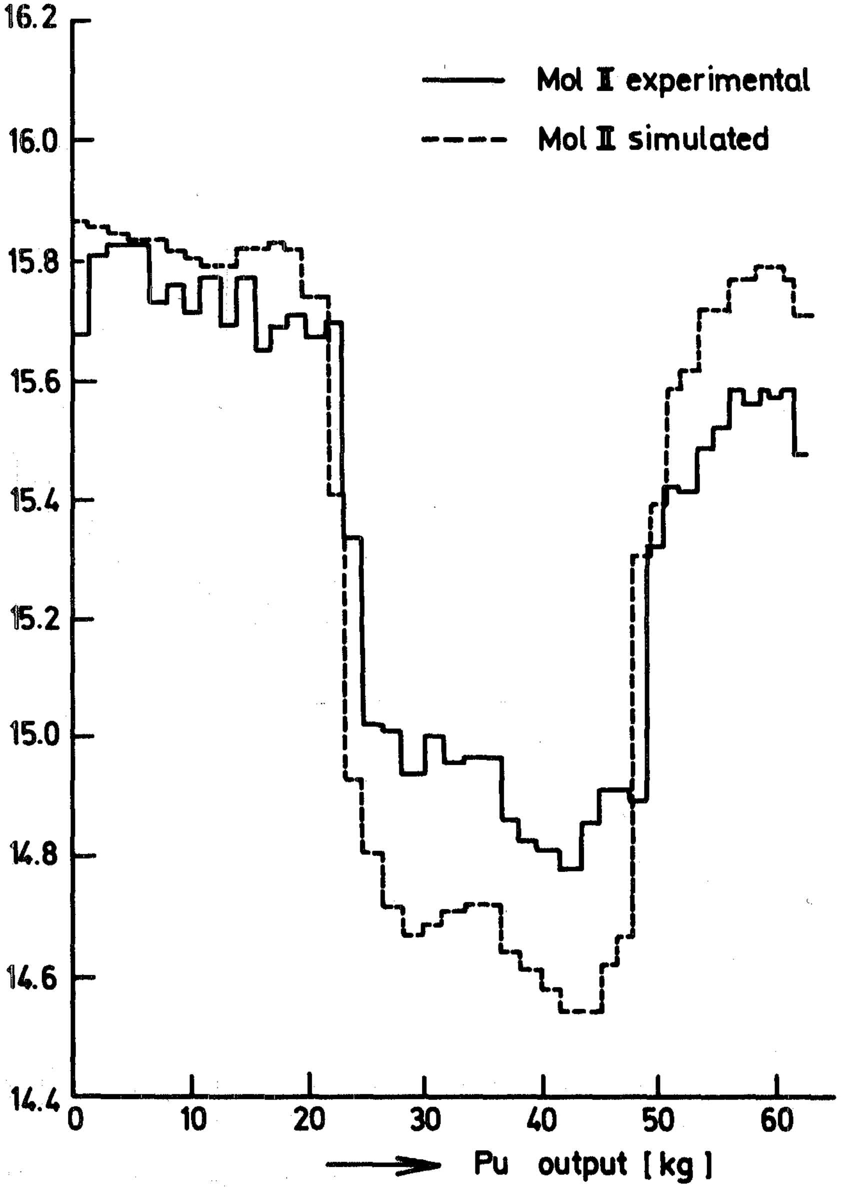


Fig. 4.15b Comparison of Predicted and Experimental Plutonium 240 Concentrations for Mol II Campaign with 5th & 6th Batches Delayed

Annex 4.I (by F.de Greef)

SIMULATED MIXER SETTLER RESPONSE

An attempt has been made in order to evaluate the implications of the simplified description of the mixer-settler batteries' behaviour with respect to the selfmixing of the fissile material there inside. The information may be obtained observing the response of the system to a suitable step shaped input function like e.g. the concentration of a particular Pu isotope. The behaviour of the mixer-settler batteries of the second purification cycle for Pu has been studied making use of a simplified mathematical model, suitably implemented on an analogous computer. The differential equations describing the behaviour of the fissile material have been derived, in the model, within the following assumptions:

- The single stage of the MXS is considered as a box of total volume V (mixer+settler) and partial volumes of aqueous (aq) and organic (org) phases defined as follows:

  $$V_{aq} = \frac{V\,F_{aq}}{F} \qquad\qquad V_{org} = \frac{V\,F_{org}}{F}$$

  where F_{aq} and F_{org} indicate the flowrates of the aqueous and organic phases respectively and $F = F_{aq} + F_{org}$ is the total flow rate.

- The partition coefficient D, defined as the ratio of the Pu concentrations (at equilibrium) in the two phases ($D = P_{org}/P_{aq}$) is constant throughout every stage of the system despite of any variation of the NHO_3 and TBP concentrations.

- The flow rates are constant in time.

- The phases are completely unmixible (no TBP in aqueous phase)

Under these assumptions every stage of the MXS is described by an equation of the following type, i being the index of the stage in question:

$$\frac{d\,P_{org}(i)}{dt} = \frac{\beta}{\tau}\left(P_{org}(i+1) - P_{org}(i)\right)$$
$$- \frac{\alpha}{\tau}\left(P_{org}(i) - P_{org}(i-1)\right)$$

where:

$$\beta = \frac{F_{aq}}{F_{aq} + D\,F_{org}}, \qquad \alpha = \frac{D\,F_{org}}{F_{aq} + D\,F_{org}},$$

$$\tau = \frac{V}{F} .$$

The complex of the MXS is then described by a suitable system of differential equations of the above type, in which the actual structural data as flow rates, operative volumes and interconnections are taken into account.

From this system the steady state conditions may be easily derived by setting all the time derivatives zero.

Unfortunately, the process data available from the flow sheet are not sufficient to derive, in the above mentioned model, an unique set of values for the partition coefficient relative to each of the four blocks in which the MXS system may be divided (Fig. A.1). From the numerical point of view it is possible only to derive consistent sets of D, if once two of them are fixed a priori.

For the calculations D_1 and D_4 have been choosen as fixed and D_2 and D_3 have been calculated. A set of the values is given in table A.I and corresponding time responses to an input step function are shown in fig. A.2.

On the average the mixing takes place over an interval of 3-4 hours. This means that a quantity of 600-800 g is mixed, because the steady state flow rate for Pu through the system is 200 g/h.

Table A.I

MXS 237-3			MXS 237-4		
case	D_1	D_2	D_3	D_4	case
I	2,6	2,080	0,6185	0,9	1
II	2,8	1,046	0,6060	1,9	2
III	3,0	0,8085	0,5920	2,9	3
IV	3,2	0,6940	0,5780	3,9	4
V	3,4	0,6210	0,5640	4,9	5
VI	3,6	0,5675	0,5505	5,9	6

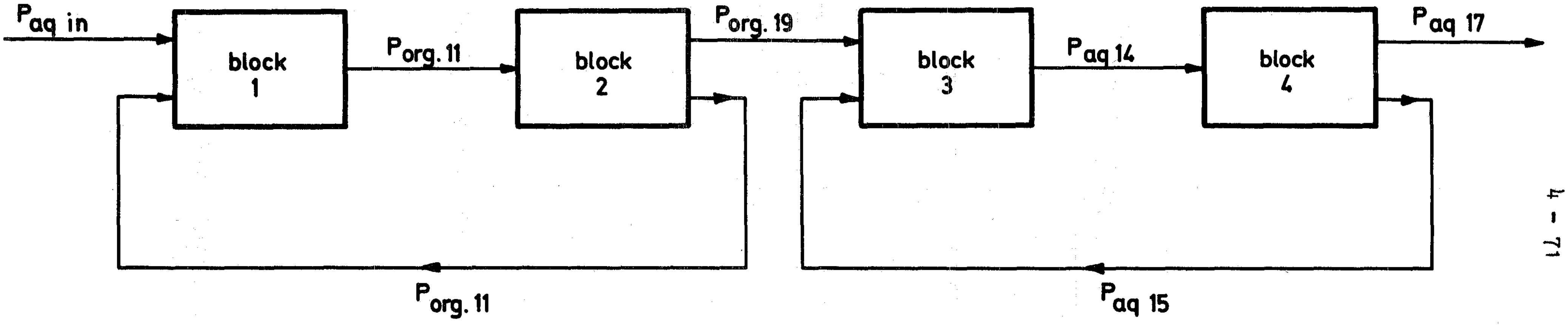


Fig. 4.A.1 Mixer settler block diagram

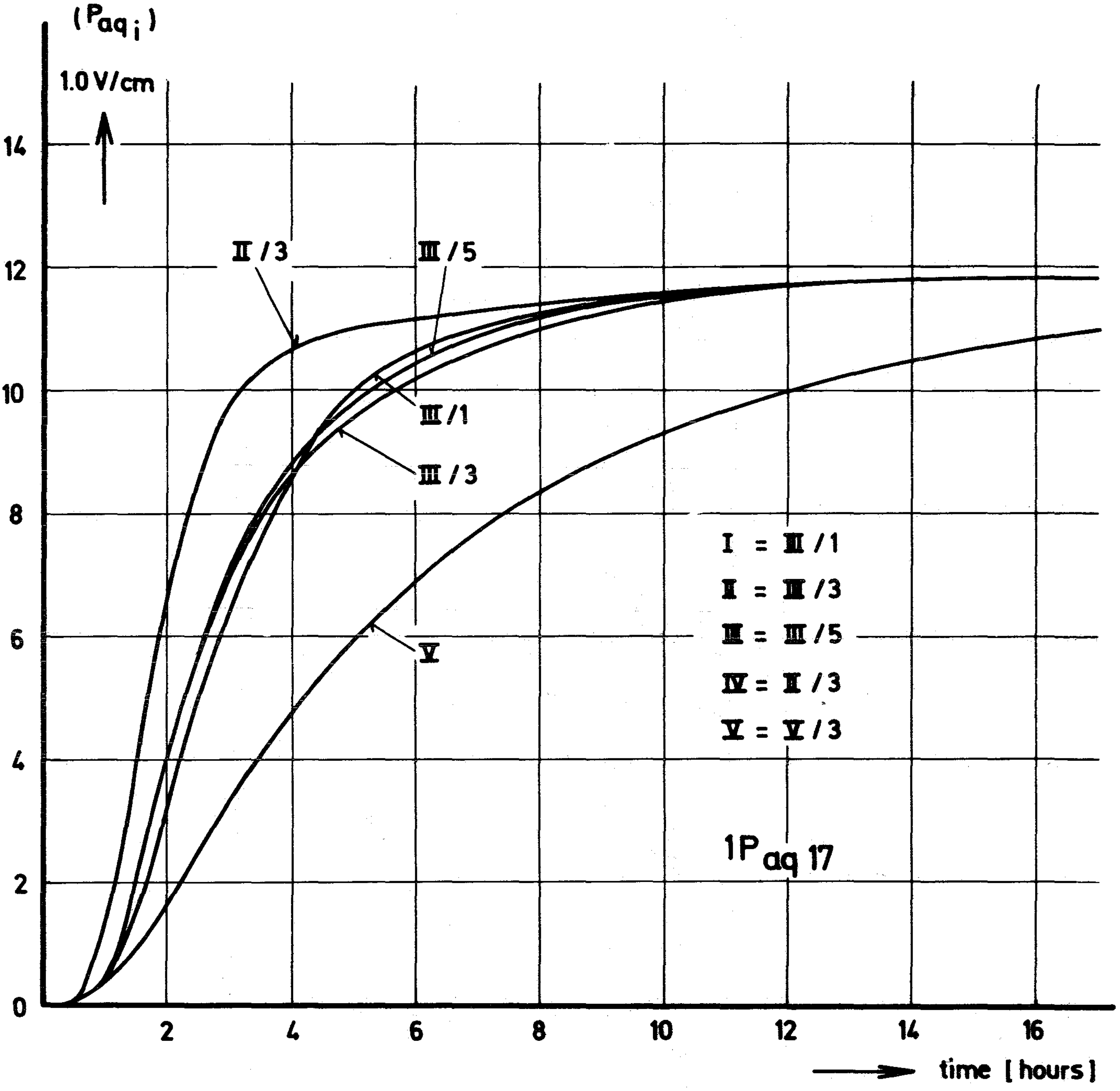


Fig. 4.A.2 Calculated mixer settler responses

Annex 4.II

DETAILS ABOUT MONTE-CARLO PROCEDURES

In order to create "simulated campaigns" two different procedures are used:

a) One simulates single campaigns for special (artificial) conditions of the plant and/or a special form of the input signal, e.g. one tries to simulate the actual Mol III experiment.

b) One simulates a series of campaigns with the aim to study systematically the influence of variations in certain parameters.

E.g. one could be interested in the accuracy for the calculated hold-up of the plant under conditions, which are similar to those of the real experiments, with respect to the batch-to-batch variation.

In this case it seems reasonable to start with the hypothesis that the tracer concentrations and volumes of the single batches inside both superbatches have known distributions. In our calculations we have chosen normal distributions with prescribed mean values C_1, C_2, V_1, V_2 and variances $\sigma_{C1}^2, \sigma_{C2}^2, \sigma_{V1}^2$ and σ_{V2}^2. By a suitable procedure it is possible to generate values for the tracer concentrations randomly. +)

For one campaign, which is of the type described under (a) above, the input superbatches are constructed by putting together single batches with different artifically generated concentratinn values C_1^i and C_2^i as well as volumes V_1^i and V_2^i. Using this input the simulation gives both physical and process inventory at the time of the introduction of the concentration step.

+) Let p(c') be the probability density function of a continuous variable c' - in the case under study

$$p\,(c') = \frac{1}{\sqrt{2\Pi\sigma}}\, e^{-\frac{(C-c')^2}{2\sigma^2}}$$

It is possible to generate a series of pseudorandom numbers R in the interval (0,1) by a digital computer. The real numbers C, implicity defined by the equation R $\int_0^c p(c'/C,\sigma)\,dc'$, result to be distributed according to p, as required

The next operation is to build up a series of such campaigns. For doing this the whole procedure beginning with the choice of the input values C_1^i, C_2^i, V_1^i, V_2^i from the same distributions which have been used for the first campaign is repeated as many times as required.

After having run all these campaigns, one ends up with distributions for the physical and book inventory values. By these one gets an answer to the problem of the interconnection between these values and the batch-to-batch variation.

The method is the same as the one used for following error propagation by Monte-Carlo techniques and the results may be interpreted under this aspect, too.

Chapter 5

Experimental Demonstration of a New Physical Inventory Technique by Means of Isotope Analysis

by

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Summary

A new physical inventory technique which correlates isotopic abundances of subsequent input and product batches could be experimentally demonstrated both for U and Pu under industrial conditions during a running campaign at the EUROCHEMIC reprocessing plant.

The agreement of the evaluated physical inventories with the corresponding book inventories was in all cases within the calculated 95 % confidence interval.

The evaluation and error analysis was performed by means of Monte Carlo techniques providing distribution functions and confidence intervals.

In particular following accuracies could be achieved

i) physical Pu inventory (≈ 12 kg) less than 5 % RSD
ii) physical U inventory (≈ 1800 kg) " " 2 % "

It could be shown that the superbatch size of VAK Plutonium was not big enough to clean the plant from former material. However, the conditions of JEX-70 fuel allowed the evaluation of a 3-component system. Thus the total inventory Plutonium could be determined. The unmixed inventory material passing the product catch tanks covered 70 % and 80 % of the total Pu- and U-inventory respectively.

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5. Experimental Demonstration of a New Physical Inventory Technique by Means of Isotope Analysis

5.1 General

The main safeguards activities result in a statement of the amount of material unaccounted for over a specific period and material balance area, giving the limits of accuracy of the amounts stated.

A nuclear material balance is closed by a physical inventory which normally takes place after a campaign.

In case of reprocessing plants a final wash-out of the process area has to precede because there are in most cases a couple of process units and pipes which cannot be inventorized adequately.

Safeguarding these plants there is a vital interest to shorten the periodes between two physical inventories because accumulating measurement errors on nuclear material flows are increasing the error limits of MUF thus there is no clear inspector statement any more possible.

On the other hand short inventory periods decrease the load factor of the plant which does not hit economic requirements. The new physical inventory technique described here is avoiding the latter disadvantage of conventional inventory techniques because it can be performed during the running campaign by suitable correlations between isotopic abundances associated with subsequent input and product batches. In addition no intimate knowledge of the units within the chosen material balance area is required by the safeguards authority.
On occasion of the first MIST experiment carried out at Nuclear Fuel Services /̄5-1_7 in 1969 the theory of this method was developed /̄5-2_7 and first experimental demonstration could be achieved at the second integral safeguards exercise in EUROCHEMIC /̄5-3_7.

This successful experiment which was limited to the Uranium flow encouraged the members of the EURATOM/GfK Steering Committee to choose again as a main objective of JEX-70 the experimental demonstration of this inventory technique applied at the Uranium and Plutonium flow.

The preceding chapter was investigating the feasibility and accuracy of this inventory technique for the conditions at the EUROCHEMIC reprocessing plant and main emphasis was laid on the establishment of a priori statements.

This chapter describes the quantitative inventory determination relevant for safeguards taking into account a posteriori real campaign data which represent the actual fuel management of the operator.

It is to be emphasized here that the great volume of information on the different process steps required by simulation studies is not used for the actual physical inventory determination by the new technique proposed. These simulation studies represent an initial investigation phase which must not be repeated at other reprocessing campaigns suitable for the application of this new inventory technique.

5.1.1 Basic Considerations

In order to avoid the reader's pre-information of the references above a short description of the basic considerations is given here similar to that in ref. [5-3].

The new inventory technique makes use of the fact, that the fissile material inventory between input- and product-accountability-tanks, which is pushed out by incoming new material, can be measured quantitatively in subsequent product batches, provided the isotopic composition of the inventory differs sufficiently from that of the new input material. The problem is to generate a step function in the isotopic composition of the input flow by loading the dissolver in such a way that a sufficient number of fuel elements of equal initial enrichment and irradiation history will be followed by fuel elements with different isotopic abundances from the first group. It is also possible to use the different isotopic composition of irradiated fuel elements from two different reactor-batches which are processed in close sequence.

The evaluation of the physical inventory is a simple sum-up of product batches weighted by a factor which indicates the fraction of the inventory material in each individual product batch according to equation (5-1).

$$(5\text{-}1) \quad PI_{(t_1)} = \sum_{i(t>t_1)} M_{pi} \frac{x_i - c_2}{c_1 - c_2} \qquad [\text{kg U, Pu}]$$

t_1 = time of introducing the step input signal

M_p = product batch size [kg U, Pu]

c_1, c_2 = isotopic composition of the input flow which forms the step signal [%]

x_i = isotopic composition of heavy material in product batch i [%]

The weight factor of subsequent product batches illustrates operator's individual material management during the passage of the signal through the plant. Simulation studies and also experimental results indicate that this factor converges to zero following a function with a shape similar to an exponential. The dispersion of the input step signal can be minimized if the operator runs the process according to a small number of procedures mainly by special operation of the headend and product catch tanks but this only during the residence time of the signal in the plant.

The corresponding book inventory which is calculated by balancing all input, waste and product streams up to the time (t_1) when the step signal is introduced follows equation (5-2).

$$(5\text{-}2)\quad BI_{(t_1)} = PI_{(t_o)} + \int_{t_o}^{t_1} (\dot{m}_I - \dot{m}_p - \dot{m}_w)dt \qquad [\text{kg Pu,U}]$$

where: $PI_{(t_o)}$ = starting physical inventory [kg U, Pu]

$\dot{m}_I, \dot{m}_p, \dot{m}_w$ = Input, product and waste flow $\left[\frac{\text{kg U,Pu}}{\text{h}}\right]$

In case of batchwise operation the integral is replaced by sums.

The two independent inventory determinations $PI_{(t_1)}$, $BI_{(t_1)}$ should correspond inside the error limits if no uncontrolled transfer has taken place or a certain amount of fissile material has been withheld intentionally.

5.2 Generation of an Adequate Input Signal

5.2.1 Criterium

Subject of this section is the definition of the optimisation criterium applied at parameters forming the input signal with the aim to improve the accuracy of this kind of physical inventory determination.

The input step signal characterized by c_1 and c_2 (equ. 5-1) is associated with certain error bars. This can be demonstrated by the definition of c_1 and c_2 which represent the homogenized isotopic abundances of the superbatches[1] before (1) and after (2) the step signal.

$$(5\text{-}3)\quad c_1 = \frac{\Sigma M_i c_i}{\Sigma M_i} \quad [\text{W/o}] \qquad c_2 = \frac{\Sigma M_j c_j}{\Sigma M_j} \quad [\text{W/o}]$$

The summation is to be carried out in a ragen:

$$\Sigma M_i \approx \Sigma M_j \approx \text{Hold up} \qquad [\text{kg Pu, U}]$$

as discussed more in detail in chapter 4.6.

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[1] "Superbatch" is defined by a certain number of consecutive input batches with small batch-to-batch variation of isotopic abundances.

The distribution of c_i and c_j around the weighted means c_1 and c_2 respectively is due to the following two reasons:

i) The "true values" of c_i and c_j respectively vary according to the slightly different irradiation histories of fuel in subsequent dissolutions of one superbatch.

ii) Errors associated with measurements of total batch quantities of U and Pu and their isotopes are in superposition with i)

With the help of Gaussian error propagation rule on equ. (5-1) and (5-3) one finds as shown in Annex (5-III) that the main error component can be expressed by the ratio:

$$(5\text{-}4) \quad r = \frac{\text{isotopic batch-to-batch variation}}{\text{isotopic step size}}$$

The mathematical term thereof is derived in Annex 5-III:

This ratio (r) has to be minimized either by increasing the stepsize and/or by decreasing the batch-to-batch variation of a certain isotopic abundance selected for the evaluation of equ. (5-1). In fact one has to start with the optimisation by careful election of the fuel elements to be dissolved. By means of burn-up codes the fuel element shipper gives already calculated quantities of isotopes in each fuel element. This information is used for the distribution of fuel elements within the different dissolution batches with regard to the optimisation criteria ($r_{min.}$).

5.2.2 Provided input signal

In case of JEX-70 fuel elements from four different reactors were processed in close sequence without any intermediate flushout. It was intended to homogenize each particular reactor batch with respect to isotopic abundances of U and Pu and to use the isotopic step signal between different reactor batches. Table 5-1 shows the characteristic numbers of these reactor batches.

There is given additionally one type of material indicated as starting inventory. This material represents Pu being present in the rework unit in form of nitric solution which was to be processed after the former material in close sequence thus forming one additonal step signal in the Pu-flow.

The use of fuel element shipper data requires of course the possibility to identify the irradiated fuel elements in the fuel storage pont either by visual inspection or by TV-camera devices. With help of Gamma-measurements even the burn-up situation of each fuel element can be confirmed. With regard to the CANDU-fuel no special dissolution order could be established because no identification of the 719 partly broken fuel elements was possible (see chapter 3). The isotopic signal could be expected to be uniform as only burned natural Uranium was reprocessed and different burnups were randomly averaged.

Concerning VAK fuel elements there was great interest of identification because considerable differences in initial enrichment and burnups of single fuel elements had to be considered. With help of the TV-camera device one was able to identify the fuel element numbers (chapter 3) thus using the shipper data an optimal selection of the 38 fuel elements in 4 groups could be arranged with respect to an uniform isotopic composition of U and Pu in the 4 VAK-dissolution batches. The actual dissolver laoding order which was arranged with the operator can be extracted from chapter 2.5.1.2.

The homogenisation of TRINO fuel by a special dissolution order was only possible to some extent due to the small number (4) of processed fuel elements. Therefore, the operator was asked to homogenize the active feed in the headend storage tanks which was unfortunately not possible due to difficulties in the transfer system and due to time delays of the former dissolutions.

The last reactor batch indicated as CDN fuel contained a relative small amount of U and Pu in relative great number of fuel elements (table 5-1), thus no effort was done in identifying fuel elements and in establishing a special dissolution order because it was assumed that enough homogenisation of this reactor batch is randomly obtained.

5.2.3 <u>The Actual Input Signal</u>

The realized input signals of U and Pu are represented as isotope abundances vs. total heavy material plots of U and Pu respectively in Fig. 5-1/2/3. The dashed lines represent the realisations of mass-spectrometric determinations of each particular input batch whereas the continuous line gives the weighted average thereof according to equ. (5-3). The actual numbers are summarized in table 5-2/3/4.

Fig. 5-1 shows the realized U-signal which was in good agreement with the expected signal as estimated by use of shipper data. Batch-to-batch variations of the U-235 abundance compared with the step signal was sufficiently small between CANDU and VAK (see table 5-4) whereas the following signals are insufficient with regard to homogenity and to the quantities of U in these superbatches. There is a condition which was experienced from the former exercise in EUROCHEMIC and from simulation work which requires that the quantity of heavy material in one superbatch should be at least equal to the hold up of the considered MBA. This condition is not fulfilled for the last two reactor batches, so in fact only one stepsignal can be evaluated with respect to physical inventory determination of Uranium.

The realized Pu-signals which are shown in Fig. 5-2 and Fig. 5-3 are due to further discussions. By nature the batch-to-batch variations of Pu isotope abundances are considerable larger than those of Uranium because they are more sensitive to different irradiation histories. This can be extracted quantitively from table 5-5 where for each isotope the interesting ratio r (equ. 5-4) was evaluated in order to select the most suitable isotope ($r_{min.}$) for the evaluation of the inventory equation (5-1). According to these numbers one has to select Pu-241 for the first step between CANDU and VAK-fuel and Pu-240 for the second and the third step. Originally it was Pu-240 which was focussed to be used as step signal between CANDU- and VAK-fuel because the calculated quantities of Pu-240 by fuel element shipper did show suitable differences of the Pu-240 isotope abundances from both reactors.

The realized Pu-240 step signal (Fig. 5-2) between CANDU and VAK fuel however, was nearly homogeneous thus r increased up to 83 % (table 5-5) which is unsufficient for any inventory calculation. The Pu-240 step after VAK however, was very suitable because of this homogenity. CANDU and VAK fuel which could be considered as first superbatch with sufficient large quantity of heavy material followed by the TRINO, CDN and inventory Plutonium with relative low Pu-240 content and sufficient homogenity. Inspite of the low Pu-240 abundance of the 1.2 kgs Pu from CDN-reactor the resulting r was considerable small (4.7 %).

5.3 Measured System Response

In accordance with the comments made above only those isotopes were followed at the product flow as system response to the input signal which let expect the most accurate results for the physical inventory both for U and Pu.

5.3.1 Measured System Response of Pu-flow

The measured system response of Pu-flow for both step signals are plotted in Fig. 5-4 and 5-5 as isotopic abundances from the single consecutive product batches (2BP and PFP) vs.the total heavy material. In addition the corresponding input signals are drawn into the same figure. The abscissa was normalized to zero at the input step signal. The correlation between input- and product signal is given by the actual step time when the first batch of the second superbatch was transfered from the input accountability tank (221-4) to the feed adjustment tank (223-6b). This happened at April 4th, 12.00 (t_1 for the first and at April 25th, 14.00 (t_2 for the second step signal (see Fig. 5-10).

The corresponding isotope abundances of each consecutive product batch after these step times were plotted in Fig. 5-4 and 5-5 respectively. Relevant product batches were indicated by operator's batch identifications.

When following the final product signal (PFP) in Fig. 5-4 one realizes that after introducing the step there appear still 6 product batches with pure CANDU-material in total about 9 kg Pu. The mixing phase started with PC 133 and the signal climbed up till PC 142, but it did not reach neither the maximum nor the weighted average of the VAK-input signal which indicates that the VAK superbatch was not large enough to push out all CANDU-material. Therefore, one had to expect a three component mixture in the following product batches which still contained CANDU-material. This fact increased the efforts to evaluate the physical inventory because equ. 5-1 is only valid for two component mixtures whereas three component mixtures must be analysed by use of an additional suitable isotope as described in section 5.4.1.

Similar conclusions can be drawn when following the intermediate product signal (2BP) in Fig. 5-4. (The numbers can be extracted from chapter 2.5.10). As this signal represents the product signal of MBA 21 (see chapter 2, Fig. 2.2-2) it shows a certain shift to the left compared with the PFP-signal. The size of this shift is an indicator for the hold up in MBA 22 which was present there at the step time (t_1). The overlapping of both product signals in the "transient phase"[1] is due to the different batch sizes of PFP and 2BP flow and due to mixing mechanisms in MBA 22. In the "steady state phase"1) all curves should be equal which was realized within the error bars of masspec. determinations. One PFP-batch (PC 150) however, exceeded this limits which can physically not be explained without including the possibility of cross contamination either at sample preparation and analysis or by blending operations in the final product weighing and sampling unit.

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1) Transient and steady state have here to be understood as isotope changes vs heavy material and not vs time.

Fig. 5-5 shows the product signals in correlation with the second input step signal between VAK and TRINO-fuel. As mentioned in 5.2.3 the most suitable isotope abundance to be used here is Pu-240. Here a step down signal was realized which has some consequences as it will be shown in 5.4.1. As no additional step was introduced with respect to Pu-240 abundance the possibility of a 3-component-mixture could be excluded and one may observe convergence of the 3 signals at the isotope level given by the inventory material (except PC150 is again significantly different from the others). The last product batches indicate however a certain divergence which might be caused by the beginning rinse operations at the end of the campaign. Compared with the product signals of the first step (Fig. 5-4), the shift of the 2BP signal vs the PFP-signal for the second step is considerably larger which indicates a larger holdup in MBA 22.

5.3.2 System response of U-flow

The measured system response of the U-flow to the various input step signals is plotted in Fig. 5-6 in the same manner as the Pu-signals. The abscissa was normalized to the step signal between CANDU and VAK-fuel because the following 3 steps were too small with respect to an adequate inventory evaluation (see 5.2.3).

Concerning the U-product signal one observes the same chracteristic as described already for Pu-product flow. It is remarkable that the mixing phase between CANDU and VAK-fuel could be reduced to a high extent thus the product signal appeared nearly unaltered at the exit of the plant.

This chracteristic was realized due to the operator's efforts in segregating the two types of fuels as much as possible at least in the U-flow in order to safe blending losses between depleted CANDU-Uranium and slightly enriched VAK-Uranium.

Some comments have to be given here about the correction applied at the U-input signal due to additional Uranium introduced into MBA 21 as reducing agent (U IV) in the separation unit.

The flowsheet of the operator prescribes the following condition:

$$\frac{\text{Uranium(IV) flow (BXR) in mols/hr}}{\text{Plutonium flow in mols/hr}} \geq 10$$

In relation to the actual Uranium feed one may define a dilution ratio:

$$\beta = \Sigma \text{BXR}/\Sigma \text{AFU}$$

Fuel	β-condition	β-realized
CANDU	3.2 %	6.27 %
others	4.7 %	8.35 %

This material would not interfere the evaluation of the physical inventory in case it was recycled internally within MBA 21. However a considerable part of the total U(IV) did not belong to the material of this campaign or was recycled into MBA 21 after passing the product accountability station. In this case one has to consider the U(IV) flow as additional input flow. In fact both cases happened during JEX-70 and in addition different isotopic vectors were associated with U(IV)-batches as shown in Fig.5-7.

With help of the realized dilution ratios β the correlation between main and recycled flow can be calculated and is shown at the second scale of Fig. 5-7. The correction of the input signal was done by the following equation:

$$c_i^x = \frac{c_i + \beta c_r}{1+\beta} \qquad [\mathrm{W/o}] \tag{5-5}$$

$$M_i^x = M_i(1+\beta) \qquad [\mathrm{kg\ U}] \tag{5-6}$$

where:

c_i^x = corrected isotope abundance of input batch i

M_i^x = corrected mass of input batch i

c_i = measured isotope abundance of input batch i

c_r = measured isotope abundance of recycled Uranium corresponding to input batch i according to Fig. 5-7.

In case two types of recycled material were corresponding to one certain input batch one had to calculate the weighted average. The input batches corresponding to internal recycled Uranium were not corrected. With this procedure one was able to reduce two different input signals to one corrected signal which is suitable for the evaluation of the inventory equation (5-1).

5.4 Evaluation of the Physical Inventory and Error Analysis

The input and product signals both for U and Pu as discussed above were used as input data for physical inventory determinations at two different time points during the running campaign. In principle one has to evaluate the weighted average concentrations c_1 and c_2 according equ. (5-3) and enter them into equ. (5-1).

Recent studies however /‾5-4_/about the theory of this inventory determination indicate that the weighted average concentrations c_1 and c_2 are not biasless because it is not only relevant to weigh the deviation of a particular input batch from the mean of the corresponding superbatch but also its actual position within that superbatch. This fact is also shown in parameter studies of chapter 4. However, weighing of the position is only possible if one has well defined steady state conditions in the process which results in a stable transfer function between input and product signal.

This steady state conditions obviously could not be provided in JEX-70 by the operator and therefore efforts were done to solve this problem with help of a suitable error analysis by means of Monte Carlo techniques.

By introducing a random number R extracted from a (0.1) interval with uniform distribution as batch weight factor a new mean concentration in one superbatch was defined for the Monte Carlo calculations, analogous to equation (5-3).

$$(5\text{-}7) \qquad c_j = \frac{\Sigma M_{ij} R_{ij} c_{ij}}{\Sigma M_{ij} R_{ij}}$$

j indicates superbatch j
i indicates input batch i in superbatch j.

When entering equ. (5-7) in equ. (5-1) one was able to evaluate with help of a computer code (Annex 5-I) a high number (10^3-10^4) of inventories per step signal. The program was providing meanvalue, variance, standard deviation and in addition the frequency and distribution functions of the calculated inventory realisations.

The distribution functions were then subject of a chi-square-test in order to prove the hypothesis of a normal distribution. This hypothesis had to be rejected in all cases with a high probability (99.9 %) because the single distribution functions showed considerable asymmetric characteristics.

5.4.1 Physical Inventory of Plutonium

When discussing in 5.3.1 the system response to the first input step signal of the Pu-flow it was mentioned that some product batches indicated not only 2 components (CANDU and VAK fuel) but also 3 components (CANDU, VAK and TRINO fuel). The objective is to find the CANDU component in each particular product batch because it is the CANDU fuel which represents the inventory material at the first step signal.

The problems associated with the evaluation of a 3 component mixture were already discussed in [5-1]. In principle the single components of a multicomponent mixture can be evaluated provided two conditions are fulfilled:

(i) The number of components must not exceed n+1 where n is the number of available isotopes,

(ii) the isotope vectors of the different components must not be linear dependant which means in mathematical terms that the coefficient matrix of the linear equation system must be sufficiently different from zero.

Following condition i) one has to select two isotopes with respect to optimize condition ii). The criterium used here is the coefficient matrix.

$$D = \begin{vmatrix} 1 & 1 & 1 \\ c_1 & c_2 & c_3 \\ d_1 & d_2 & d_3 \end{vmatrix} \qquad (5\text{-}8)$$

where: c_j and d_j are weighted isotopic abundances average of superbatch j.

The value of D is proportional to the triangle area in a c-d-plot. D has to be maximized and the deviation of D caused by the batch-to-batch variation of the single isotopic abundances c_{ij}, d_{ij}, of batch i forming one superbatch j should be minimized.

This procedure was done by plotting a number of isotope pairs in the c-d-plot and by estimating the minimum relative deviation of D. An analytical expression thereof corresponding to r equ. (5-4) is no more possible because c_{ij} and d_{ij} are correlated.

Only with help of Monte Carlo technique one is able to solve this problem quantitatively. With respect to this optimisation procedure the most suitable isotopes were evaluated to be:

c = Pu-241 W/o
d = Pu-242 W/o.

The corresponding plot is given in Figure 5-8 which is described in the following.

The 3 components are represented as weighted means from the different input batches (small dark circles) whereas the small squares and triangles represent the different product batches of PFP and 2BP respectively. The product points are connected by pointers which indicate their time sequence because the indicated batch identification numbers are not always straight foreward.

Starting from the CANDU-point both product vectors follow nearly the same linear characteristic and exceed the maximum possible mixing area(shadowed area) at the VAK point. This fact can only be explained by blending operations with unknown material during the process or by a bias of masspec. determinations for VAK input batches which is more probable than errors of product batches because both product vectors measured in two independant laboratories correspond very good. The product vector moves then down to the TRINO-point oszillates there and leaves the mixing triangle hitting finally the PI-point characterized by the starting inventory Pu.

With help of Fig. 5-8 one may clearly define which product batches show a one- two-and three component mixture. Product batches which hit roughly (with respect to the associated error bars) the mixing area[1] of one component indicate that the Pu is not blended with other components. Product batches hitting roughly a straight line between two components are mixtures of both and those within the mixing triangle are three component mixtures.

According to this rule the product batches forming the system response to the first input step signal were devided in three groups:

i) Clean CANDU Pu: PFP-135,-136,-127,-128,-129,-130,-
2BP-1600,-1700

ii) Mixture CANDU and VAK: PFP-133,-138,-139,-140,-141,-142,-
2BP-1800,-1900,-2000,-2100,-

iii) Mixture CANDU, VAK and TRINO: PFP-145,-146,-147,-148,- 149
2BP-3100, (-3200)[2]

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[1] The mixing area of one component covers all input batches i belonging to this component.

[2] This batch may also contain other components (see Fig. 5-8) and has not been taken into account for the determination of the physical inventory.

The quantities and isotopic abundances associated with the batch identifications above can be extracted from chapter 2 Table 2.5.6-1 and 2.5.10-1. The batches in brackets may also contain other components.

The batches of the first group can be sumed with the weight factor: one, whereas the batches of the ii) and iii) group have to be weighed according to their CANDU component using the Monte Carlo technique as described above for two component systems. The technique was also developed for the 3-component systems (see Annex 5-I). The results of these calculations are summarized in Table 5-6.

The confidence interval forthe total inventory was calculated by use of the convolution integral (5-9) which describes the resulting probability density function of the sum (y) from two random variables.

$$(5\text{-}9) \quad f(y) = \int_{-\infty}^{+\infty} f_1(t)\, f_2(y-t)\,dt$$

where f_1 and f_2 are individual probability density functions of the two random variables.

In the present case, however, the f_1 and f_2 are delivered by the Monte Carlo technique (Annex 5-I) as discontinuous histograms. Their convolution must then be numerically evaluated and this has been obtained by the use of a computer code as described in Annex (5-II). The resulting distribution histogram is shown in Fig. 5-9. The considerable asymetric error bars of + 6.2 % and -7.2 % of the total inventory represent the maximum possible error range associated with the chosen confidence level of 95 % because the batch weight factor R_i in equ. (5-7) was assumed to cover the total 0,1 interval. In steady state operating reprocessing plants one may reduce significantly this range by introducing in equ. (5-7) an additional batch weight factor which considers in average the weight of a single input batch due to its position within the superbatch [5-4].

Looking at the three types of mixtures in the product batches (Table 5-6), one realizes that the greatest amount of the physical inventory (more than 70%) is unmixed material which can be determined with high accuracy according to the involved errors in weighing and analysis.

Even the two-component mixture could be evaluated within satisfactory error bars. It is only the evaluation of the 3-component mixture which involves the great range of uncertainty, and this was mainly caused by the great batch-to-batch variation of the TRINO fuel which unfortunately could not be homogenized in the head-end storage tanks due to technical difficulties. This confirms again our previous experience that one should avoid 3-component mixtures by increasing the superbatch size which is able to clean out completely the inventory material.

The system response to the second input step signal (Fig. 5-5) did show this characteristic without the 3-component mixture but the corresponding physical inventory indicated greater error bars due to the relative bad quality of the input step signal and the great dispersion of the system response over a range of nearly 20 kg Pu.

The direction of the input step signal, e.g."upstairs" or "downstairs" reflects to the calculated error bars for the two-component system in such a way that the asymetric characteristic changes its sign. This turns out when comparing the error bars of the two component systems in Table 5-6 and Table 5-7 respectively.

It is remarkable that both inventory determinations indicated about 70 % unmixed Pu. If one may increase this ratio by avoiding blending operations during the process there is also an improvement of the total accuracy of this inventory determination.

5.4.2 Physical Inventory of Uranium

The results of the Uranium physical inventory determination are summarized in Table 5-8.

In this case only MBA 21 was covered because the U-flow does not pass MBA22.

As already mentioned in 5.3.2 the operator was able to segregate to a high extent CANDU from VAK Uranium which reflects to the 83 % single component Uranium inventory. The corresponding fraction of the single component Pu-inventory was only 71 % (Table 5-6).

5.5 Book Inventory Determination and Error Analysis

The physical inventory determinations carried out so far are only of use for safegurads if the corresponding book inventories at the defined step times are available. For this purpose one has to balance each transfer (e.g. input, product and waste) crossing the boundaries of the defined MBA according to eqn. (5-2) inclusive starting inventory up to the step time.

In practice JEX-70 observers established a volume vs time plot of each relevant accountability tank and recorded by this procedure for the total time interval between beginning and ending inventory all relevant transfers. An interesting section of this plot is given in Fig. 5-10. It covers the time when VAK fuel was started to be processed and one may clearly follow the passag of VAK fuel through the plant at least for U-flow. With help of this plot one is able to account all transfers indicated with their batch identification up to the defined step time.

The time dependent sequence of all interesting transfers is compiled in chapter 2.5.

The resulting book inventories of Pu and U are summarized in Table 5-9/10/11. The standard deviations associated with each flow were calculated according to equation (5-10):

$$(5\text{-}10)\quad \delta^2_{tot} = \left(\delta^2_c + \frac{\delta^2_r}{n}\right)_{volume} + \left(\delta^2_c + \frac{\delta^2_r}{n\cdot m}\right)_{analysis} \qquad [\%]$$

δ_c = calibration error

δ_r = precision of the measurement [%]

n = number of batches
m = number of analyses per batch

Equation (5-10) is only valid if each batch shows equal volumes and concentrations which can be roughly assumed. Estimated and experienced RSD associated with different flows and measurements can be extracted from Table 2.3-1 (chapter 2).

5.6 Investigation on Significance of the Book-Physical-Inventory Difference

The use of material balance for safeguards results in a comparison of two independent inventory determinations namely

i) book inventory (BI) indicating the amount of material which should be inside the chosen MBA and

ii) physical inventory (PI) which indicates the actual inventory measured by any kind of technique.

The difference of both is defined as material unaccounted for

$$\text{MUF} = \text{BI} - \text{PI} \tag{5-11}$$

If one assumes that the measured BI and PI values are the true values MUF should be zero in the case no diversion has taken place.

In practice however BI and PI because of measurement errors are random variables and the actual MUF represents the difference of realisations of these two random variables characterized by certain distribution functions.

Therefore the zero-hyphotesis MUF = 0 has to be proved with help of statistical techniques.

One possibility of investigating any significance of MUF is the establishment of a 95 % confidence interval [1]. In case this interval overlaps the zero-point one can accept the zero-hypothesis with a 95 % confidence level.

Another possibility is to evaluate a probability statement as follows:

$$p(\text{MUF} \leqq 0) \geqq 5\ \%$$

which represents a more strict one site test with regard to the required confidence level.

The Monte Carlo technique applied at the physical inventory determination provided already the distribution function thereof whereas a normal distribution

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[1] The confidence level can be estimated by game theoretical investigations. In common safeguards practice the 95 % confidence interval is often used which covers roughly a ± 2σ-range in case of normal distributions.

was assumed for the book-inventory determinations. Both distribution functions were accumulated with help of convolution integrals according to Annex 5-II.

The resulting MUF-distribution functions were evaluated with help of both statistical techniques as described above and all tests did prove the zero hypothesis on MUF within the chosen confidence level of 95 % as shown in Table 5-12.

5.7 Conclusions

The satisfactory results of this inventory experiment in spite of many difficulties, which were involved either by the fuel characteristics or by operation (a lot of recyclings happened in the Plutonium cycle and homogenisation procedures during head end operations could not be followed) prove the great potential of this new inventory technique.

In general the new inventory technique is most suitable for reprocessing plants with high annual throughput and comparatively small hold up because of:

i) avoiding interruptions of normal fuel processing by rinsing operations which are to precede to an adequate conventional physical inventory determination. This hits commercial requests because the operator may process more fuel per year.

ii) meeting safeguards requirements in view of timely detection of diversion /‾5-5_/ as a greater number of physical inventories per year may be performed. An example will illuminate this statement. It is expected that future large scale reprocessing plants on commercial basis will process up to 5 tons Uranium per day; thus a normal power reactor batch containing 20-30 tons of spent fuel will be processed within two weeks inclusive fuel residence time in the process. As it was experienced from present day spent fuel characteristics that the differences in isotopic abundances (major and minor isotopes) between fuel from different power reactors are big enough to generate adequate input step signals, it may be possible to perform monthly physical inventories.

Concerning the analytical load required for this inventory technique there is no additional request if operator's analyses and isotopic measurements at normal input and product sampling tanks can be used provided verification efforts are excluded.

The main problems associated with this new inventory technique can be summarized as follows:

i) Generation of an adequate input signal e.g. the superbatch size of fairly uniform isotopic composition. A good deal of the efforts to get an adequate superbatch by precampaign homogenisation of the different fuel elements forming subsequent dissolution batches can be covered with help of computer codes. It is recommended to start this selection already before shipment of the fuel elements in order to avoid time consuming rearrangements in the storage pond of the reprocessing plant.

ii) Dispersion of the isotopic step signal during its passage through the plant. Problems may occur if the hold up of the bigest tank in line e.g. a product sampling tank exceeds certain limits because it's integration effect may cause intolerable dispersion or homogenisation of the isotopic signal. These limits are mainly a function of the superbatch size and may be estimated by model simulation studies as carried out in chapter 4. From experimental data of JEX-70 one can roughly estimate that the ratio

superbatch size vs hold up of bigest tank in the line ≥ 3.

If this condition is not fulfilled one can avoid integration of the corresponding unit by operating it with lower hold up or by intermediate sampling between two increments in case the unit is installed at the end of the line (product sampling tank) just during the relative short residence time of the signal in the plant.

iii) The successful application of this inventory technique claims for experienced personal following closely input signal and system response and being able to interprete them with respect to limiting conditions of the method. Having once all data together required for one inventory determination one is able to evaluate with help of already existing Monte Carlo codes mean value and confidence limits. These codes are not plant specific but can be applied in any reprocessing plant with batchwise operation at input and product accountability stations.

5.8 References

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Table 5-1: Shipper data on irradiated fuel elements processed during JEX-70

Material	CANDU	VAK	TRINO	CDN	Starting inventory[1]	Total
No. of fuel elements	719	38	4	1507	-	-
Exposure /‾$\frac{MWd}{kg}$_7	4-8	13-22	8-14	10	-	-
U initial	9595.	2025	1237	706.	-	-
U final /‾kg_7	9504.[2]	1979	1214	694.	-	13391.
Initial U-235 enrichment /‾w/o_7	natural	2.33-2.60	2.72-3.90	4.00-4.50	-	-
Final U-235 enrichment /‾w/o_7	0.27	1.08	2.05	3.06	-	-
Pu /‾kg_7	30.35	11.45	7.11	1.37	11.8	62.08
Pu-239 /‾w/o_7	70.2	66.16	75.9	-	78.7	-
Pu-240 /‾w/o_7	24.35	18.23	15.0	-	14.6	-
Pu-241 /‾w/o_7	4.4	13.13	8.5	-	5.6	-
Pu-242 /‾w/o_7	1.05	2.48	0.6	-	0.9	-
No. of dissolutions	9	4	2	6[3]	-	-

[1] present in the rework unit to be processed after the normal run (measured data)

[2] estimated

[3] cladding and fuel were dissolved together

Table 5-2: Input signal of superbatch I (CANDU)

Batch Identif.	M_i g Pu	Pu-isotopes w/o					M_i kg U	U-isotopes w/o			
		238	239	240	241	242		234	235	236	238
1	2	3	4	5	6	7	8	9	10	11	12
AFU 600	3386.7	0.13	71.63	23.44	3.72	1.09	598.7	0.005	0.281	0.078	99.64
" 610							433.5	0.005	0.274	0.074	99.65
" 700	3381.0	0.13	71.24	23.71	3.81	1.11	612.5	0.004	0.271	0.075	99.65
" 710							391.8	0.004	0.271	0.073	99.65
" 800	3218.4	0.13	71.71	23.43	3.67	1.05	635.9	0.005	0.275	0.073	99.65
" 810							360.7	0.005	0.271	0.073	99.65
" 900	3434.4	0.12	73.05	22.43	3.41	0.985	700.4	0.005	0.302	0.066	99.63
" 910							414.6	0.005	0.306	0.063	99.63
Σ	13420.5						4148.1				
$\bar{c}$		0.127	71.914	23.247	3.651	1.058		0.0047	0.282	0.0719	99.643
10^4 var c		0.05	2020	616	68	5.9		-	0.24	0.0286	-
10^2 c		0.22	45	24.6	8.2	2.4		-	0.49	0.169	-

Table 5-3: Input signal of superbatch II (VAK)

Batch Identif.	M_i g Pu	Pu-isotopes w/o					M_i kg U	U-isotopes w/o			
		238	239	240	241	242		234	235	236	238
1	2	3	4	5	6	7	8	9	10	11	12
AFU 100	3103.5	0.597	67.78	22.13	7.53	1.97	619.5	0.012	1.056	0.228	98.70
AFU 200	2109.6	0.629	66.03	22.96	8.08	2.30	415.9	0.012	1.019	0.234	98.73
AFU 210											
" 300	4309.0	0.742	65.35	23.31	8.18	2.42	513.2	0.012	1.033	0.259	98.70
" 310							268.1	0.012	1.032	0.260	98.70
AFU 400	702.7	0.528	68.31	21.64	7.74	1.78	144.5	0.012	1.088	0.234	98.67
Σ	10224.8						1961.2				
c		0.66	66.432	22.765	7.933	2.214		0.012	1.041	0.242	98.705
10^4 var c		16.8	3990	975	269	142		-	0.621	0.486	-
10^2 c		4.1	63.2	31.2	16.4	12.		-	0.788	0.697	-

Table 5-4. Input signal of superbatch III (TRINO), IV (CDN) and V (physical inventory)

Batch ident.	M_i g Pu	Pu-isotopes w/o 238	239	240	241	242	M_i kg U	U-isotopes w/o 234	235	236	238	Superbatch
1	2	3	4	5	6	7	8	9	10	11	12	13
AFU 100	3420.3	0.44	75.46	15.74	7.18	1.19	337.8	0.014	1.796	0.247	97.94	III
" 110							235.7	0.014	1.775	0.251	97.96	
AFU 200	3149.8	0.36	78.73	14.07	5.94	0.90	301.9	0.014	2.305	0.227	97.46	
" 210							310.0	0.014	2.304	0.224	97.46	
$\sum$	6570.1						1185.5					III
$\bar{c}$		0.40	77.027	14.939	6.586	1.050		0.014	2.054	0.237	97.696	
10^4 var c		8.01	13320.	3474.	7690.	420.		-	168.	0.339	-	
$10^2 \sigma$ c		2.83	115.	58.9	87.6	20.5		-	12.98	0.58	-	
CDN	1222.9	0.065	86.63	11.79	1.35	0.164	688.1	0.0181	3.010	0.276	96.696	IV
P.I.	11800.	0.30	78.65	14.64	5.55	0.862	-	-	-	-	-	V

Table 5-5: Batch-to-batch variation vs stepsize r[1] for the different isotopes of Pu and U

Step signal	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	U-235	U-236
CANDU/VAK	7.70	14.14	82.75	4.29	10.52	1.22	4.22
VAK/TRINO	19.16	12.42	8.52	66.23	20.37	12.82	181.66
CANDU+VAK/ (TRINO+CDN+ INVENTORY)	-	-	4.69	-	-	-	-

[1] $$r = \left[\frac{varc_1 + varc_2}{(c_1 - c_2)^2} \right]^{1/2} \cdot 100 \; [\%]$$ (see equ.5-4)

Table 5-6: Plutonium physical inventory determination by means of isotope analysis at April 4th, 12.00 in material balance area MBA 21+22 and (MBA 21)

Type of mixture	Inventory [g Pu]	Relative inventory [%]	95 % Confidence interval [g Pu]	No.of Monte Carlo trials
Single components	8755 (7802)	71 (70)	± 20 (28)	-
2 components	2426 (2850)	20 (26)	+ 289 (+ 520) - 411 (- 730)	10 000
3 components	1141 (432)	9 (4)	+ 710 (+ 660) - 809 (- 740)	10 000
Total [1]	12352 (11088)	100	+ 762 (+ 725) - 887 (- 825)	-

[1] The total inventory is not obtained by adding the means of the 3 contributions but represents the mean of the distribution function relative to their sum as described in detail in Annex 5-II.

Table 5-7: Plutonium physical inventory determination by means of isotope analysis at April 25th, 14.00 in material balance area MBA 21+22 and (MBA 21)

Type of mixture	Inventory [g Pu]	Relative inventory [%]	95 % Confidence interval [g Pu]	No. of Monte Carlo trials
Single component	7672 (3786)	70 (63)	± 20 (± 38)	-
2 components	3423 (2199)	30 (37)	+ 1080 (+ 840) - 900 (- 900)	10 000
Total 1)	1108 (5979)	100	+ 1080 (+ 840) - 900 (- 900)	-

---

1) see footnote of table 5-6

Table 5-8: U-Physical inventory determination by means of isotope analysis at April 4th, 12.00 in MBA 21

Type	Inventory [kg U]	Rel. inventory [%]	95% Conf. level [kg U]	No.of Monte Carlo calculations
Single component	1425	83	+ 12/-12	-
2 components	289	17	+ 33/-35	1000
Total:	1714	100	+ 38/-40	-

Table 5-9: U-Book-inventory at April 4, 12.00 in MBA 21

Flow	kg U ± SD	
PIb.	+ 873. ± 43	
ΣAFU-RAR+JD(CANDU)	+ 9427. ± 25	
Recycled U^{IV}	+ 537. ± 5	
RAR 100 (VAK)	- 8.	
$\sum_{100}^{1900}$ 3 UP + 2 batches (PIb)	- 8973. ± 40	
ΣHAW	- 1.	± 4
ΣJWC	- 13.	
ΣASRW	- 12.	
ΣBSRW	- 1.	
ΣARIN	- 9.	
Book-inventory	+ 1820. ± 64.	

Table 5-10: Pu-Book Inventory Determination at First and Second Step Signal in MBA 21 + 22

Flow (g Pu)		April 4th, 12.00	April 24th, 14.00
i)	Beginning physical inventory[1]	+ 819 ± 45 (1σ)	+ 819 ± 45 (1σ)
ii)	Active feed (AFU)	+ 30 151 ± 115 (1σ)	+ 40 373 ± 149 (1σ)
iii)	Recycled acid (RAR)	- 401 ± 22 (1σ)	- 722 ± 40 (1σ)
iv)	Pu-final product (PFP)	- 17 600 ± 21 (1σ)	- 28 059 ± 33 (1σ)
v)	High active waste (HAW)	- 130 ± 19 (1σ)	- 175 ± 32 (1σ)
vi)	Solvent recovery waste (SRW)	- 64 ± 10 (1σ)	- 106 ± 16 (1σ)
vii)	Rinses (A/B RIN)	- 10 ± 2 (1σ)	- 18 ± 4 (1σ)
viii)	Solid waste drums	- 166 ± 18 (1σ)	- 252 ± 25 (1σ)
ix)	Book inventory	+ 12 599 ± 130 (1σ)	+ 11 860 ± 170 (1σ)

---

[1] Without 11800 g Pu in the rework unit to be processed after the normal run.

Table 5-11: Pu-Book-inventory determination at first and second step signal in MBA 21

Flow (g Pu)	April 4th, 12.00	April 24th, 14.00
i) Beginning inventory[1]	+ 261. ± 26 (1σ)	+ 261 ± 26 (1σ)
ii) Active feed (AFU)	+ 30 151. ± 115 "	+ 40 373 ± 149 "
iii) Recycled Pu (3AW)	+ 837. ± 44 "	+ 952 ± 48 "
iv) Recovered acid (RAR)	- 401. ± 22 "	- 722 ± 40 "
v) Pu-battery product (2BP)	- 19 454. ± 55 "	- 35 145 ± 90 "
vi) High active waste (HAW)	- 130. ± 19 "	- 175 ± 32 "
vii) Solvent recovery waste (SRW)	- 64. ± 10 "	- 106 ± 16 "
viii) Rinses (A/B RIN)	- 10. ± 2 "	- 18 ± 4 "
i) Book inventory	+ 11 190. ± 141 "	+ 5 420 ± 190 "

---

[1] without 11 800 g Pu in the rework unit to be processed after the normal run

Table 5-12: Final results of the inventory experiment
(Error ranges given as 95 % confidence intervals)

MBA	Steptime	April 4th, 12.00		April 25th, 14.00
		g Pu	kg U	g Pu
1	2	3	4	5
21	i) Book-inventory	11190 ± 282	1820 ± 125	5420 ± 380
	ii) Physical inventory	11088^{+725}_{-825}	1714^{+38}_{-40}	5979^{+840}_{-900}
	iii) MUF	108^{+794}_{-806}	106 ± 134	-559^{+930}_{-1110}
	iv) p (MUF ≤ 0)	43.8 %	5.7 %	89.5 %
21+ 22	i) Book-inventory	11748 ± 260	U-flow does not pass MBA 22	11860 ± 340
	ii) Physical inventory	12352^{+762}_{-887}		11080^{+1080}_{-900}
	iii) MUF	275 ± 900		700^{+1100}_{-1000}
	iv) p (MUF ≤ 0)	30 %		5.9 %

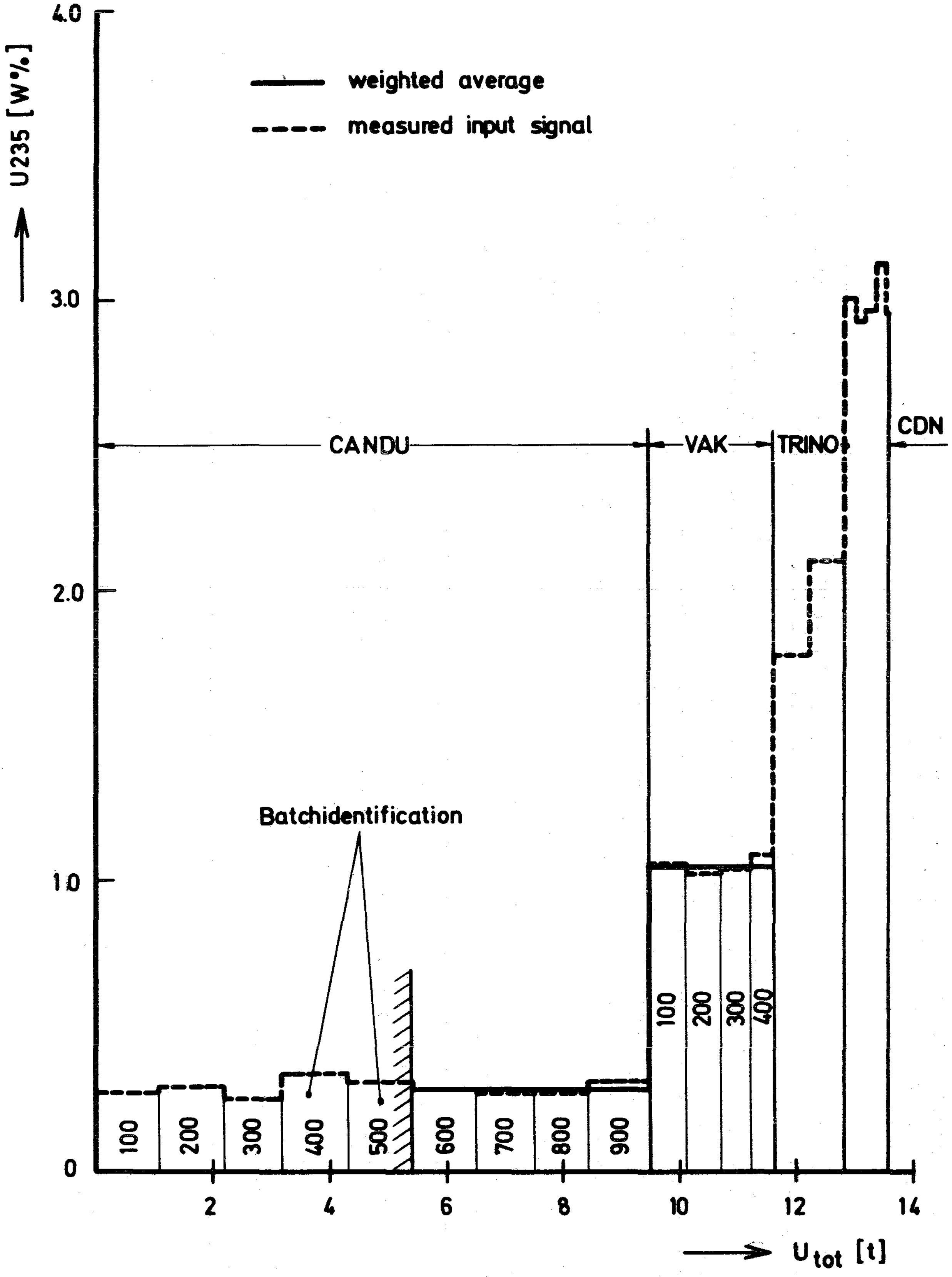


Fig. 5-1 Meas. Inputsignal (Operator's Data) U235 W/o vs. U (tot) of the U - Inventory - Experiment in EUROCHEMIC, Mol, Belgien

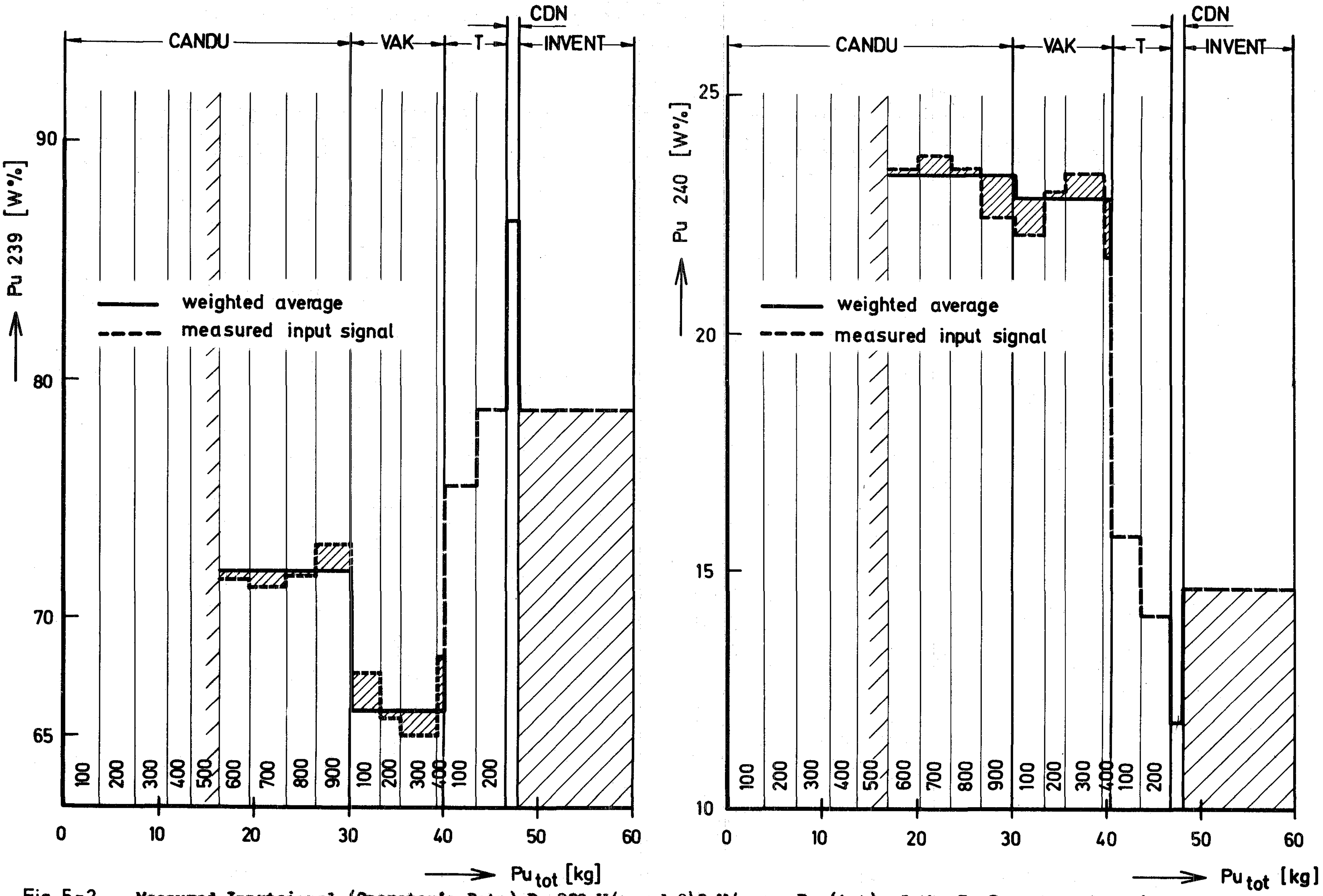


Fig. 5-2 **Measured Inputsignal (Operator's Data) Pu 239 W/o and 240 W/o vs. Pu (tot) of the Pu-Inventory-Experiment in EUROCHEMIC, Mol, Belgien**

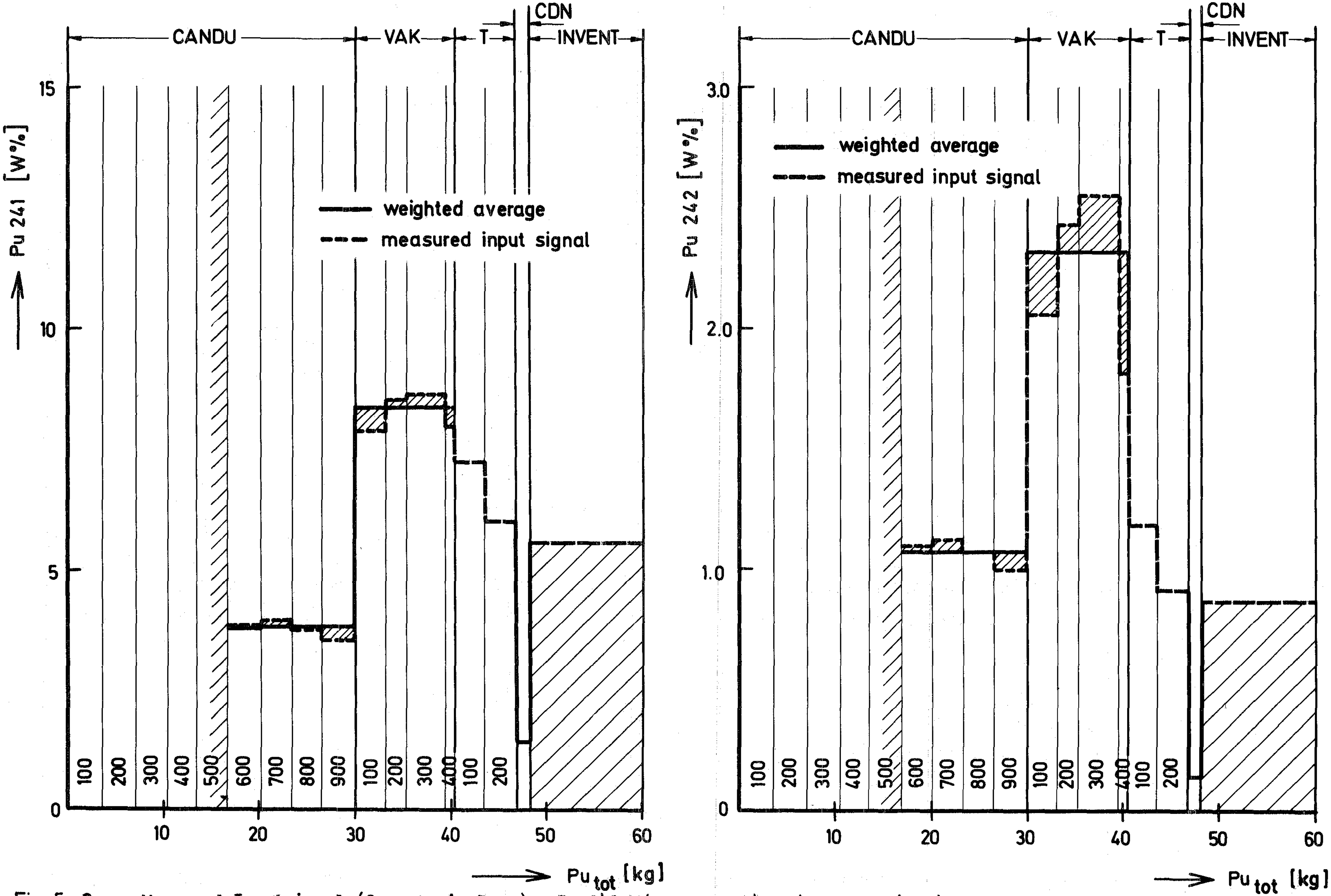


Fig. 5 - 3 **Measured Inputsignal (Operator's Data)** Pu 241 W/o and Pu 242 W/o vs. Pu (tot) of the Pu-Inventory-Experiment in EUROCHEMIC, Mol, Belgien

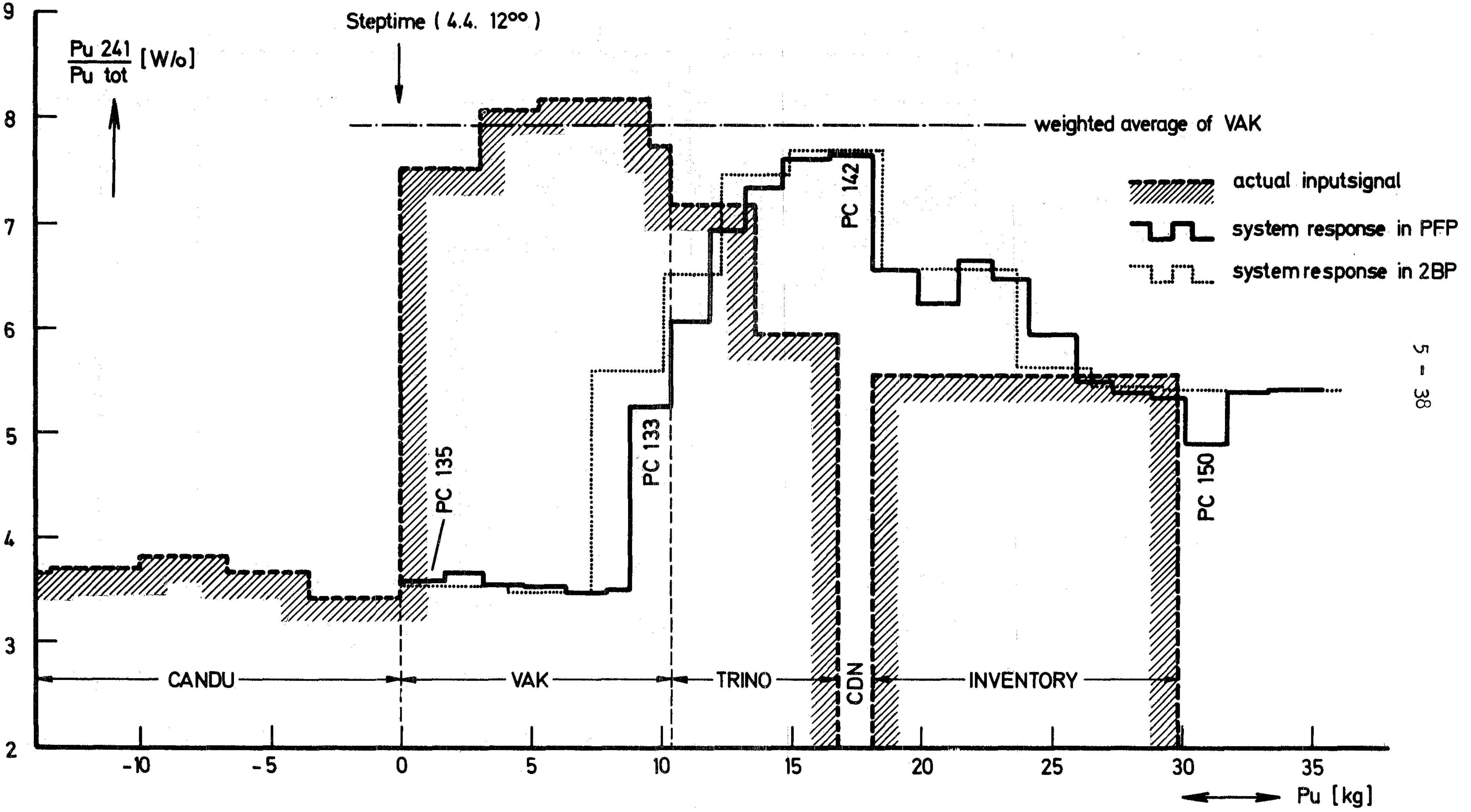


Fig. 5-4 Inputsignal and Systemresponse of Pu 241 isotope abundance

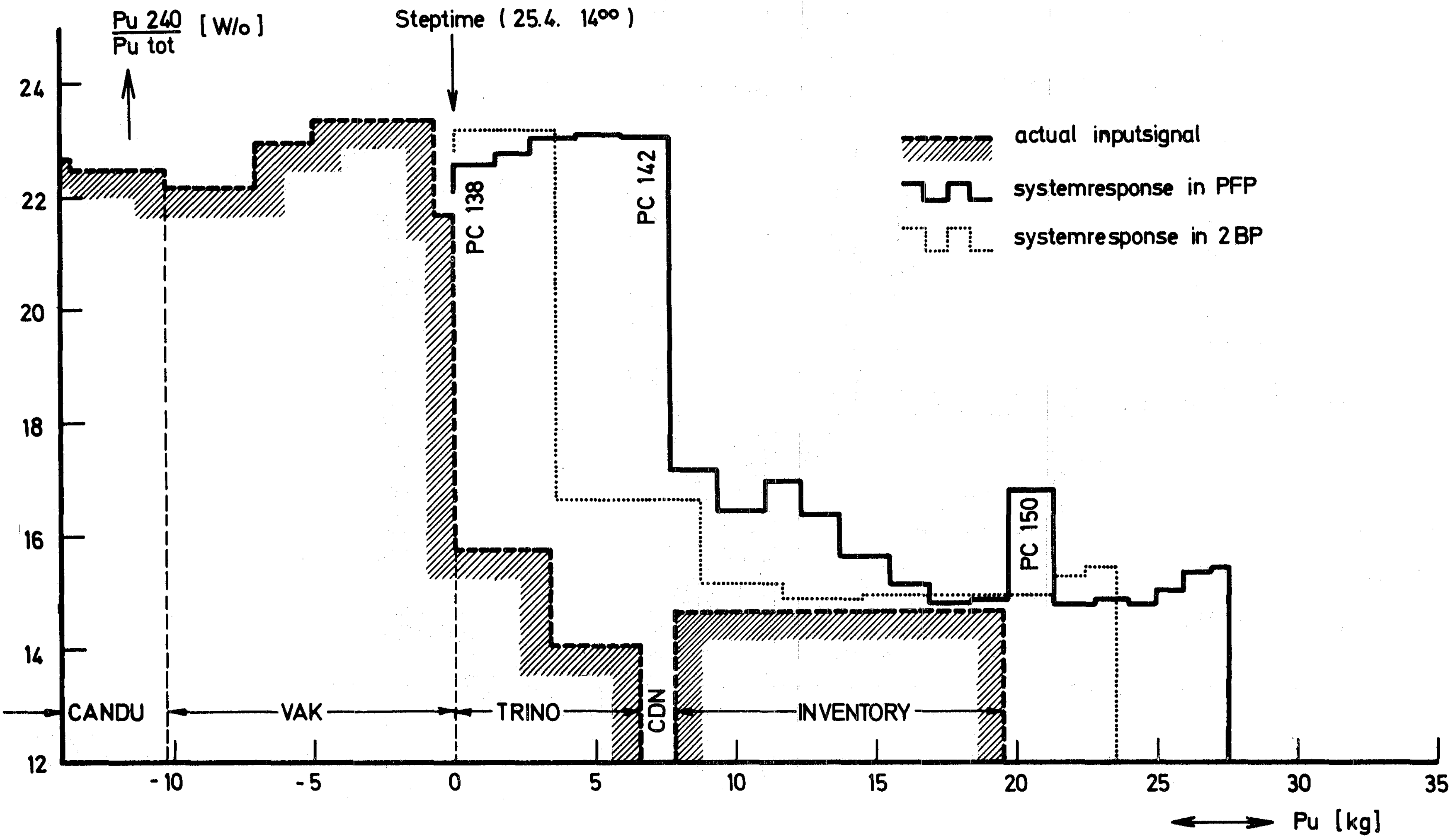


Fig. 5-5 Inputsignal and Systemresponse of Pu 240 isotope abundance

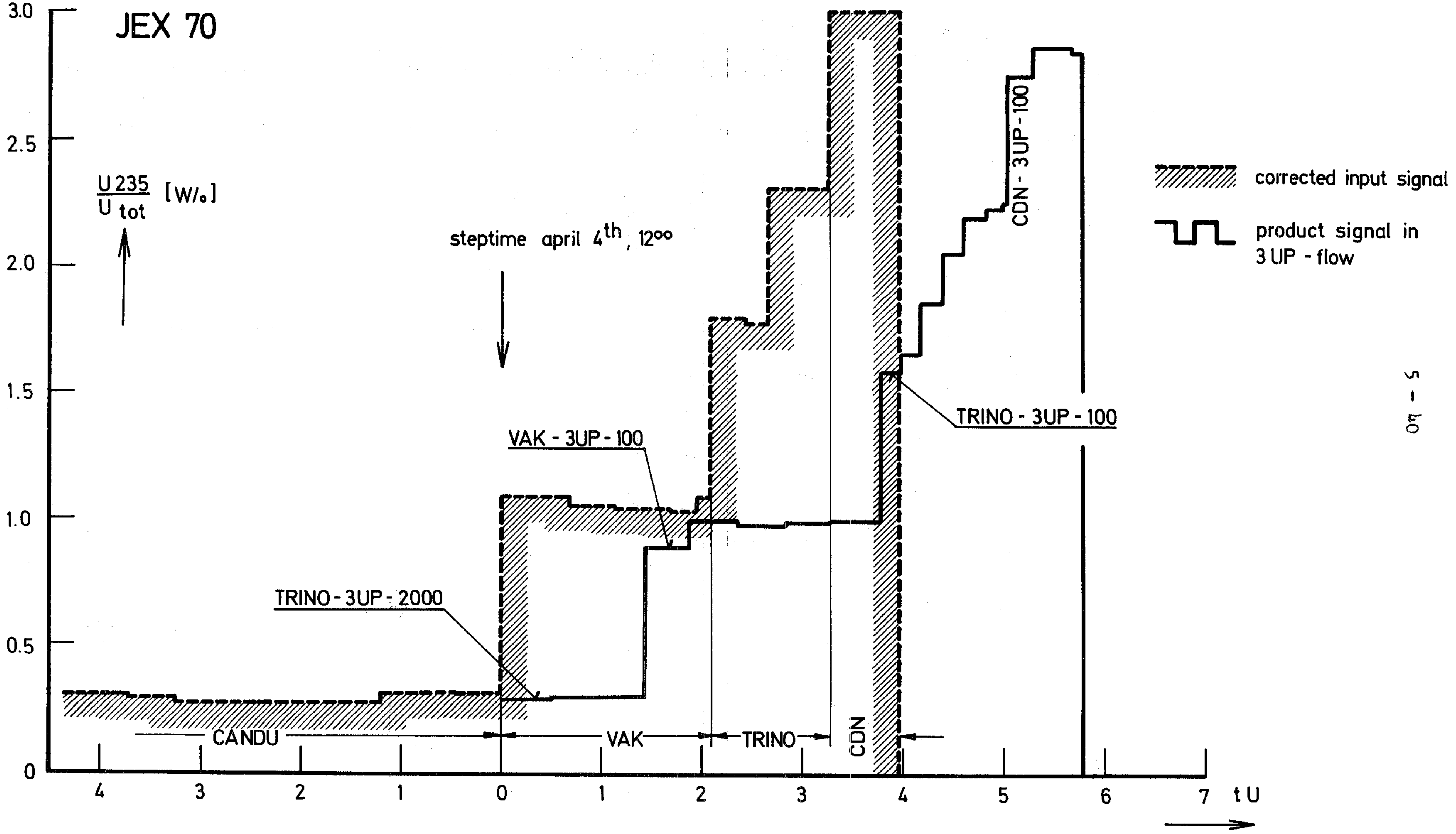


Fig. 5 - 6 Inputsignal and Systemresponse of U 235 Isotope Abundance vs. Heavy Material

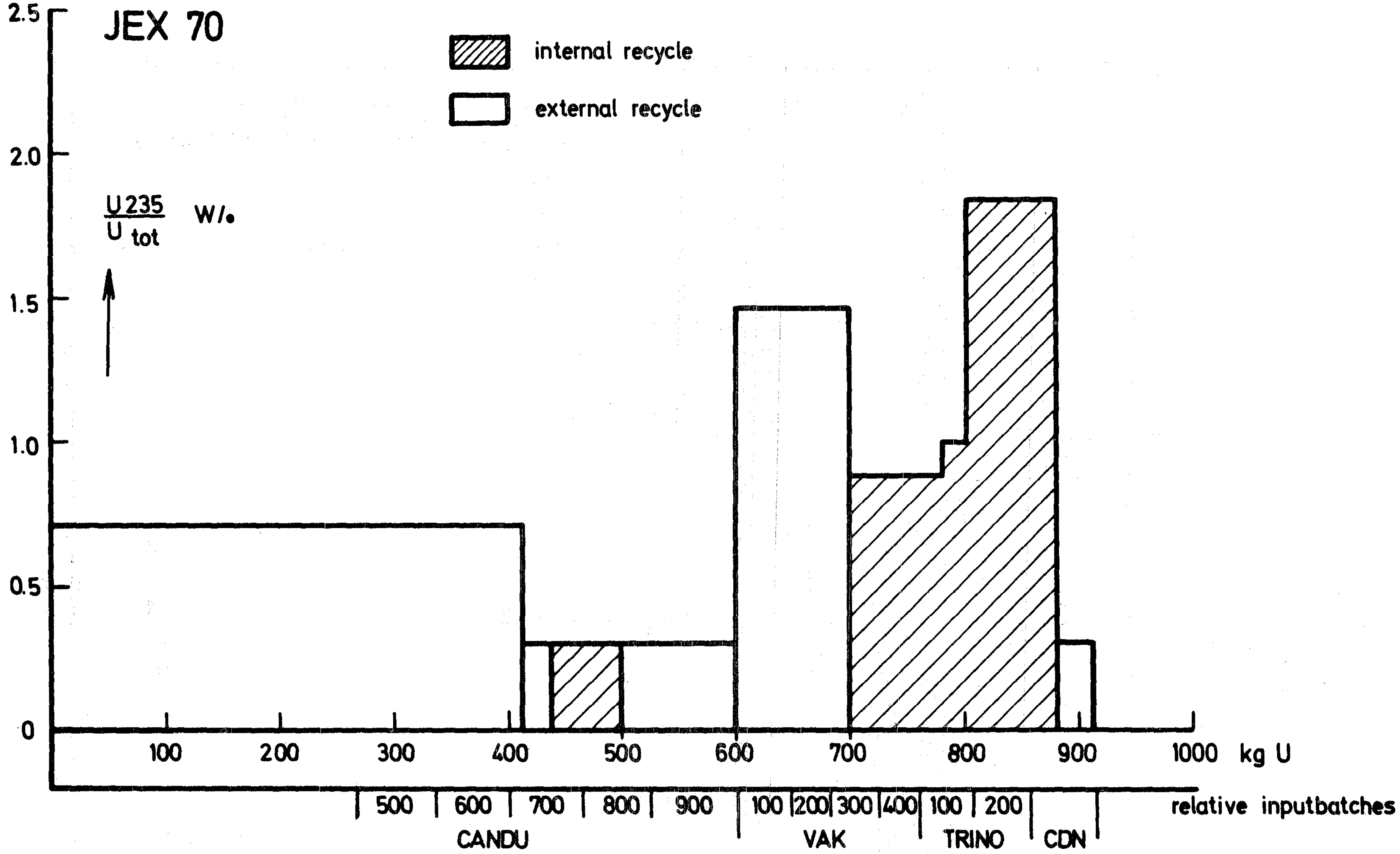
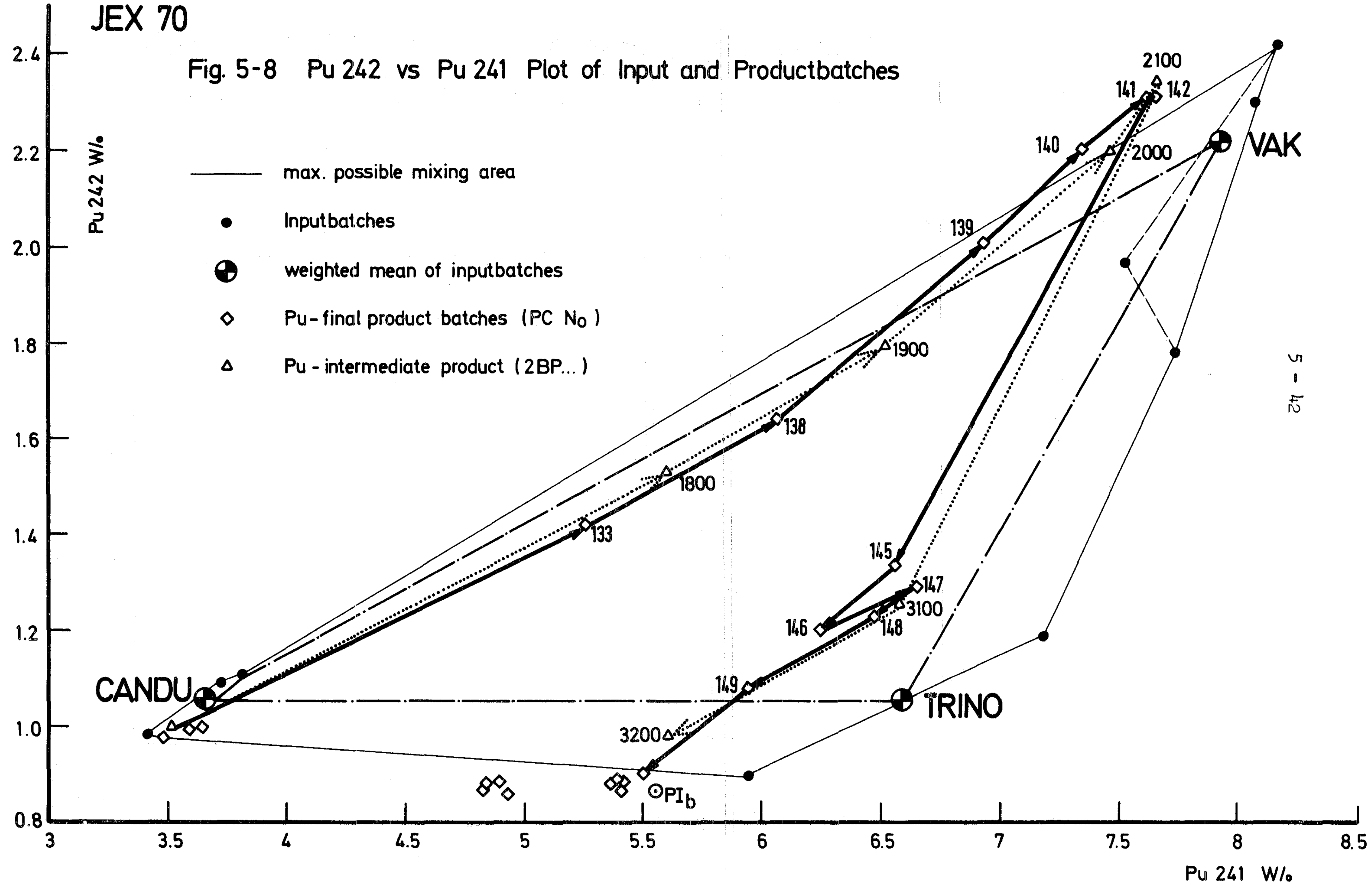


Fig. 5-7 U 235 Isotope Abundance of Recycled Uranium (BXR)

JEX 70

Fig. 5-8 Pu 242 vs Pu 241 Plot of Input and Productbatches



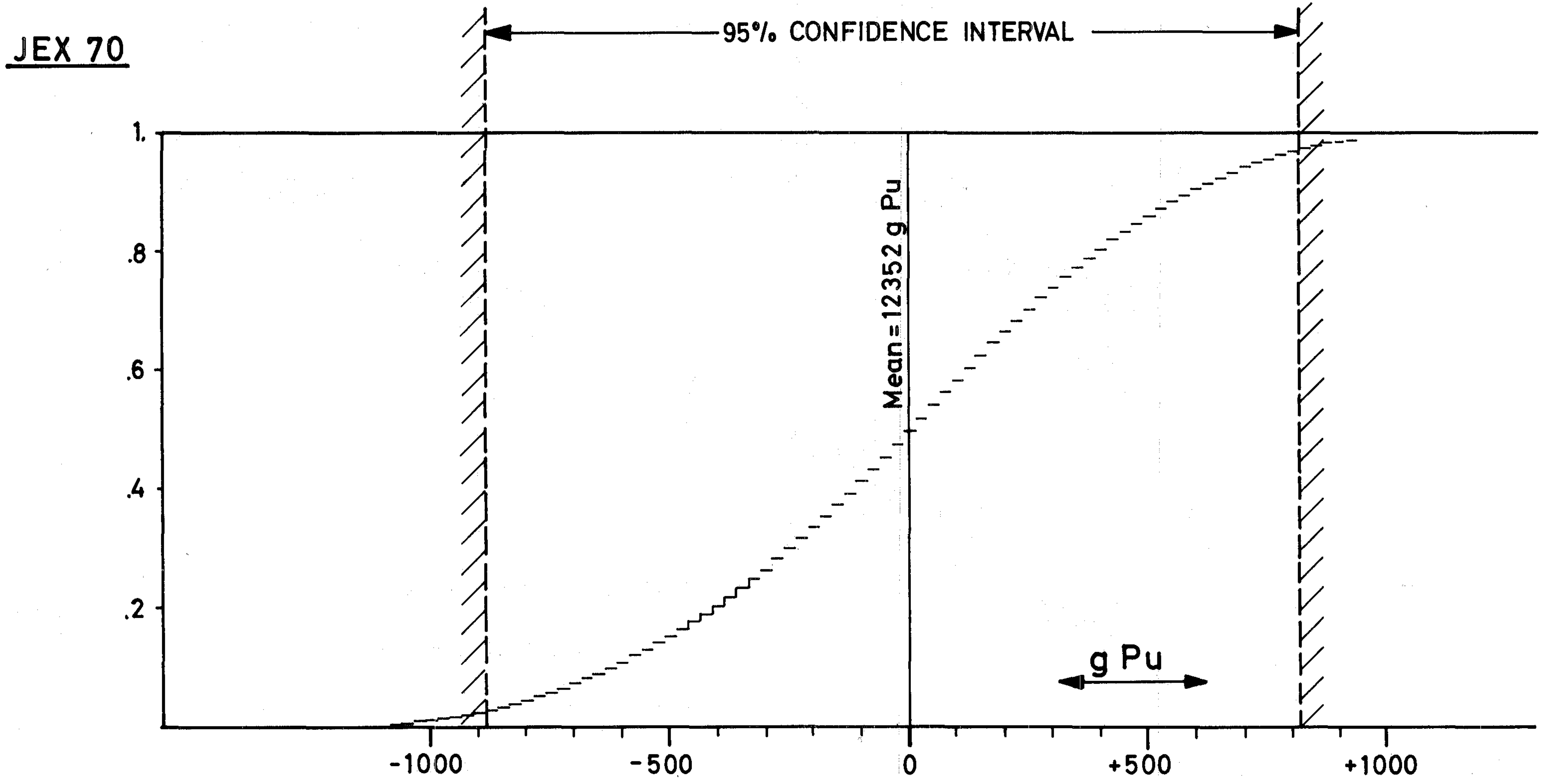
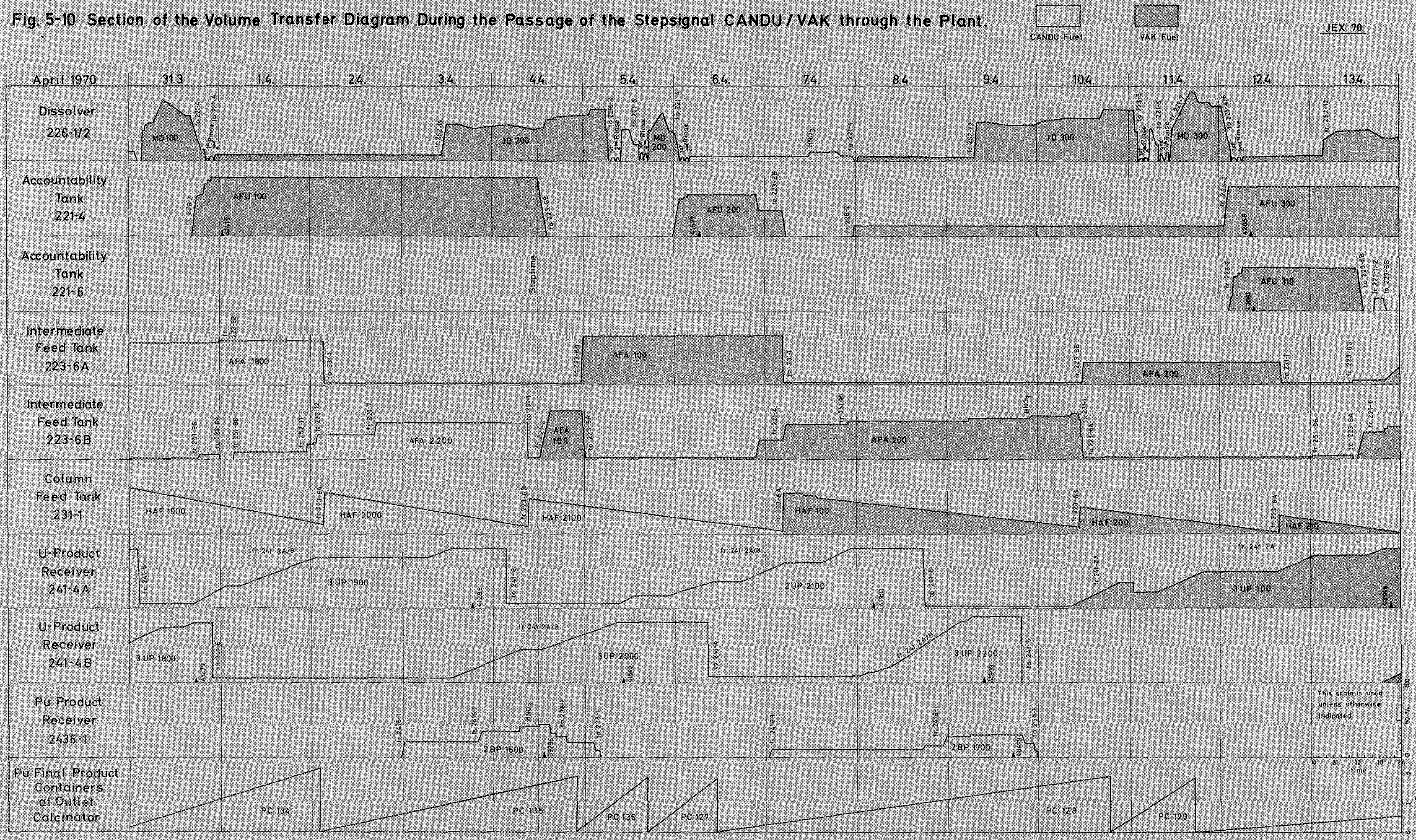


Fig. 5-9 Distribution Histogram of the total Pu-Inventory in MBA 21 and 22 at the First Isotopic Stepsignal CANDU/VAK.

Fig. 5-10 Section of the Volume Transfer Diagram During the Passage of the Stepsignal CANDU / VAK through the Plant.

JEX 70



Annex 5-I

Monte Carlo Technique Applied at Inventory Determinations for Two- and Three-Component Systems (Computer Code)

by

A. Rota

5.I.1 Two component system

As pointed out in paragraph 5.4, the use of the weighted average concentrations c_1 and c_2 may give not an unbiased estimation of H_2, the part of the PI calculated on the basis of a "two component" (single tracer) mixture. Because until now the theory is not sufficiently developed to indicate how to calculate the values of c_1 and c_2 for a better estimation of H_2, the following approach has been attempted.

Let

$$H_2 = f_2(M_i, x_i, c_1, c_2) \qquad (5\text{-}12)$$

be the correct formula (see (5-1)) to be used when the tracer concentrations for all the batches of the superbatches 1 and 2 are constant, and respectively equal to c_1 and c_2.

Let us assume now that the independent variables M_i, x_i, c_1 and c_2 are realizations of random variables everyone of which has a known prescribed pdf (probability density function). For the values M_i and x_i the pdfs have been assumed to be normal with mean values equal to the measured ones and standard deviations equal to the standard errors of the related measurements. The variables c_1 and c_2 are given by equation (5-7); in its right-hand term the numbers R_i - as already seen - are random variables uniformly distributed in the (0,1) interval. Consequently, c_1 and c_2 are also random variables, and their mean values and standard deviations may be calculated. Note that (5-7) assures that c_j assumes values inside the interval: minimum (c_i), maximum (c_i).

If in (5-12) are introduced the mean values of each independent variable, a value $\bar{H}_2$ is obtained.

The pdf of H_2 is obtained by a Monte Carlo technique: the evaluation of (5-12) is performed many times (1000-10000) and every time the independent variables are randomly selected from the above defined distributions. A frequency curve for H_2 is obtained and it is interpreted as pdf for the dependent random variable H_2.

As for (a) the function f_2 of (5-12) is not a linear function of all the independent variables in the relevant range of variation and (b) the pdf for c_1 and c_2 are not necessarily symmetric, the pdf of H_2 is not expected to be symmetric. This means, among other things, that its mean value $\overline{H}_2$ may be different from $\overline{\overline{H}}_2$.

Fig. 5.I-1 gives a block diagram of the computer code suitably written to perform the necessary calculations. Table 5.I-1 and Fig. 5.I-2 gives, as an example, the print out of the program for the calculations related to the "two component" mixture (CANDU and VAK materials, when U-235 is used as tracer isotope.

5.I.2 Three component system

In the case of a "three component " system, the theory [5-2] provides, for the calculation of the PI, the following formula.

(5-13)
$$H_3 = \Sigma_i M_i \frac{T_i}{D}$$

(i = index of the output batches resulting from the mixture of 3 super-batches)

where

$$T_i = \begin{vmatrix} 1 & 1 & 1 \\ x_i & c_2 & c_3 \\ y_i & d_2 & d_3 \end{vmatrix}$$

$$D = \begin{vmatrix} 1 & 1 & 1 \\ c_1 & c_2 & c_3 \\ d_1 & d_2 & d_3 \end{vmatrix}$$

c_j and d_j (j=1,2,3) are the concentrations of two tracers (e.g. Pu-241 and Pu-242) in the j-th input superbatch. x_i and y_i are the concentrations of the same isotopes in the i-th output batch.

The inadequacy of the theory for real cases derives from the same reasons pointed out in the case of the "two component" systems. It follows that the evaluation of the experimental data may be obtained following a procedure similar to the one outlined in the previous paragraph.

In this case, however, it is necessary to pay some attention to the fact that the selection of random values for the pairs c_j, d_j must respect the physical correlation existing between these parameters. The use of the following system

$$(5\text{-}14) \qquad c_j = \Sigma M_i R_i c_i / \Sigma M_i R_i$$

$$d_j = \Sigma M_i R_i d_i / \Sigma M_i R_i$$

logically justified as equation (5-7) (the subscript indexes have the same meaning), indicates that single values of c_j and d_j are obtained as randomly weighted means of the concentrations of the input batches c_i and d_i. It follows that, in every realization of the pair of random variables c_j, d_j, the same contribution of the individual input batches to the means must be considered. The use of the same weighting factors ($M_i R_i$) in both equations of system (5-14) assures the respect of the physical correlation existing between c and d inside each single super batch.

Provided that the conditions for the "three component" mixture are fulfilled (mainly $D \neq 0$) it is possible to use (5-12) in order to obtain the same information derived in the "two component" case.

As before, the pdf of H_3 is obtained by a Monte Carlo technique: the left term of eq. (5-13) is evaluated many times as function of independent variables randomly selected from the mentioned distributions. The analysis of the resulting sample of H_3 gives as results $\bar{H}_3$, σ_{H_3}, frequency and distribution curve of H_3.

Fig. 5.I-4 gives a block diagram of the computer code which performs the above mentioned calculations, Table 5.I-2, Table 5.I-3 and Fig. 5.I-5 gives, as an example, the results related to the "three component" system for the the Pu PI; Pu-241 and Pu-242 are the tracers used and CANDU, VAK, TRINO are the superbatch identifications (see paragraph 5.4.1).

Table 5.I-1: Program print for Monte Carlo calculations of U-inventory two component systems.

I. Input data

```
Input batches  Mi(kg U)            U235 W/o           c1 (eqn. 5-3)

                  1          8             0.2896  /
                636.2998            0.3060                 0.1463
                460.7000            0.2990                 0.1059
                651.0000            0.2780                 0.1496
CANDU           391.7998            0.2710                 0.0901
                642.2000            0.2750                 0.1476
                383.2998            0.2710                 0.0881
                744.3999            0.3020                 0.1711
                440.5999            0.3060                 0.1013

                                                      c2 (eqn. 5-3)
                  2          5             1.0601  /
                671.2000            1.0330                 0.3225
VAK             450.5999            1.0520                 0.2165
                546.8999            1.0450                 0.2628
                268.0999            1.0320                 0.1288
                144.5000            1.0380                 0.0694
```

Product batches

```
             Mp(kg U)                  U235 W/o

       1   443.6399      1.2000      0.8830      0.0050
       2   484.3799      1.2000      0.9970      0.0050
       3   474.3298      1.2000      0.9600      0.0050
       4   428.4500      1.2000      0.9840      0.0050
       5   434.4399      1.2000      0.9960      0.0050
       6    95.3600      0.3000      0.9930      0.0050
```

II. Results

II.1 Median values calculated with weighted means c_1 and c_2

```
H( 1) =  101.96
H( 2) =   39.65
H( 3) =   61.61
H( 4) =   42.30     kg U      CANDU-component in single U-product batches
H( 5) =   36.13
H( 6) =    8.30

                                                 Median value
STIMA DESUNTA DA DATI MISURATI                   289.9597  kg U
```

II.2 Mean value of Monte Carlo trials (1000)

```
VMED,VAR,SDEV,PERC   288.1104  kg U       323.6250    17.9896     6.2440
```

Table 5.I-2 Program Print for Monte Carlo Calculations of Pu-Inventory Three-Component Systems.

(Input Data)

```
    INPUT BATCH DATA
    CANDU REACTOR

    PU MASS (G)    PU-41 CONC.    PU-42 CONC.

     3434.3999         3.4100         0.9850
     3218.3999         3.6700         1.0500
     3381.0000         3.8100         1.1100
     3386.7000         3.7200         1.0900

    REACTOR  BATCHES        MEAN  VALUES

     1       4         3.6514         1.0586
    VAK REACTOR

    PU MASS (G)    PU-41 CONC.    PU-42 CONC.

     3103.5000         7.5300         1.9700
     2109.5999         8.0800         2.3000
     4309.0000         8.1800         2.4200
      702.7000         7.7400         1.7800

    REACTOR  BATCHES        MEAN  VALUES

     2       4         7.9318         2.2147
    TRINO REACTOR

    PU MASS (G)    PU-41 CONC.    PU-42 CONC.

     3420.2998         7.1800         1.1900
     3149.7998         5.9400         0.9000

    REACTOR  BATCHES        MEAN  VALUES

     3       2         6.5855         1.0510

    OUTPUT BATCH DATA

        PU-MASS (G)         PU-41 CONC.         PU-42 CONC.
NO.  VALUE     ST.DEV.   PERCENT   ST.DEV.   PERCENT   ST.DEV.

 1 1722.8198   17.2232    6.5600    0.0624    1.3400    0.0134
 2 1623.9399   16.2394    6.2400    0.0624    1.2000    0.0120
 3 1268.8398   12.6884    6.6500    0.0665    1.2900    0.0129
 4 1378.8298   13.7883    6.4700    0.0647    1.2300    0.0123
 5 1810.2500   18.1025    5.9400    0.0594    1.0800    0.0108


INIZIALIZZAAIONE GAUSS   357  INIZIALIZZAZICNE RANDOM   357.0


NUMBER OF TRIALS = 10000
```

Table 5.I-3: Program Print for Monte Carlo Calculations of Pu-Inventory Three Component Systems.

(Results)

```
PLUTONIUM INVENTORY (3 COMPONENTS MIXTURE) = G 1156.82

TRIAL  PU-41/1 PU-42/1    PU-41/2 PU-42/2    PU-41/3 PU-42/3       D(k)        H_3(k)

  250   3.6807  1.0753     7.7753  2.1215     6.3966  1.0068    -3.1221     1024.5908
  500   3.6845  1.0681     7.9623  2.2595     6.3778  1.0024    -3.4899      850.1619
  750   3.6670  1.0635     7.9273  2.2109     6.8331  1.1089    -3.4397     1547.8901
 1000   3.6868  1.0678     8.0677  2.3110     6.7975  1.1005    -3.7238     1349.2751
 1250   3.6634  1.0593     8.0967  2.3455     6.6458  1.0651    -3.8104     1405.8572
 1500   3.6400  1.0539     7.9507  2.2332     6.4367  1.0162    -3.4607      994.0913
 1750   3.6059  1.0462     7.9589  2.2509     6.7701  1.0941    -3.6033     1335.8127
 2000   3.6781  1.0656     8.0002  2.2917     6.6089  1.0564    -3.6333     1118.6252
 2250   3.6561  1.0613     8.0779  2.3129     6.0736  0.9312    -3.6009      463.3394
 2500   3.7091  1.0715     7.8487  2.1305     6.8313  1.1084    -3.1534     1560.9438
 2750   3.7119  1.0802     7.9315  2.2301     6.3804  1.0030    -3.3945      896.1802
 3000   3.5581  1.0320     7.9636  2.2343     6.8959  1.1236    -3.6098     1580.5120
 3250   3.7280  1.0872     8.0596  2.3176     6.5627  1.0456    -3.6678     1109.2256
 3500   3.5893  1.0402     7.7816  2.1315     6.0760  0.9318    -3.1681      481.5728
 3750   3.7462  1.0891     7.9480  2.2209     6.3449  0.9947    -3.3380      915.4729
 4000   3.6201  1.0505     8.0387  2.2498     6.8784  1.1195    -3.6031     1486.0286
 4250   3.6542  1.0576     7.9357  2.2051     6.6683  1.0703    -3.4040     1277.9197
 4500   3.6895  1.0714     8.0228  2.2975     6.6551  1.0672    -3.6542     1373.0630
 4750   3.6832  1.0662     7.8700  2.1522     6.6824  1.0736    -3.2260     1281.1736
 5000   3.6277  1.0506     7.9279  2.1803     6.8146  1.1045    -3.3683     1509.2212
 5250   3.6905  1.0704     7.7938  2.1476     7.0738  1.1652    -3.2558     1914.4958
 5500   3.6294  1.0562     7.8291  2.1482     6.6728  1.0714    -3.2595     1214.5369
 5750   3.7443  1.0887     8.0404  2.3140     6.2193  0.9653    -3.5627      667.2920
 6000   3.7145  1.0819     8.0808  2.3023     6.8004  1.1012    -3.6817     1597.6587
 6250   3.6668  1.0569     8.0170  2.2443     6.7041  1.0787    -3.5115     1333.8894
 6500   3.6346  1.0529     7.7518  2.0863     5.9767  0.9086    -3.0145      444.7131
 6750   3.6841  1.0679     8.0697  2.3143     7.0840  1.1675    -3.8008     1648.8291
 7000   3.5570  1.0256     8.0225  2.2786     6.8012  1.1014    -3.7264     1355.1489
 7250   3.6399  1.0588     7.9148  2.2028     6.6645  1.0694    -3.4147     1217.8215
 7500   3.5836  1.0350     7.8151  2.1263     6.1401  0.9468    -3.1631      352.6511
 7750   3.6262  1.0509     7.9366  2.2227     6.5060  1.0324    -3.4545     1032.4756
 8000   3.5874  1.0360     8.0813  2.3407     6.5239  1.0366    -3.8289     1101.4741
 8250   3.6114  1.0431     7.9338  2.1974     6.4097  1.0099    -3.3739     1030.8423
 8500   3.6342  1.0519     7.8260  2.1468     6.9394  1.1337    -3.2760     1544.4487
 8750   3.6699  1.0644     7.8996  2.2166     6.5745  1.0484    -3.4145     1109.8967
 9000   3.7177  1.0768     7.9623  2.2354     6.3462  0.9950    -3.3926     1024.3081
 9250   3.5321  1.0190     7.9484  2.2180     6.5795  1.0496    -3.5189     1082.0349
 9500   3.6959  1.0720     7.9020  2.1983     6.6668  1.0700    -3.3546     1234.9937
 9750   3.5673  1.0321     8.0299  2.2785     6.5888  1.0517    -3.6785     1135.9932
10000   3.7426  1.0857     7.8327  2.1488     7.0224  1.1531    -3.2109     1670.5618

MEANS  3.6495  1.0573     7.9186  2.2060     6.5757  1.0479    -3.4011     1140.9507

TRIAL N.   P.I.(MEAN VALUE)   STANDARD DEV.   PERCENT ST. ERROR


 10000         1140.95           415.37             36.41
                                              20    27    59   102   130   138   158   183   192   202   220
                                                   239   257   287   307   332   359   382   432   478   537
                                                   494   485   471   402   411   302   312   299   282   257
 PROCESS INVENTORY DISTRIBUTION,Step=50 g Pu       238   228   230   181   174    96    61    28     7     1
```

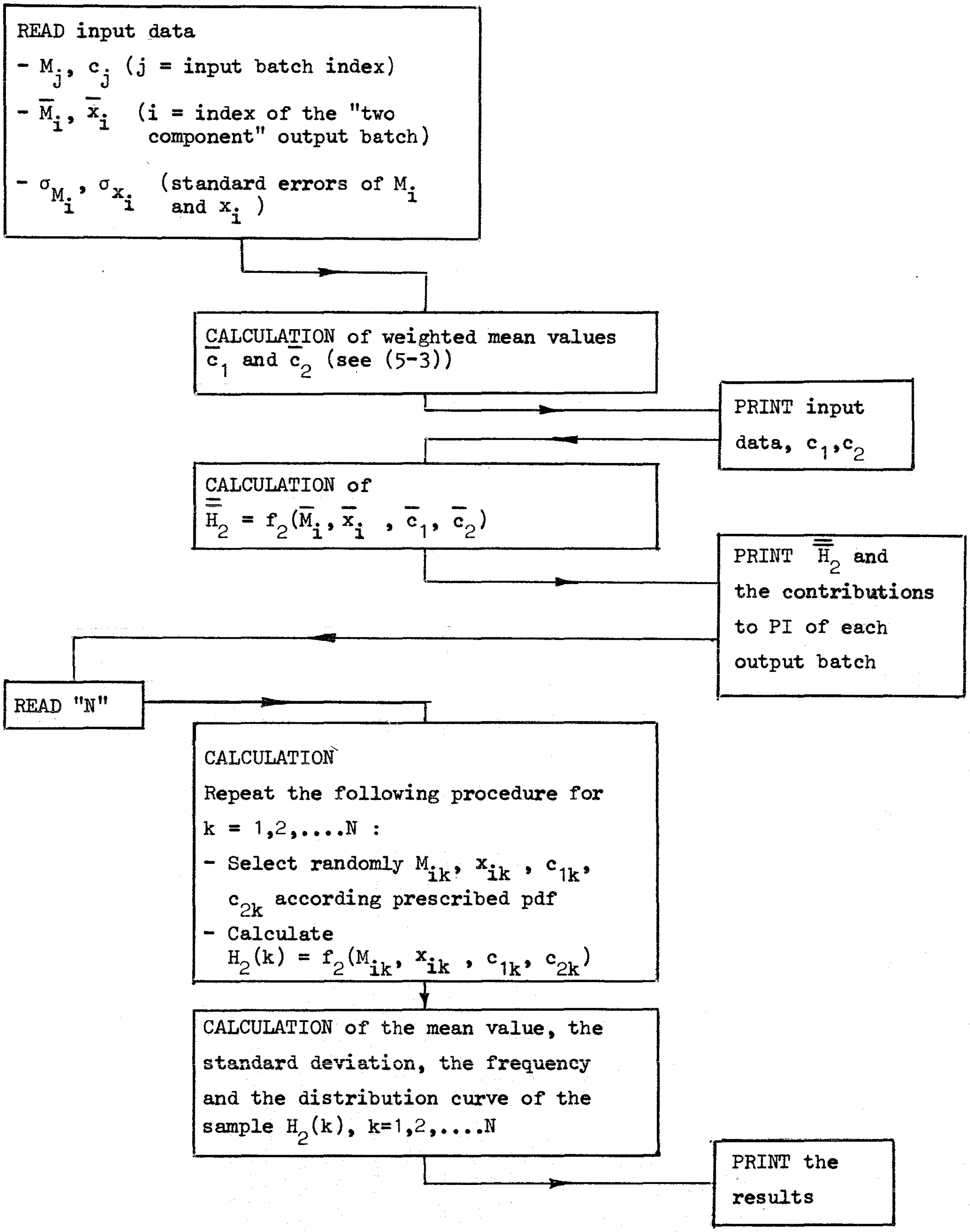
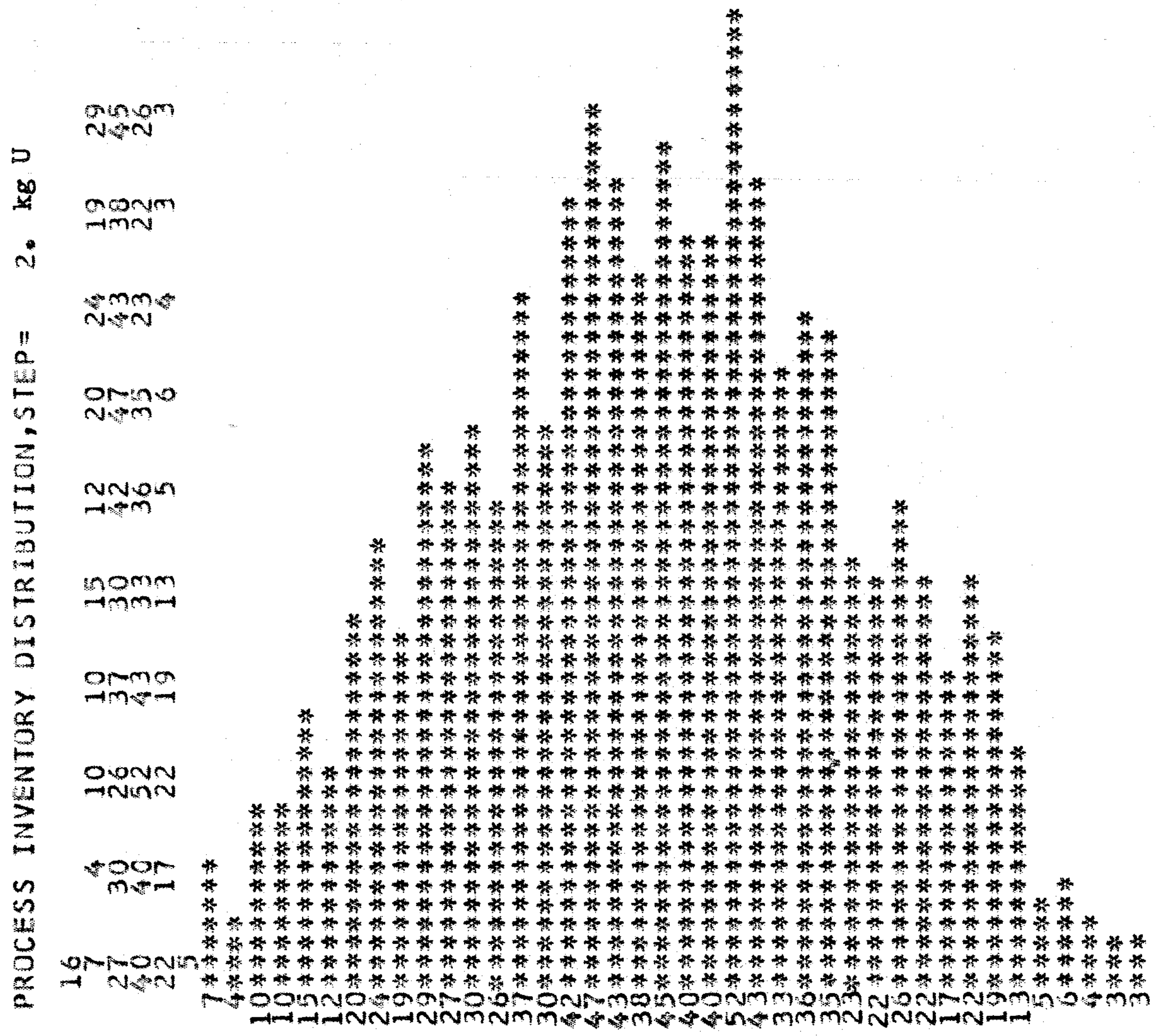


Fig. 5.I-1: Block diagram of the computer code for the evaluation of the "two component" experimental data.

Fig.5.I-2 : Frequency Histogram of U-Inventory Results Calculated by Means of Monte Carlo Technique (two Component System only)



```
   16    23    27    37    47    62    74    94   118   137
  166   193   223   249   286   316   358   405   448   486
  531   571   611   663   706   739   775   810   833   855
  881   903   920   942   961   974   979   985   989   992
  995  1000




 1*
 2**
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```

Fig. 5.I-3: Distribution Histogram of
U-Inventory Results Calculated
By Means of Monte Carlo Technique
(Two Component System Only)

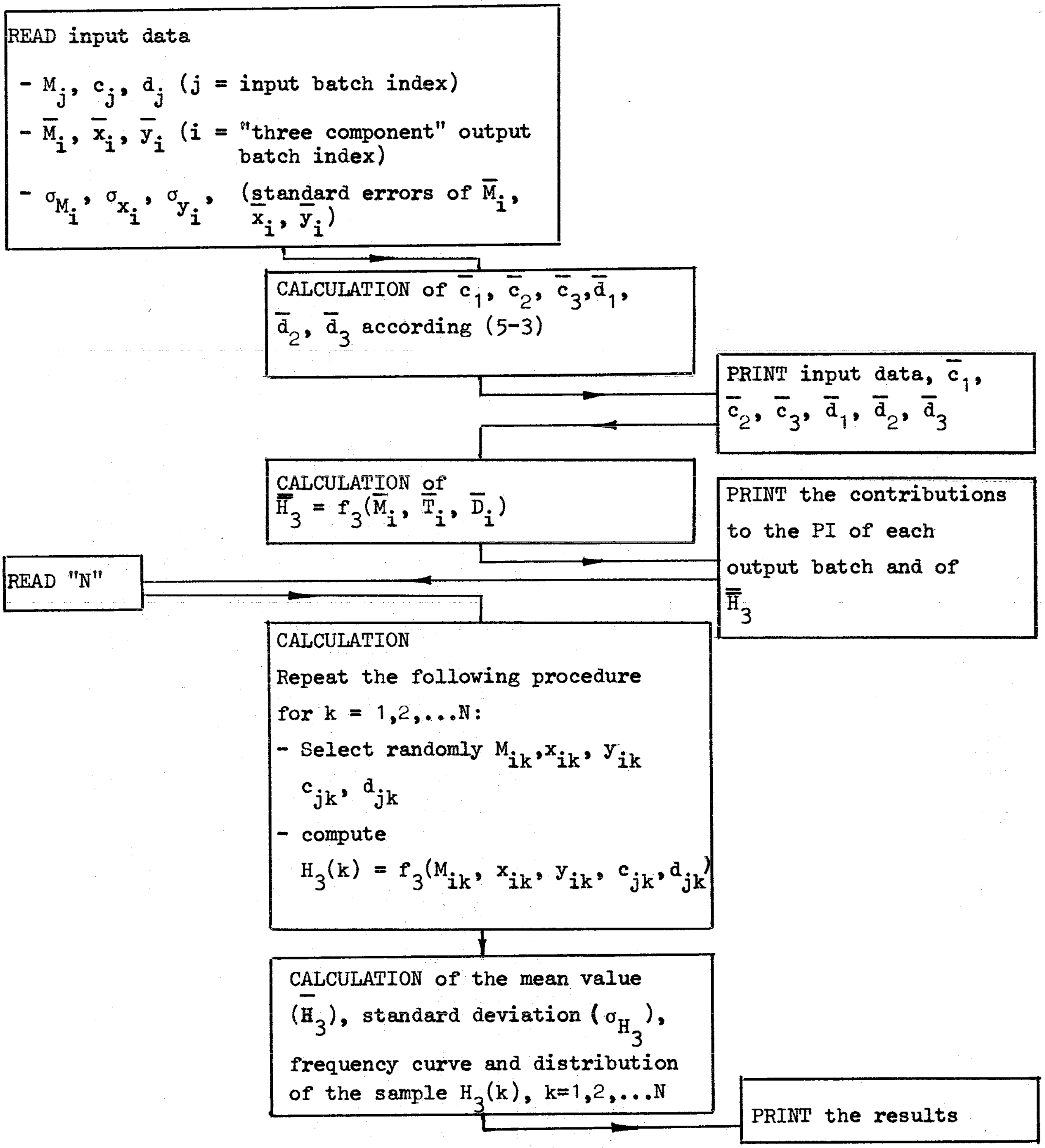


Fig. 5.I-4: Block diagram of the computer code for the evaluation of the "three component" experimental data.

Annex 5-II

Evaluation of Frequency and Distribution Function of Total Physical Inventory and Book-Physical-Inventory Difference by Means of Convolution Integrals.

by

A. Rota

5.II.1 General

The evaluation of the JEX-70 PI data from the point of view of the safeguard involves mainly the comparison between the PI itself and the correspondent Book Inventory (BI). In turn PI is obtained as sum of two or three terms, namely

$$PI = H_1 + H_2 \ (+H_3)$$

where H_j is the contribution to the PI of the "j component" system (see, e.g. Table 5.6).

The most important result for safeguard purposes concerns the value of MUF, as usual defined by the relationship:

$$MUF = BI-PI$$

As far as all the involved parameters can be interpreted as random realizations of unknown quantities, it is important to know, for each of them, the pdf. The pdf of H_1, H_2, H_3, and BI are known: the pdf.s of BI and H_1 are assumed to be normal; those of H_2 and H_3 are calculated from the experimental results by the procedure described in Annexe 5.I and are available in form of hystograms. (Analytical expressions for H_2 and H_3 are not available.)

5.II.2 Evaluation of convolution integrals

The calculation of the pdf and of the distribution of PI and MUF is obtained by convolutions of the type here described. Let p and q be independent random variables and f_1 and f_2 the corresponding pdf.s. The analytical expressions for the pdf.s of the random variables

$$s = p+q$$
$$r = p-q$$

are given, respectively by the following convolution integrals:

$$g(s) = \int f_1(t) \cdot f_2(s-t)dt$$
$$h(r) = \int f_1(r+t) \cdot f_2(t)dt$$

As far as, in the present case the f are, or may be expressed, in form of hystograms, the above integrals are discretized as follows:

(5-15)
$$G(S) = \sum_{K1}^{K2}{}_K(F1(K).\ F2(S-K)$$

$$H(R) = \sum_{J1}^{J2}{}_J F1(R+J).F2(J)$$

(The capital letters used for the function names and vairables corresponds to the small letters, which indicate continuous function and variables).

Let N_{11}, N_{12} ($N_{11}<N_{12}$) define the integer interval outside which F1 is identically zero and let N_{21},N_{22}($N_{21}<N_{22}$) have the same meaning for F2. From these limits it is possible to deduce analogous intervals for the functions G and H:

$$N_{11} + N_{21} < S < N_{12} + N_{22}$$

$$N_{11} - N_{22} < R < N_{12} - N_{21}$$

As it useless to include in the sums (5-5) those terms that certainly do not give any contribution, the sum limits result defined as follows:

$$K1 = \text{Max}\ (N_{11},\ S-N_{22})$$
$$K2 = \text{min}\ (N_{12},\ S-N_{21})$$
$$J1 = \text{Max}\ (N_{21},\ N_{11}-R)$$
$$J2 = \text{min}\ (N_{22},\ N_{12}-R)$$

A computer code that makes use of the above derived relationships has been set up. Particular care must be paid for a correct definition of the histogram intervals and for their homogenization.

The code allowed the calculations of the pdf.s and of the distributions for both PI and MUF. An example of part of the results obtained is given in Fig.s 5.II-1 and 5.II-2.

Fig. 5.II-1: Frequency Function of the Book-Physical Inventory Difference of Pu in MBA 21 at Step time April 25th,14.00 hours.

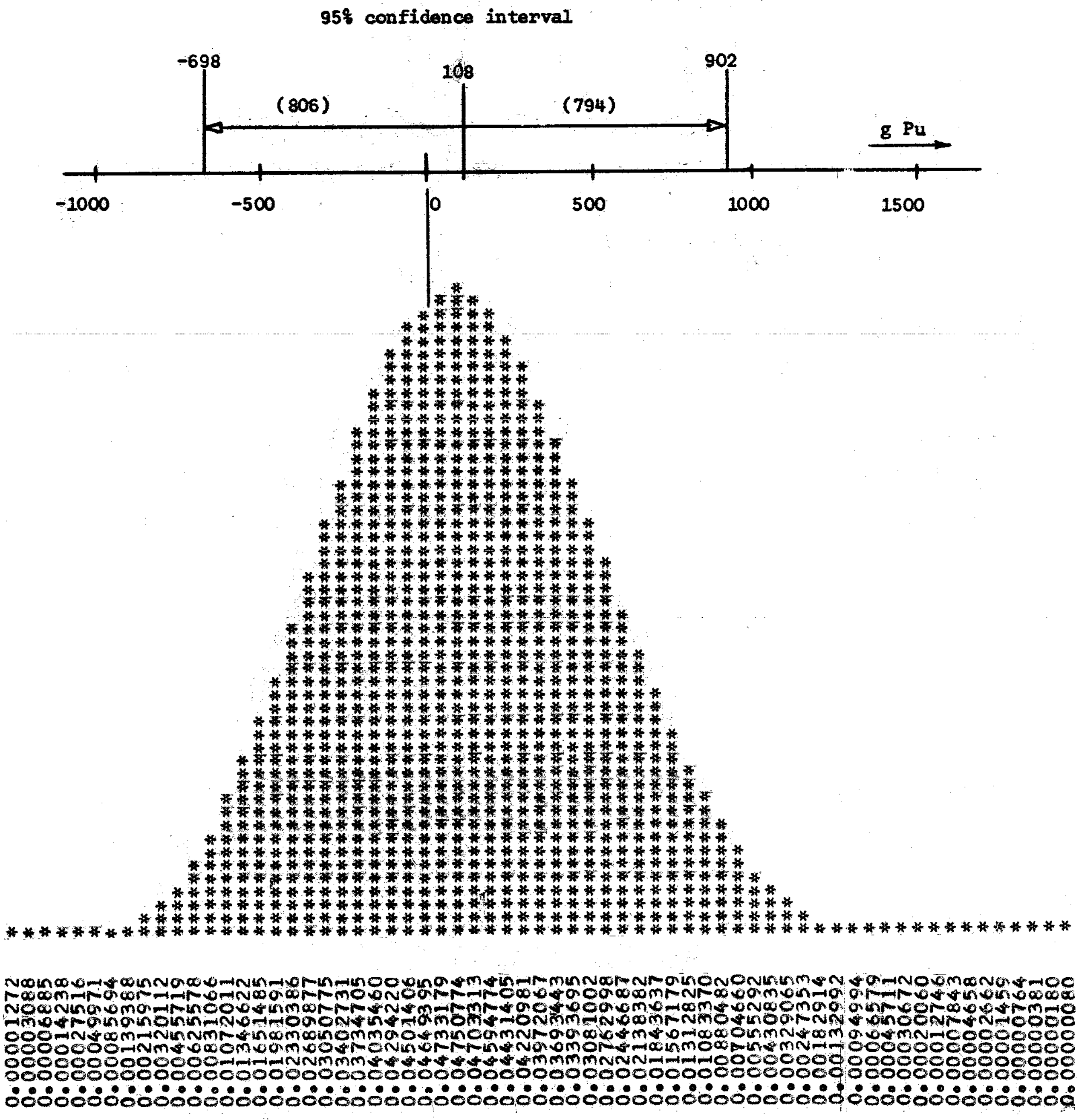
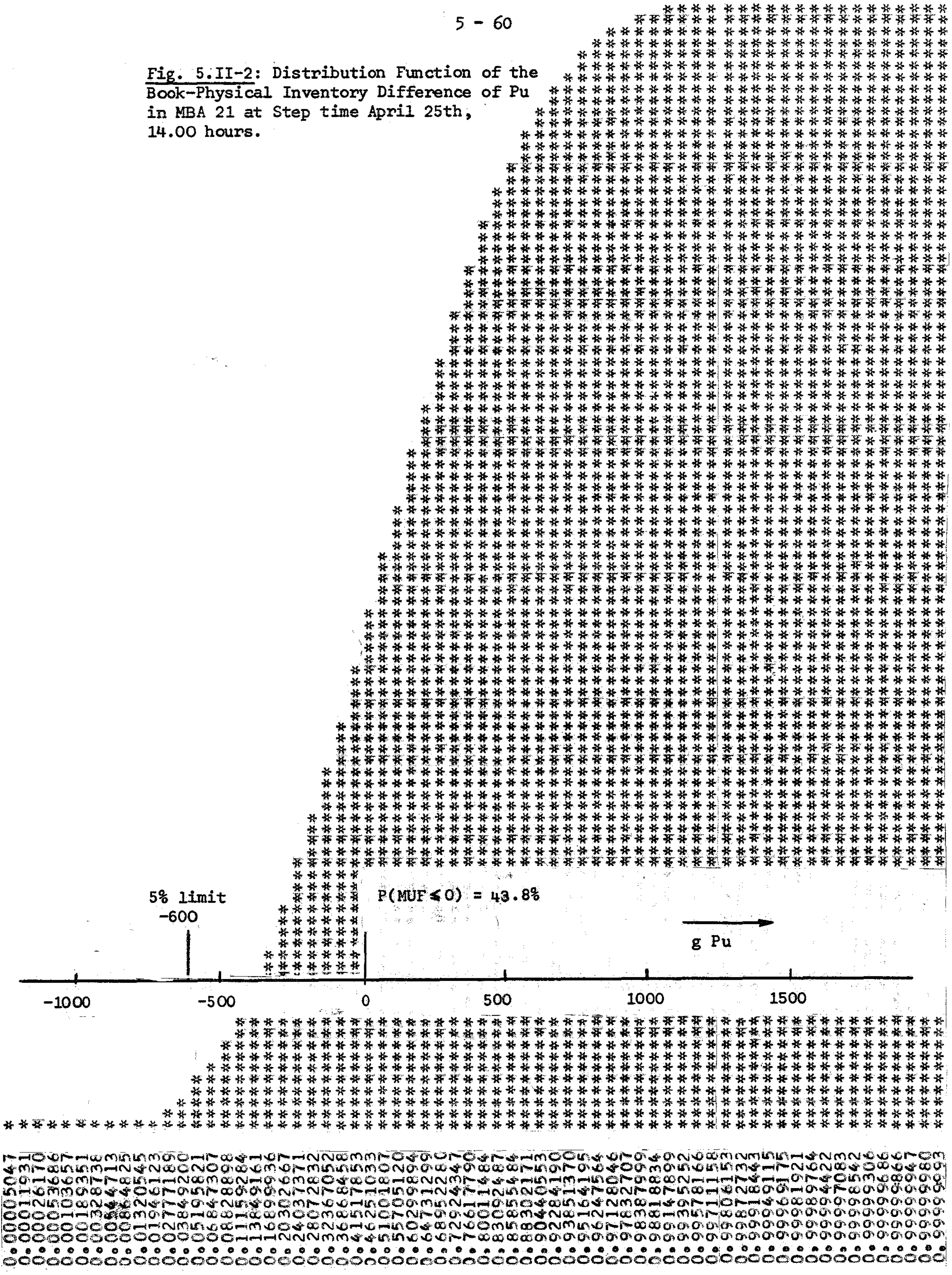


Fig. 5.II-2: Distribution Function of the Book-Physical Inventory Difference of Pu in MBA 21 at Step time April 25th, 14.00 hours.



Annex 5.III

Analytical Error Analysis on Inventory Determination of Two-Component Systems

by

R. Avenhaus and R. Kraemer

5.III.1 General

Subject of this appendix is an analytical derivation to quantify approximately in advance the variance of the self tracing inventory determination taking into account

i) variance of weighing and analysis on product batches (var M)

ii) variance of isotopic measurements (var x)

iii) batch-to-batch variance of the tracer isotope in one superbatch (var c)

5.III.2 Error propagation

In case only 2 component mixtures occur in subsequent product batches the inventory equation (5-16) is valid.

$$I = \sum_a M_a \frac{x_a - c_2}{c_1 - c_2} \tag{5-16}$$

Assuming that the relative standard deviation of each independant parameter in equ. (5-16) is small (e.g. $< 10\ \%$) one may apply the Gaussian error propagation formula:

$$\text{var } I = \left(\frac{\partial I}{\partial M_a}\right)^2 \text{var } M_a + \left(\frac{\partial I}{\partial x_a}\right)^2 \text{var } x_a + \left(\frac{\partial I}{\partial c_1}\right)^2 \text{var } c_1 + \left(\frac{\partial I}{\partial c_2}\right)^2 \text{var } c_2 \tag{5-17}$$

with

$$\left\{\begin{array}{l} \dfrac{\partial I}{\partial M_a} = \sum\limits_a \dfrac{x_a - c_2}{c_1 - c_2} \;;\quad \dfrac{\partial I}{\partial x_a} = \sum\limits_a \dfrac{M_a}{c_1 - c_2} \\[2ex] \dfrac{\partial I}{\partial c_1} = \sum\limits_a M_a \dfrac{-x_a + c_2}{(c_1 - c_2)^2} \;;\quad \dfrac{\partial I}{\partial c_2} = \sum\limits_a M_a \dfrac{x_a - c_1}{(c_1 - c_2)^2} \end{array}\right. \tag{5-18}$$

It is assumed that the relative standard deviations

$$\delta M = \frac{\text{var } M_a}{M_a} \;;\quad \delta x = \frac{\text{var } x_a}{x_a} \tag{5-19}$$

are constant, whereas var c_1 and var c_2 represent the batch-to-batch variance which is still to be developed.

When entering (5-18) and (5-19) in (5-17) and dividing by $(5\text{-}16)^2$ one gets (5-20)

$$(5\text{-}20) \qquad \frac{\text{var } I}{I^2} = \delta_M^2 + \left(\frac{\Sigma M_a x_a}{\Sigma M_a (x_a - c_2)}\right)^2 \delta x^2 +$$

$$+ \frac{\text{varcc}_1}{(c_1 - c_2)^2} + \frac{\text{var } c_2}{(c_1 - c_2)^2} \cdot \left(\frac{\Sigma M_a (x_a - c_1)}{\Sigma M_a (x_a - c_2)}\right)^2$$

With help of Fig. 5.III-1 some approximations can be estimated.

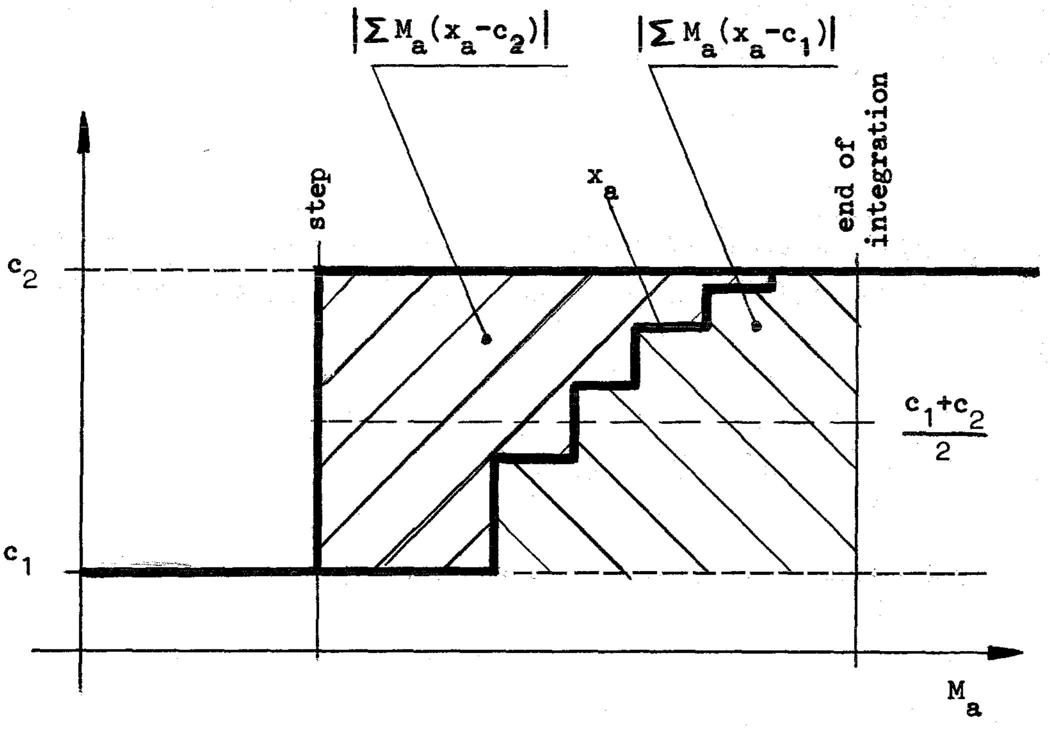


Fig. 5.III-1: Step function and system response

Looking at Fig. 5.III-1 one realizes that both shadowed areas are approximately equal which depends of course from the integration limits. But from former experience this assumption is justified which brings the factor of $\text{var}(c_2)$ to one.

A further approximation

$$\Sigma M_a x_a \approx \frac{c_1 + c_2}{2} \Sigma M_a \qquad \text{and}$$

$$M_a \approx M = \text{const}$$

simplifies in equ. (5-20) the factor of δ_x^2 thus it remains:

$$(5\text{-}21) \qquad \frac{\text{var I}}{I^2} = \delta M^2 + \frac{(c_1+c_2)^2\delta_x^2 + \text{var } c_1 + \text{var } c_2}{(c_1-c_2)^2}$$

5.III.3 Batch-to-batch variance (var c)

Let the random variable c be the batch weighted isotopic mean concentration in one superbatch. Then an unbiased estimate for the expectation value Ec of c_i is given by

$$(5\text{-}22) \qquad \hat{E}c = \frac{\sum\limits_i M_i c_i}{\sum\limits_i M_i} \qquad \text{[W/o]}$$

where the c obtained in the single input batches (M_i) are considered as realisations of this random variable c.

The batch-to-batch variance is defined as the variance of c; an unbiased estimate of the batch-to-batch variance is given by

$$(5\text{-}23) \qquad \hat{\text{var}}\ c = \frac{1}{1-\frac{\sum\limits_i M_i^2}{(\Sigma M_i)^2}} \; \frac{\sum\limits_i M_i(c_i-\hat{E}c)^2}{\Sigma M_i}$$

for, as one can show,

$$E\ \hat{\text{var}}\ c = E(c^2) - (Ec)^2 = \text{var } c.$$

In case all $M_i = M = \text{const}$ equ. (5-23) becomes

$$(5\text{-}24) \qquad \hat{\text{var}}\ c = \frac{1}{1-\frac{nM^2}{(nM)^2}} \; \frac{M\sum\limits_i(c_i-\hat{E}c)^2}{nM} = \frac{1}{n-1}\sum_i (c_i-\hat{E}c)^2$$

which clarifies the meaning of the first factor in equ. (5-23).

JEX - 70

Charpter 6

Minor Isotopes Safeguards Techniques-
Application of Isotopic Correlations
to Spent Fuels of JEX - 70+)

by

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+) ref. No. BNWL-SA-3749

ABSTRACT

Data from the MOL III experiment are used to demonstrate that the Pu and U isotopic data from the head end dissolver accountability tank can be used successfully to verify the Pu content of a reactor loading. It is shown that the data can also be used to confirm that the material which has been dissolved originated in the designated reactor by utilizing the characteristics of the inherent element and isotopic constitutent makeup of the dissolved material. In this sense the results provide a method of characterizing the reactor under consideration further by improving the reactor parameter estimates. Since the data from a commercial reactor loading is from one of a series of repeated reactor loadings the results should exhibit a statistical regularity and this property can be used in estimating the present results from historical results and in anticipating and predicting future repeated reactor loading output results.

The data from the MOL III experiment and particularly from the CANDU reactor indicate that average U and Pu isotopic data from dissolver batches clearly portray the underlying functional relationships between Pu, U, and their isotopic compositions. Thus an excellent basis is provided for judging the consistency of the data.

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ABSTRACT

Minor Isotopes Safeguards Techniques - Application of Isotopic Correlations to Spent Fuels of JEX-70 +)

By

D. E. Christensen, R. A. Schneider and K. B. Stewart

6.1. INTRODUCTION

Minor Isotopes Safeguards Techniques, denoted by the acronym MIST, is a programmatic title used in the United States to identify a collection of safeguards techniques which depend on the use of the isotopic compositions of the nuclear materials. These techniques utilize all the isotopes present at normally measurable amounts. A key part of the MIST program is the safeguards application of isotopic correlations. It is in that context of the MIST program that this section of the MOL III Experiment (JEX-70) has been designated MIST applications.

The potential safeguards value of isotopic correlations arises from the inherent relationships between the formation of Pu and the growth and depletion of the U and Pu isotopes during the irradiation process. As a result of the underlying interdependence provided by these relationships, the isotopic composition data tend to be internally self-consistent and at the end of irradiation, the isotopic compositions of U and Pu give testimony to the Pu content and confirm previous safeguards information about the fuel.

The key point for the application of these principles is at the input accountability tank at the chemical processing plant. Here, in many current processes, the unaltered ratios of the important nuclides are present in the dissolver solution. Current practice for input accountability in

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+) Work Done Under the Sponsorship of the U.S. Arms Control and Disarmament Agency and the U.S. Atomic Energy Commission.

reprocessing spent power reactor fuel is to measure the total U, total Pu, and the corresponding U and Pu isotopic compositions for each batch. From data previously obtained on slightly enriched U fuels, the following empirical generalizations were apparent.

A. The integrating effect of dissolving whole rods and bundles provides an unusually high degree of consistency in the burnup relationships when viewing data from successive chemical plant input batches of the same spent fuel.

B. Spent fuel data from the same reactor, having the same design and initial enrichment, portray the sets of burnup relationships which trace smooth curves over a wide range of exposure. In addition, some of the relationships between Pu content and the isotopic compositions were linear and have a consistency equivalent to the measurability of the relationship.

From the evidence, several potentially valuable safeguards applications were recognized by workers in both Europe(1) and the U.S.(2,3) These applications include verification of the Pu content of spent fuels and confirmation of previous safeguards information.

6.1.1. Verification of the Pu Content of Spent Fuels

It was recognized that the correlation relationships may be used to verify the Pu content of spent fuels in two main ways. The first approach, the historical method, is based simply on accumulating the data (Pu/U ratios and U and Pu isotopic compositions on dissolved batches of spent fuels) for a particular reactor and fuel design, developing the correlations and then applying the correlations to future similar spent fuels. It was also recognized that both the facility operator and the safeguards agency could use the historical method as a cross check on input measurements of successive batches.

A second method of potential application is to use the correlation relationships as a means of verifying those input batches which are measured by the plant operator only. That is to say the agency establishes relationships between the variables by using data from a few batches measured by the agency. The plant operator data on other batches, should, within the limits of statistical error, then bear the same relationships. In practice, both methods could be used simultaneously in that the safeguards agency could always make some redundant measurements but could vary the intensity of independent measurement with the nature and extent of the previously established data base. Again, it was recognized that the safeguards agency as well as the facility operator could use the isotopic correlations developed from chemical plant data to test the consistency of measurements made on a series of input batches.

6.1.2. Confirmation of Previous Safeguards Information

The continuous nature of the burnup paths and the feature that they are characteristic of spent fuel from a given reactor can be used to confirm previous safeguards information. Typical applications would include confirmation of the initial enrichment, the reactor type, and the exposure. When extensive historical data are available, the confirmation may be extended to include reported changes in fuel design and reactor operating conditions.

Since much of the previous experimental work, particularly the U.S. work, was limited as to reactor type and fuel design, it was important that the concepts be tested and demonstrated on a broader scale. The MOL III experiment which included spent fuel from a CANDU reactor (natural U, heavy water moderated) offered an excellent opportunity to test and demonstrate the concepts further.

During the planning stage of the MOL III experiment, the following objectives were formulated for the isotopic correlation part of the experiment:

1. Develop from the input accountability data and the preprocessing data the relationships between Pu concentration in the fuel and the U and Pu isotopic compositions. Similarly develop the relationships which provide the internal consistency checks on isotopic composition measurements made on successive input batches of the same fuel type.
2. Test the constancy of certain relationships by comparing the observed batch to batch variation with the apparent measurability of the variables.
3. Using the results of 1 and 2 above, illustrate the various potential safeguards applications of the isotopic correlation technique and the extent to which such application can be applied in a quantitative manner.

During the planning stage, it was well recognized that full achievement of these objectives might be limited by practical considerations. Two possible obstacles existed. The first limitation stemmed from the expected fairly narrow exposure range of the CANDU fuel as well as the fact that the fuel could not be segregated according to exposure. As a consequence, there was a good possibility that successive dissolution batches might be too uniform in exposure. In addition, the nature of Eurochemic head end process is such that many of the input batches do not contain the unaltered ratios of the key nuclides as present in the spent fuel. This occurs because normally, the fuel is declad by chemical attach which could preferentially dissolve a "richer" outer layer of the fuel rods. Also, the declad fuel is usually dissolved in recycle acid which often times contains significant quantities of U and Pu. The "true" ratios of the nuclide in the spent fuel are then arrived at by making a correction for the quantities and isotopes added with the recycle acid. Here it was expected that the effect would be to increase the variation of the input data rather than to prevent the realization of the objectives of the experiment. By contrast, if successive dissolution batches turned out to be of nearly the same exposure, then the correlation part of the experiment would reduce largely to a measurability test. Fortunately, a useful exposure range of about 1850 MWD/tonne U did result for the dissolution batches of the CANDU fuel.

6.2. SUMMARY AND CONCLUSIONS

Provisional accountability data reported by Eurochemic on input batches as well as preirradiation data were used to form isotopic correlations. These were developed in some depth for CANDU and CdN fuel. The limited number of input batches for TRINO and VAK fuel precluded similar consistency checks for those fuels. The data were treated from the standpoint of random error, since only plant data were available at the time of writing. It is planned to consider the effects of systematic error (biases) when the data from the other participating measurement groups are available.

The relationships of safeguards interest were examined by quantitative methods of statistical analysis and by graphical means. The between-batch consistency for dissolution batches of the same fuel was also compared to the apparent measurability of the nuclide ratios deduced from duplicate ratio measurements made on the same dissolution batch. The results are illustrated in detail in the subsequent parts of this report.

6.2.1. Verification of Pu Content

Since the CANDU reactors represent a class of reactors which produce Pu from a uniform starting material (natural U), special emphasis was given to CANDU fuel. Results show that ^{235}U depletion, ^{236}U growth, and the $^{240}Pu/^{239}Pu$ ratio all provide useful historical cross-checks of the Pu content. Thus, for the processing of more CANDU fuel which was irradiated under similar conditions, one would expect to see the values of the relationships repeated within their limits of uncertainty as shown below:

Expected Eurochemic Measured Values for Similar Future CANDU Fuels

$\frac{Pu/U}{^{235}D}$	$\frac{Pu/U}{\Delta^{236}U}$	$\frac{Pu/U}{^{240}Pu/^{239}Pu}$
7458 ± 1.3%	45581 ± 2.4%	10043 ± 1.4%

where the limits of uncertainty are at the 90% confidence level.

^{235}D = wt.% $^{235}U_o$ - wt.% $^{235}U_f$. It should be noted that the values and corresponding uncertainties shown above are based on the assumption that the plant measurement system reproduces itself. Changes in the measurement method or shifts in measurement biases could result in values of somewhat different magnitudes and uncertainties. The same rationale applies to redundant measurements made by other parties using different methods and mass spectrometers. Values for the relationships useful in verifying Pu content were also obtained for TRINO, VAK, and CdN fuels. Again, these "historical" bases could be applied to future cores from those reactors if sufficient supporting data exist to assure that those factors which control the conversion ratio are the same. In general, it has been found that the conversion ratio for identical conditions is fairly constant over a wide range of exposure. However, parameters, such as the initial enrichment, cladding, fuel design, fuel-to-moderator ratio, that influence the conversion ratio, also change the relationships. Although in many cases those changes are small and can be predicted by theory with some exactness, the best use of historical values for the relationships is in truly iterative situations. When the expected changes in the relationships between successive cores from a given reactor are large, the safest approach appears to be that of placing more emphasis on increasing the number of independent safeguards measurements.

An appreciation of the general agreement expected between the measured values for the isotopic correlations obtained during the MOL III experiment and corresponding historical values can be found in the table on page 9 of this Summary. The table compares measured values with reactor statements for CANDU fuels. It is not, however, a direct comparison, but rather a comparison with predicted values based on previous experimental data. Table IV on page 22 in the body of the text also shows some direct comparisons with previous measurements for TRINO and VAK fuels for the term $\frac{Pu/U}{^{235}D}$ where ^{235}D is defined as the depletion in ^{235}U.

The consistency found for the isotopic correlations can also be used to advantage in minimizing the number of independent measurements made by the safeguards agency. For example, dissolution batches of fuel from the same reactor which differ only in exposure (e.g. same conversion ratio) form a homogeneous population in that all have the same correlation relationships Here random sampling for verification is possible. This is demonstrated for CANDU fuel in Table II on page 13 where it can be seen that the independent measurement of any one batch would confirm plant measurements made on all batches.

6.2.2. Confirmation of Previous Information

The measured isotopic and Pu concentration data for CANDU fuel clearly confirm previous safeguards information about the fuel. This is shown below by the very close agreement between observed values and values stated by the reactor operator on the preprocessing data sheet.

Table I

Measured Versus Reactor Stated Values for CANDU Fuel

Comparison Unit$^{(1)}$	Measured By Chem. Plant	Stated By Reactor
$\frac{Pu/U}{^{235}D}$	7458	7320
$\frac{Pu/U}{\Delta^{236}U}$	45581	47860
$\frac{Pu/U}{^{240}Pu/^{239}Pu}$	10047	10300
Average MWD/tonne U	∿5950	∿6000
Wt. % ^{239}Pu	72.31	72.55
Wt. % ^{240}Pu	22.94	22.48
Wt. % ^{235}U	0.2857	0.2715
Wt. % ^{236}U	0.0697	0.0673

(1) Weighted Average of all 9 Batches

In addition to the confirmatory checks shown in the above table, the initial enrichment (natural U) was confirmed by graphical means. Similar agreements were found for the other reactors. However, only limited supporting data were available to insure the validity of these comparisons.

6.2.3. Internal Consistency of the Data - Verification of Analytical Measurements

The internal consistency of the isotopic and plutonium concentration data may also be used as a means of checking analytical measurements for random errors. A data point is considered for possible remeasurement or other confirmatory tests on the basis that it is not consistent with the main body of data. Two complementary methods of consistency testing - graphical and statistical analyses - are described in the main body of the text. It should be noted that this phase of the data analysis effort is a basic part of the overall safeguards application. It is the first step in Pu verification, rather than a separate and unrelated effort. Pu verification subsequently uses the isotopic correlations as a vehicle for testing whether the reported Pu/U ratio is biased by comparison to history or to current independent measurements. The internal consistency test does not reveal, persistent, proportional biases, rather it serves to reveal any data point which is not consistent with the majority of the data points.

6.2.4. Potential for Improving Reactor Predictions

Another potential application illustrated by the experimental data is the value of providing a data feed-back loop from the chemical plant to reactor for the purpose of improving the quality of reactor calculations. The relationships themselves are a good example of this. For example, the term $\frac{Pu/U}{^{235}D}$ appears to be constant over a wide range of exposure. Thus each batch measurement provides one experimental estimate of this constant. A complete campaign can provide a number of replicates. Similar theory-experiment check points exist for the Pu concentration and U and Pu isotopic data. Attention is drawn to this aspect of potential application only to encourage those engaged in reactor calculations to consider the data from this standpoint. The subject is not discussed further in this report.

6.3. NUMERICAL RESULTS

6.3.1. Verification of Pu Content

The data consist of measurements made on a total of 20 dissolution batches which were processed during the MOL III experiment. The six different initial enrichments of the 20 batches of reactor fuels were as follows.

Reactor	Batches	Initial Enrichment (^{235}U Weight Percent)
CANDU	9	0.7114
CdN	5	4.48
VAK	2	2.33
	1	2.51
	1	2.40*
TRINO	1	2.92
	1	3.31

*An average value of the 2.33 and 2.51 enriched fuels was assumed.

The initial U data were obtained from the data sheets as received except for CANDU fuel which initially was natural U fuel. In the correlation investigation, no attempt was made to use any data received other than the numbers listed as totals for each batch which had been corrected for jacket dissolution and recycle acid.

For safeguards purposes the provisional input accountability data as received need to be transformed into more appropriate variables. Table II gives a display of some of the data in a manner which is useful for further analyses. Here ^{235}D and $\Delta^{236}U$ mean, respectively, the depletion in ^{235}U and the increase in ^{236}U induced by reactor irradiation.

The table itself indicates some of the general properties that the data suggest. That is to say each reactor and enrichment has its own "fingerprint" as regards to the manner in which the measured variables behave. Even with the sampling variation which is present, the possible contamination with Pu and isotopic material in the recycle acid, and the existence of measurement error, the various ratios for a reactor and enrichment exhibit a high degree of consistency. The anomalous results which occur on occasion such as those involving Pu/U in batch 800 are not hard to earmark, at least as candidates for further investigation.

In Table II the batches for a reactor are ordered according to decreasing weight residual percent ^{235}U so that for a reactor other variables in the table which are exposure-dependent will tend to be indicated if the inherent effect is strong enough. For more details on the original data see Section IV.

The consistency in the $(Pu/U)/^{235}D$ and $(Pu/U)/\Delta^{236}U$ ratios depend upon uniform initial enrichments. It is understood that the CdN batches were made up of mixed initial enrichments so that this probably accounts for the relatively high variation in these ratios for the CdN reactor.

Table II

Relationships Between Pu Content and U and Pu Isotopic Concentrations

Reactor	Batch No.	$\frac{Pu/U}{^{235}D}$ (gms/tonne)	$\frac{Pu/U}{\Delta^{236}U}$	$\frac{Pu/U}{^{240}Pu/^{239}Pu}$	$\frac{\Delta^{236}U}{^{235}D}$
CANDU	400	7361	46110	10282	0.1597
	500	7369	46979	10291	0.1569
	900	7472	46995	9927	0.1590
	200	7567	46172	9963	0.1639
	600	7588	43063	10048	0.1762
	800	7282	44353	9757	0.1642
	700	7585	44980	10026	0.1686
	100	7460	45546	10117	0.1645
	300	7438	46027	9980	0.1616
CdN	400	1271	8305	13299	0.1530
	100	1196	7586	13374	0.1574
	300	1185	7709	13229	0.1536
	500	1153	7502	13003	0.1536
	200	1177	7498	12025	0.1569
VAK	100	3857	21822	14925	0.1768
	200	3858	21877	14364	0.1764
	300	3792	21283	15282	0.1781
	400	3905	22462	16135	0.1741
TRINO	100	5574	26577	30056	0.2102
	200	5163	24909	28829	0.2063

Table III gives a summary of these results using the following definitions.

$\overline{y}$ = the average value of the variable for the reactor

s_y = the observed standard deviation of the individual batch results

$s_{\overline{y}}$ = the observed standard deviation of the average

$F = t_{0.90}(f)\ s_{\overline{y}}$ = the 90% confidence limit term in the sense that 90% confidence limits on the mean are $\overline{y} \pm F$.

$\%F = F(100\%)/_{\overline{y}}$ = the 90% confidence limit term in relative percent

$\%F\sqrt{2}$ = the 90% confidence limit term in relative percent for a prediction interval involving a similarly replicated set of data.

Suppose that the members of a set of fuel assemblies, S_a: $A_1, A_2, \ldots, A_n$ come from n different reactor locations within one loading. The members of another set of assemblies S_b: $B_1, B_2, \ldots, B_n$ are irradiated to the same exposures in the reactor where the location within the reactor for A_i is the same as for B_i. If a variable y is exposure-dependent then the variance of the variable for assemblies A_i and B_i, which have been dissolved as independent batches, are positively correlated in the context of a population of measurements over all the fuel assemblies. The same sort of reasoning obtains if the fuel assemblies in set S_a have different

Table III

A Summary of Results Involving Pu Content and U and Pu Isotopic Concentrations

		Variable			
Reactor	Statistic	$\frac{Pu/U}{^{235}D}$	$\frac{Pu/U}{\Delta^{236}U}$	$\frac{Pu/U}{^{240}Pu/^{239}Pu}$	$\frac{\Delta^{236}U}{^{235}D}$
CANDU	$\bar{y}$	7,458	45,581	10,043	0.1638
	s_y	108	1,274	170	0.0058
	$s_{\bar{y}}$	36.1	425	56.5	0.0019
	F	67.1	790	105.1	0.0036
	%F	0.9%	1.7%	1.0%	2.2%
	$\%F\sqrt{2}$	1.3%	2.4%	1.4%	3.1%
CdN	$\bar{y}$	1,196	7,720	12,986	0.1549
	s_y	44.6	338	555	0.0021
	$s_{\bar{y}}$	19.9	151	248	0.0009
	F	42.5	322	529	0.00198
	%F	3.5%	4.2%	4.1%	1.3%
	$\%F\sqrt{2}$	4.9%	5.9%	5.7%	1.8%
VAK	$\bar{y}$	3,853	21,861	15,176	0.1763
	s_y	46.4	482	742	0.00167
	$s_{\bar{y}}$	23.2	241	371	0.00083
	F	54.6	567	873	0.00196
	%F	1.4%	2.6%	5.8%	1.1%
	$\%F\sqrt{2}$	2.0%	3.7%	8.1%	1.5%
TRINO	$\bar{y}$	5,369	25,743	29,443	0.2083

initial enrichments, one to another, but the assemblies A_i and B_i are identically enriched. Then for a variable y, which is a function of enrichment there will be a positive correlation between the results from assemblies A_i and B_i

Because of these conditions the variance $s_{\bar{y}}^2 = s_y^2/n$, where s_y is computed from the y values for the different batches from a given reactor loading, will tend to overestimate the true variance of the average y values between identical reactor loadings. In this sense then the confidence limits in Table III tend to be conservative for $(Pu/U)/^{240}Pu/^{239}Pu$ since the variable is exposure dependent.

These considerations are not pertinent to the variables $(Pu/U)/^{235}D$ and $(Pu/U)/\Delta^{236}U$ and $\Delta^{236}U/^{235}U$. for the CANDU and CdN reactors since these variables are not exposure-dependent and the fuel assemblies initially contained uniform levels of enrichment. For the VAK and TRINO reactors, however, the fuel assemblies had different initial enrichments so that different $(Pu/U)/^{235}D$ and $(Pu/U)/\Delta^{236}U$ values are expected for the different batch results for these variables. Confidence limits in the case of the TRINO data are not given because the initial enrichments for the batches are so different that the confidence limits have little validity. It is known, for example, that the $(Pu/U)/^{235}D$ changes about 7-9% per unit change in the percent initial enrichment, so that the observed variation in the TRINO values are to be expected. Thus the use the observed variation in the case of TRINO would result in unrealistic confidence limits.

Let y = Pu/U and x = ^{235}D. If y/x is constant over batches for a given reactor and initial enrichment (as the data suggest) then y and x are related by the function $y = \beta x$. Similar considerations hold when $x = \Delta^{236}$U. Graphs of the relationship $y = \beta x$ then are very useful for enhancing the comprehension of how the data act as a whole, pinpointing anomalous results, characterizing the different reactor and enrichment situations and judging whether the model $y = \beta x$ is an accurate reflection of the underlying relationship. Figures 1 and 2 indicate the relationships in Table II by the use of graphs.

The data observed in the MOL III experiment indicate that the model $y = a + bx$ is appropriate when y = Pu/U and x = ^{240}Pu/^{239}Pu for the limited range of exposures for a given reactor. The quality of these relationships is shown for the CANDU and the CdN reactors in Figure 3 in the linear range. The least-squares fits give the following results:

Reactor	Relationship	$(s/\bar{y})$ x 100%	r
CANDU	$y = 442 + 8638x$	0.013	0.98
CdN	$y = 1256 + 3766x$	0.014	0.82

The indices which indicate the quality of the fit are $(s/\bar{y})$ x 100%, the residual standard deviation on a relative percent basis, and r, the correlation coefficient.

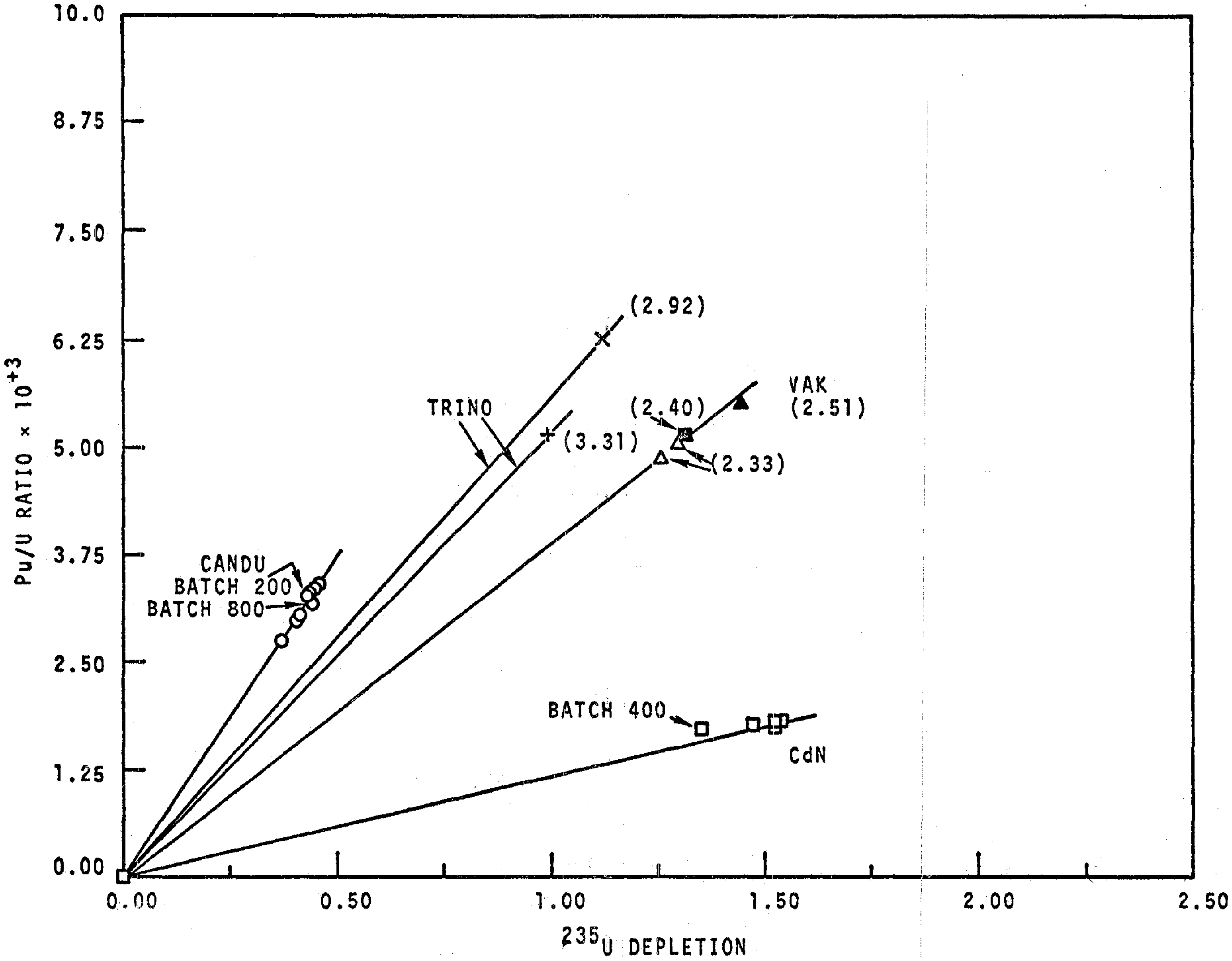

FIGURE 1. Pu/U Ratio Versus ^{235}U Depletion for the MOL III Experiment. The Curves Shown Have Been Drawn in by Inspection

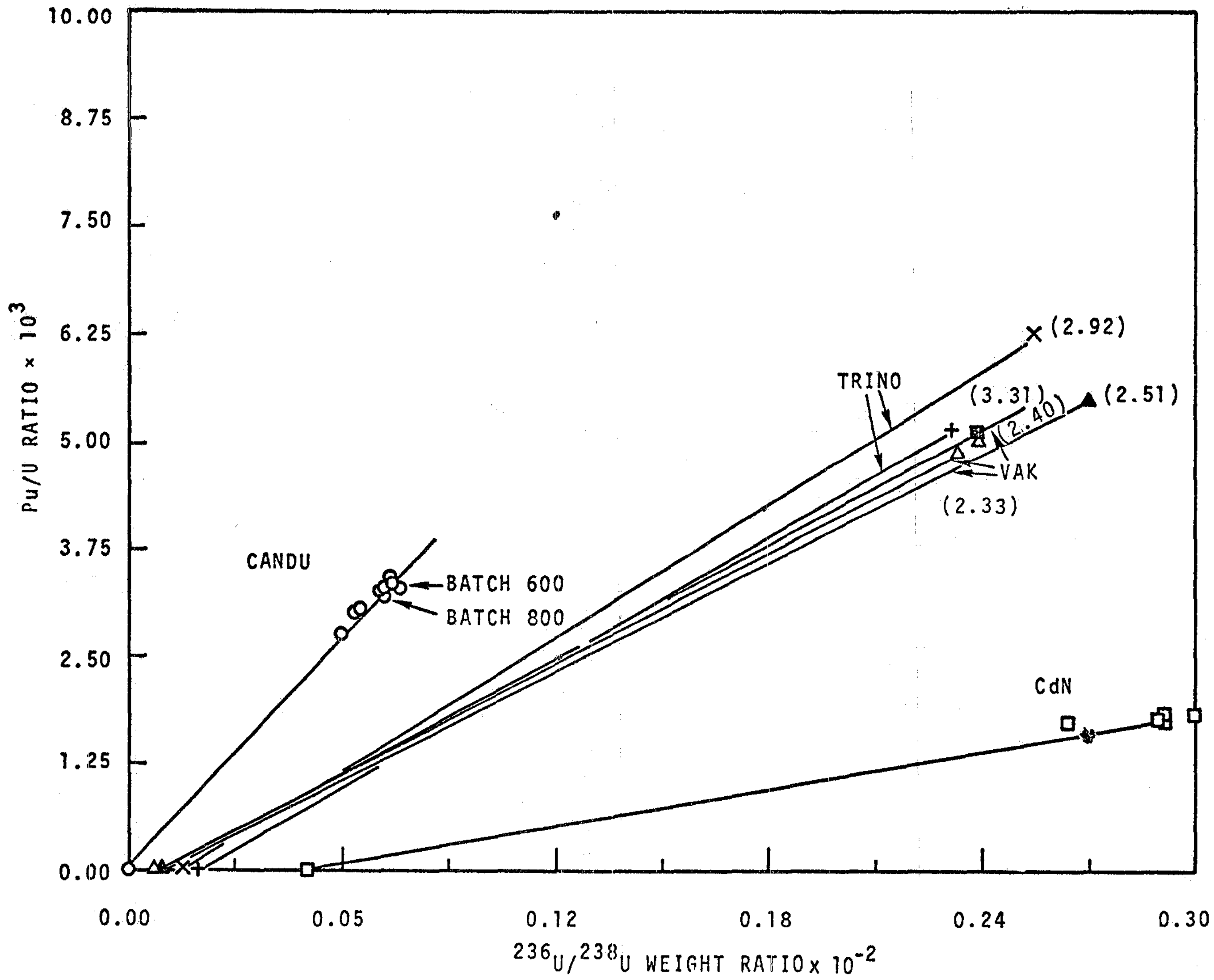

FIGURE 2. Pu/U Ratio Versus $^{236}U/^{238}U$ Weight Ratio for the Mol III Experiment. The Curves Shown Have Been Drawn in by Inspection.

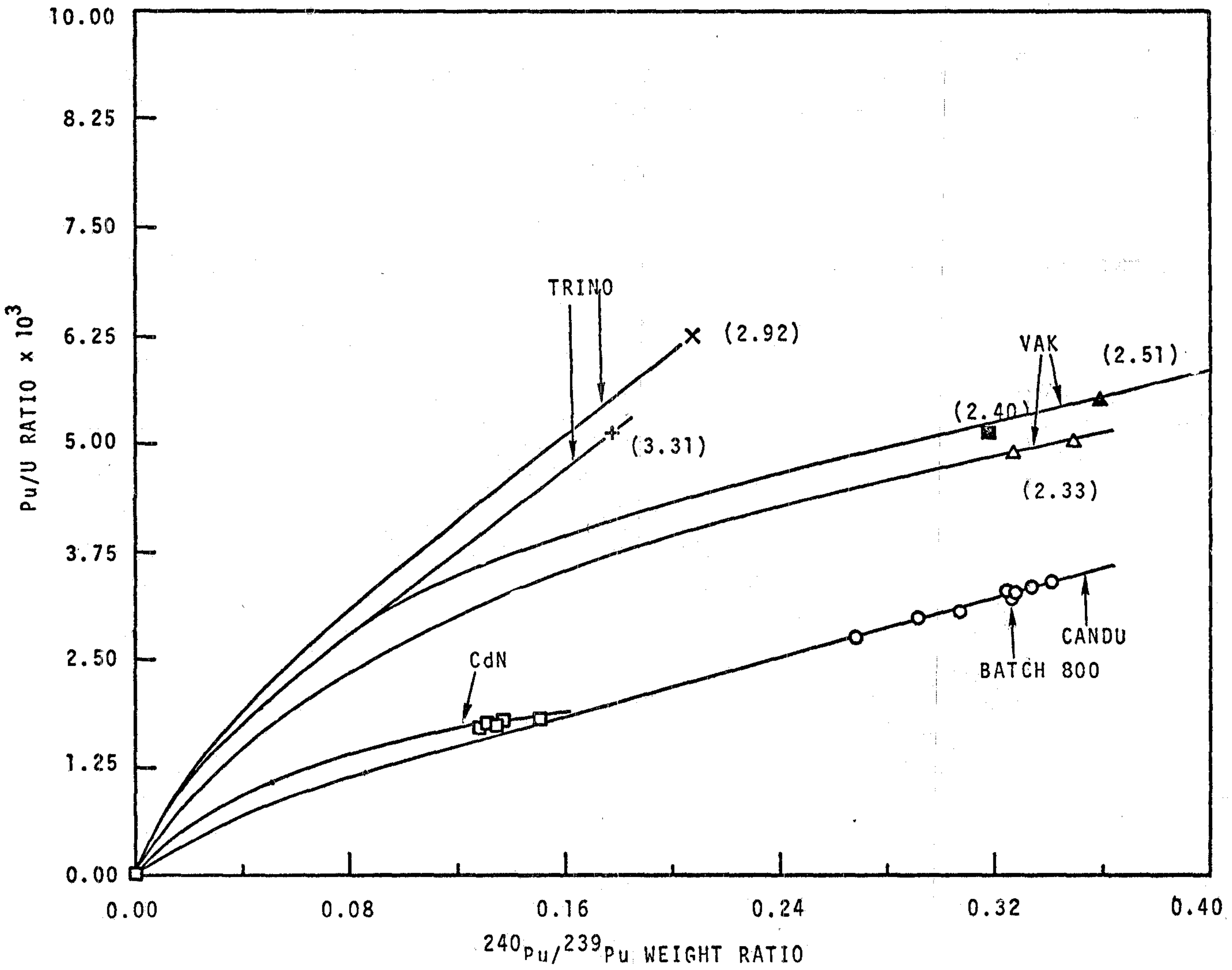

FIGURE 3. Pu/U Ratio Versus ^{240}Pu/^{239}Pu Weight Ratio for the Mol III Experiment. The Curves Shown Have Been Drawn in by Inspection.

6.3.2. Confirmation of Previous Information

A complementary part of the concept of Pu verification is the concept of confirming that the spent fuel entering the chemical plant is, indeed, the stated fuel. Here the isotopic correlations as well as the data themselves are used to match the "stated" or historical fingerprint with the observed fingerprint. The detail of the print or the number of characteristics which can be matched is of course, highly dependent on the extent of the historical information. In general, the information to be confirmed for safeguards purposes include the data features which identify the particular reactor or reactor class, the stated values for the end-of-life nuclear materials content, and the initial composition of the fuel. For purposes of illustration, available historica information is compared to measured values in Table IV. Here the endeavor is to demonstrate the principles involved rather than make an exhaustive comparison of all available data or all potentially useful comparisons. As is evident from the data in the table, the measured values clearly confirm the previous information about the fuels. The use of the technique to confirm starting compositions is shown graphically in Figures 4 and 5. If a relationship $y = a + bx$ exists, where $x = {}^{235}U$ weight percent, the initial enrichment can be estimated by setting $y = 0$ and solving for x. The best relationship of this kind occurs when $y = Pu/U$. In Figure 4 the initial ${}^{235}U/{}^{238}U$ value for a given reactor can be estimated graphically by finding the abscissa value on the line which corresponds to the initial ${}^{236}U/{}^{238}U$ ordinate value.

Table IV

Comparison of Preprocessing Information With Measured Chemical Plant Data

Reactor Fuel	Identifying Characteristic(1)	Observed Value	Reactor Statement
CANDU	$\frac{Pu/U}{^{235}D}$	7458	7320
"	$\frac{Pu/U}{\Delta ^{236}U}$	45581	47860
"	$\frac{Pu/U}{^{240}Pu/^{239}Pu}$	10047	10300
"	Wt. % ^{235}U	0.2857	0.2715
"	Wt. % ^{236}U	0.0697	0.0673
"	Wt. % ^{239}Pu	72.31	72.55
"	Wt. % ^{240}Pu	22.94	22.48
"	Average Exposure (MWD/tonne)	∼5950	∼6000
"	Pu/U (gms./tonne)	3176	3193
TRINO	$\frac{Pu/U}{^{235}D}$	5397	5469 (∼5350)(2)
"	$\frac{Pu/U}{^{240}Pu/^{239}Pu}$	29295	29751
"	Pu/U (gms./tonne)	5682	5857
"	Wt. % ^{235}U	2.063	2.045
"	Wt. % ^{239}Pu	77.01	75.93

(1) Weighted Average of all Input Batches of Each Fuel

(2) Estimated From Historical Measured Values Previously Reported by Eurochemic (5).

Table IV

(Continued)

Reactor Fuel	Identifying Characteristics(1)	Observed Value	Reactor Statement
VAK	$\frac{Pu/U}{^{235}D}$	3841	4363 (∼4140)(2)
"	$\frac{Pu/U}{\Delta^{236}U}$	21640	24944
"	$\frac{Pu/U}{^{240}Pu/^{239}Pu}$	15000	20882
"	Wt. % ^{235}U	1.048	1.073
"	Wt. % ^{236}U	0.2462	0.240
"	Wt. % ^{239}Pu	66.18	65.76
"	Wt. % ^{240}Pu	22.77	18.25
"	Pu/U (gms./tonne)	5161	5796
CdN	$\frac{Pu/U}{^{235}D}$	1205	1386
"	Wt. % ^{235}U	3.008	3.057
"	Pu/U (gms./tonne)	1774	1972

(1) Weighted Average of all Input Batches of Each Fuel.

(2) Estimated From Historical Measured Values Previously Reported by Eurochemic (5).

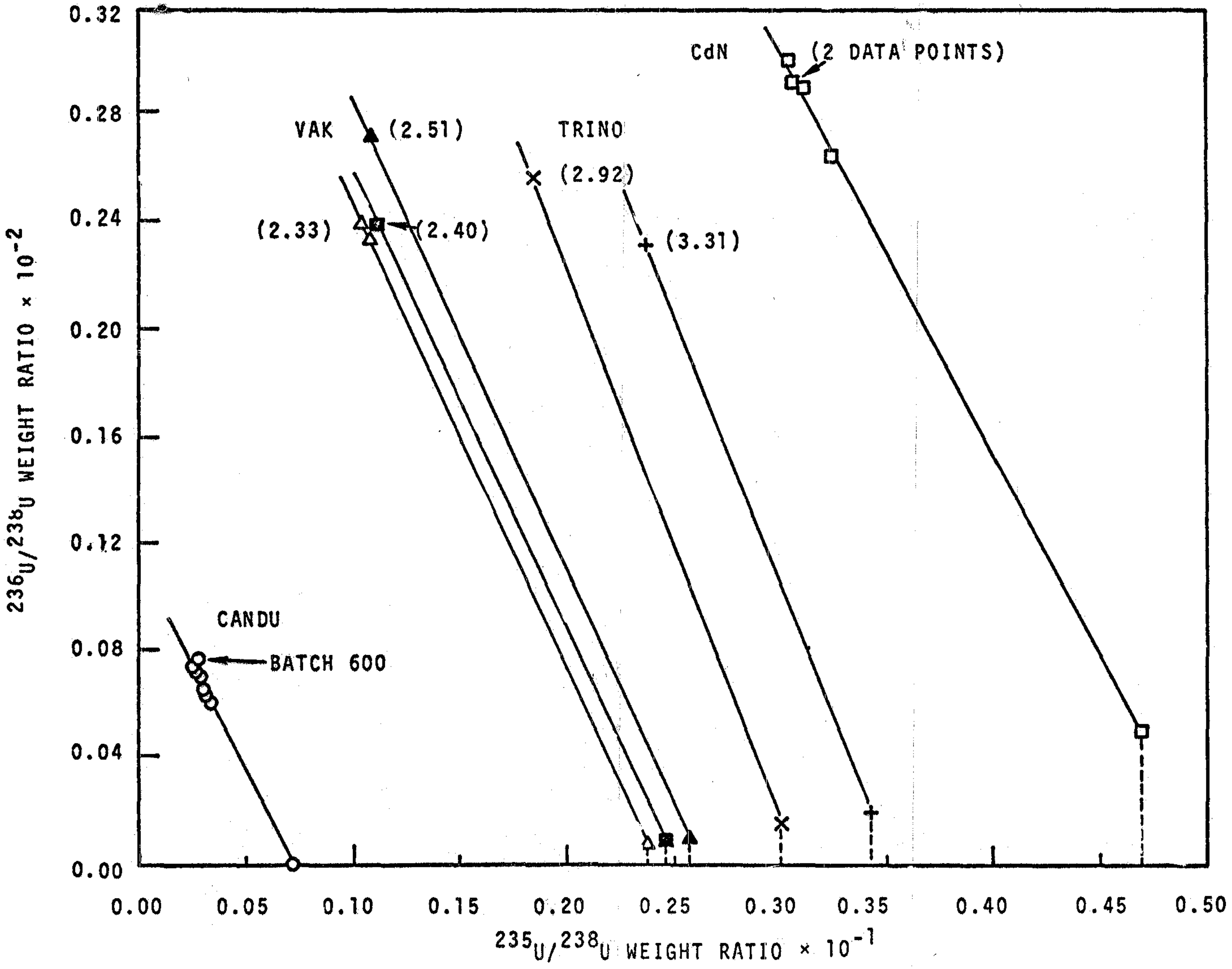

FIGURE 4. $^{236}U/^{238}U$ Weight Ratio Versus $^{235}U/^{238}U$ Weight Ratio for the MOL III Experiment. The Curves Shown Have Been Drawn in by Inspection

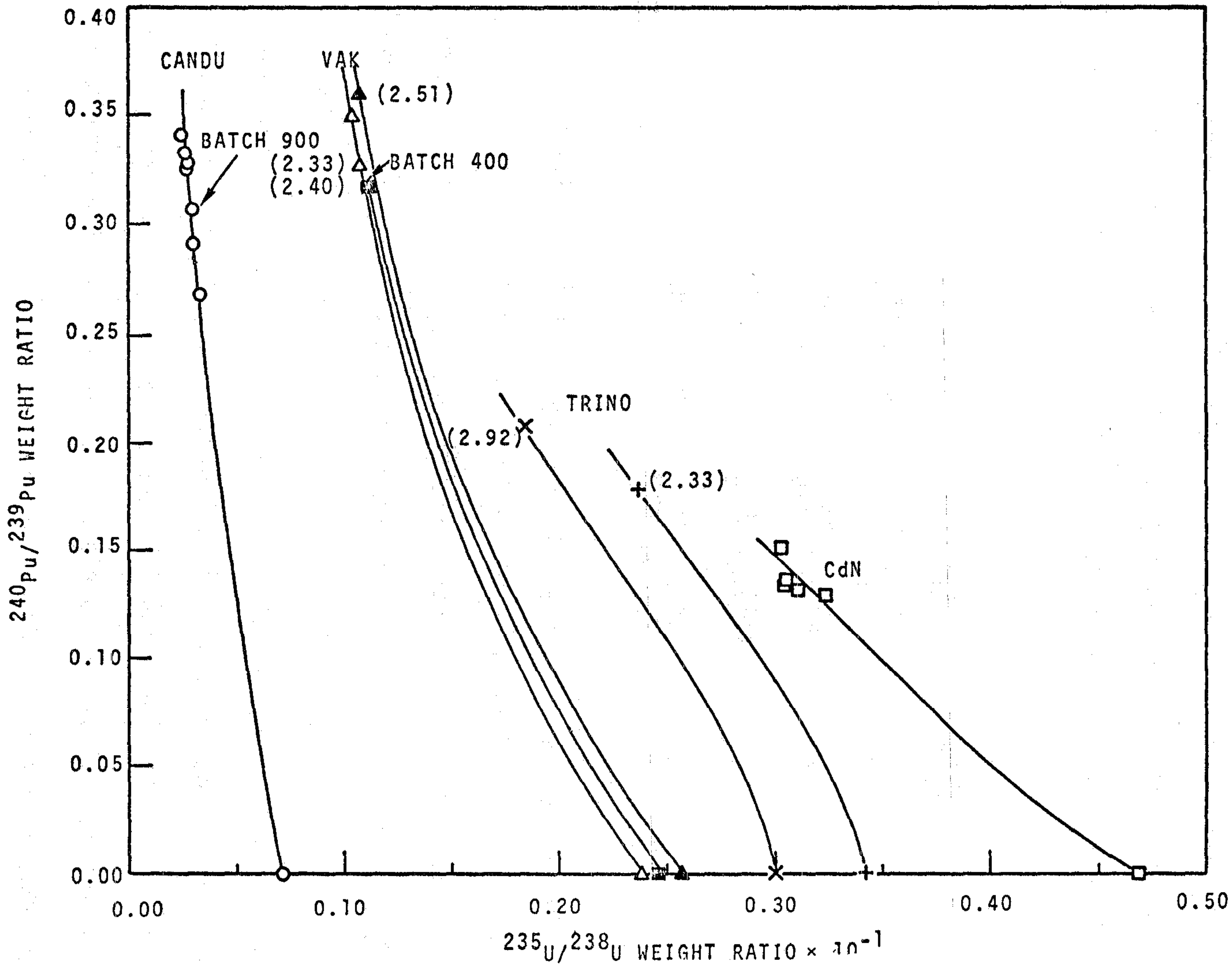

FIGURE 5. ^{240}Pu/^{239}Pu Weight Ratio Versus ^{235}U/^{238}U Weight Ratio for the Mol III Experiment. The Curves Shown Have Been Drawn in by Inspection

6.3.3. Internal Consistency of the Data

6.3.3.1. General Description of the Results by the Use of Graphs

The results which have been reviewed previously indicate that the Pu content and the U and Pu isotopic concentrations show strong patterns of consistency. In addition to these results, the following graphical relationships are relevant and are shown in Figures 4, 5, 6, and 7.

Figure	y = f(x)	x
4	$^{236}U/^{238}U$	$^{235}U/^{238}U$
5	$^{240}Pu/^{239}Pu$	$^{235}U/^{238}U$
6	$^{240}Pu/^{239}Pu$	$^{236}U/^{238}U$
7	$^{240}Pu/^{239}Pu$	$^{236}U/^{235}U$

If the safeguards inspectorate knew the exact conditions of the load, the reactor and the irradiation he could, theoretically at least, determine the constituent makeup of the irradiated material. However the inspectorate does not wish to assume the reactor's stated parameter values without an adequate check. It is known, however, that the functional relationships exist. What is not known, a priori, is the extent to which the functional relationships are retained on a batch basis when a dissolution batch contains an entire fuel assembly. There are also effects due to the possible contamination by dissolver acid and to sampling variation and measurement error. Figures 4, 5, 6, and 7 in addition to Figures 1, 2 and 3 are useful in assessing the extent to which these functional relationships are retained. The figures are also useful in depicting and understanding the general form of the

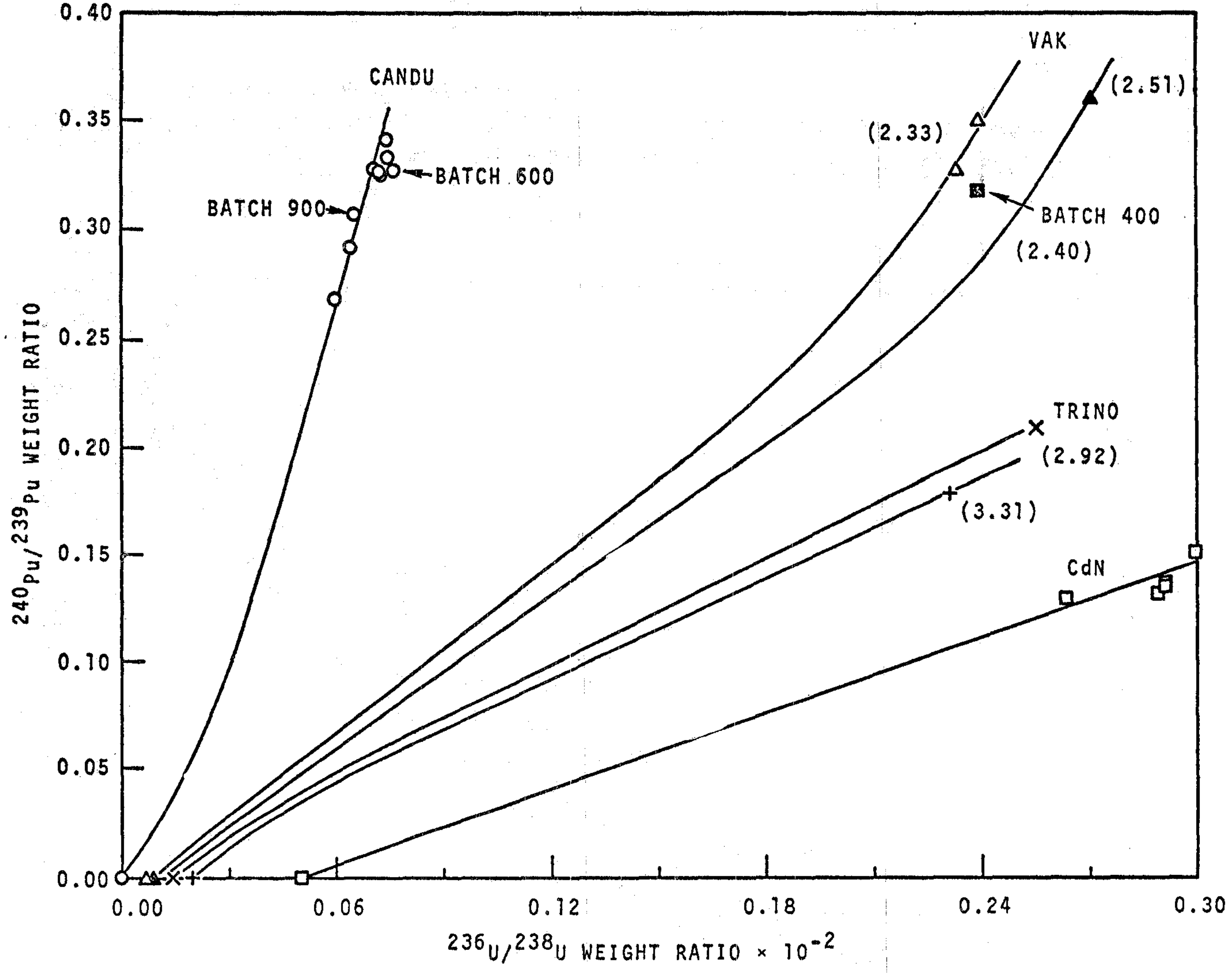

FIGURE 6. ^{240}Pu/^{239}Pu Weight Ratio Versus ^{236}U/^{238}U Weight Ratio for the Mol III Experiment. The Curves Shown Have Been Drawn in by Inspection

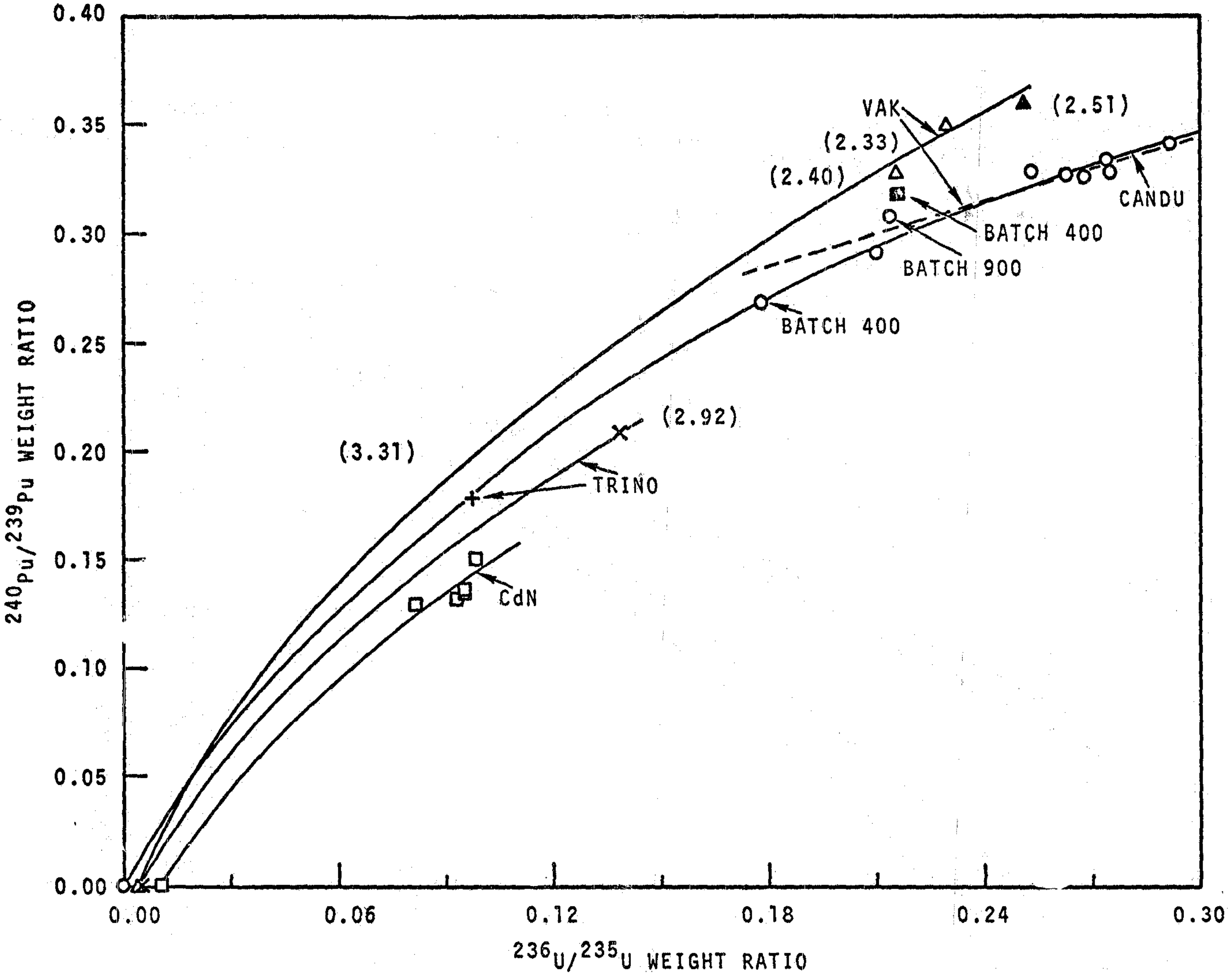

FIGURE 7. ^{240}Pu/^{239}Pu Weight Ratio Versus ^{236}U/^{235}U Weight Ratio for the Mol III Experiment. The Curves Have Been Drawn in by Inspection.

relationships and in earmarking results which appear to be anomalous.

The procedure to this point in assessing internal consistency is as follows.

1. The original plant measurement data are ordered according to decreasing weight percent ^{235}U. This is a simple but effective procedure for evaluating the data consistency since increasing or decreasing magnitude should be a property which is invariant for the different measurement variables.
2. The original data are transformed to variables which are more meaningful for eliciting the nature of the underlying batch to batch relationships for the different reactors where the previous batch ordering is retained.
3. These data are then displayed in graphical form in order to obtain an empirical basis for determining the general form of the equations, for comparing reactors and enrichments and for isolating the values which appear to be anomalous.

The main conclusions to this point which are pertinent to assessing the data consistency are as follows:

1. The underlying relationships between the Pu/U and isotopic values of the batches have a strong enough imprint to show through imperfections in the measurements and the head end process.
2. The analyses give very firm evidence that the model $y = \beta x$, or $y/x = \beta$ is, within the limitations of measurement and sampling errors, correct when $y = Pu/U$ and $x = {}^{235}D$ or $x = \Delta^{236}U$.

3. The measurements which are apparently anomalous are rather easy to separate out. A statistical basis for adjudging their anomalous character also needs to be developed and this is done in the next section.

6.3.3.2. The Use of Regression Procedures to Study Consistency

The graphical methods of Section C.1 are very useful for displaying the data and for understanding what the data indicate in regards to reactor and enrichment differences, batch to batch consistency and the functional form of the underlying relationships between variables. In addition, it is also desirable to have numerical and statistical methods for assessing the overall consistency exhibited by the data and for judging whether an individual batch result for a given variable is reliable.

In order to do this, least-squares fits to the data were obtained within the range of the data based on models of degree 0 or 1. The models are justified on empirical grounds in the sense that a) the range of the average exposures in the batches from a set is small, b) the least-squares fits are obviously effective and c) higher degree models do not improve the quality of the fits.

The correlation coefficients and the relative standard deviations of the residuals can be used as indices to indicate the overall quality of the fit. The residuals, the differences between the observed dependent variable and the predicted dependent variables, can be used to assess the quality of the observations. In practice it is better to normalize a particular residual by dividing the residual by its estimated standard deviation. The residuals expressed as percentages of the predicted dependent variables are also useful.

The following fits were made for both the CANDU and the CdN data.

Fit	Dependent Variable	Independent Variable	Model
1	$\frac{(\text{Pu/U g/tonne})}{^{235}\text{D}}$	----	y = c
2	$\frac{(\text{Pu/U g/tonne})}{\Delta^{236}\text{U in wt\%}}$	----	y = c
3	$\Delta^{236}\text{U}/^{235}\text{D}$	----	y = c
4	(Pu/U g/tonne)	$^{240}\text{Pu}/^{239}\text{Pu}$	y = a + bx
5	$^{240}\text{Pu}/^{239}\text{Pu}$	^{235}D	y = a + bx
6	$^{240}\text{Pu}/^{239}\text{Pu}$	$\Delta^{236}\text{U}$	y = a + bx
7	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{236}\text{U}/^{235}\text{U}$	y = a + bx

The least-squares fit for c in the model $y = c$ is $\hat{c} = \overline{y}$

The formulae for the three residual forms are as follows:

Form	Definition	Formula
residual	observed y - predicted y	$r_i = y_i - \hat{y}_i$
(normalized residual)	$\dfrac{\text{residual}}{\left(\text{standard deviation of the residual}\right)}$	$\dfrac{r_i}{s_{r_i}}$
(percent residual)	$\dfrac{\text{residual} \times 100\%}{\text{predicted } y}$	$\dfrac{r_i \times 100\%}{\hat{y}_i}$

The normalized form of the residual is the most easily interpreted in the context of the consistency of the Pu/U ratios and the isotopic data since r_i/s_{r_i} should be less than 2 most of the time. Exact critical values for normalized residuals are hard to establish, however. [4] Results for CANDU data are presented in Tables V and VI. Results for CdN are given in Tables VII and VIII.

The conclusions and indications which are shown by the least-squares analysis are as follows:

1. The high correlation coefficients and the low relative standard deviations of the residuals from the CANDU data indicate that the fits are good.
2. There are no extremely bad residuals although some of the normalized residuals from CANDU suggest that outliers exist in batch 600, for fits 2, 3, and 6 since all of the values for these fits have absolute magnitudes near 2. The same type of situation is encountered in batch 400, fit 7, and batch 800 fits 1 and 4. Since batch 400 has the smallest exposure this may indicate that the linear model is not completely adequate over the whole range.
3. The least-squares results from the CdN data, as judged by the correlation coefficients and the residual relative standard deviations, are not as good as for CANDU data. This may delimit the sensitivity required for isolating suspect observations.

A residual which indicates a defective observation may be caused by either a bad independent or dependent variable. For this reason other

Table V

The Results of the Least-Squares Fit of Pu and Isotopic Data From the CANDU Reactor

Fit	Model	Correlation	Relative Standard Deviation
1	$y = \bar{y} = 7457.7$		0.014
2	$y = \bar{y} = 45{,}581$		0.028
3	$y = \bar{y} = 0.1638$		0.034
4	$y = 442.5 + 8637.9x$	0.98	0.013
5	$y = -0.0712 + 0.910x$	0.97	0.017
6	$y = 0.04565 + 3.881x$	0.94	0.028
7	$y = 0.1697 + 0.5933x$	0.97	0.020

Legend

Fit	Dependent Variable	Independent Variable	Model
1	$\frac{(\text{Pu/U g/tonne})}{^{235}D}$	----	$y = c$
2	$\frac{(\text{Pu/U g/tonne})}{\Delta^{236}U \text{ in wt\%}}$	----	$y = c$
3	$\Delta^{236}U/^{235}D$	----	$y = c$
4	(Pu/U g/tonne)	$^{240}Pu/^{239}Pu$	$y = a + bx$
5	$^{240}Pu/^{239}Pu$	^{235}D	$y = a + bx$
6	$^{240}Pu/^{239}Pu$	$\Delta^{236}U$	$y = a + bx$
7	$^{240}Pu/^{239}Pu$	$^{236}U/^{235}U$	$y = a + bx$

Table VI

Various Residual Forms Used to Check on the Internal Consistency of CANDU Data

Legend:

	Dependent	Independent
1	$(Pu/U)/^{235}D$	
2	$(Pu/U)/\Delta^{236}U$	
3	$\Delta^{236}U/^{235}D$	
4	Pu/U	$^{240}Pu/^{239}Pu$
5	$^{240}Pu/^{239}Pu$	^{235}D
6	$^{240}Pu/^{239}Pu$	$\Delta^{236}U$
7	$^{240}Pu/^{239}Pu$	$^{236}U/^{235}U$

The Residuals Normalized

The Number of the Fit

Batch	1	2	3	4	5	6	7
400	- .9	.4	- .7	- .1	- .5	-1.5	-1.6
500	- .9	1.1	-1.2	1.0	-1.6	- .2	- .5
900	.1	1.1	- .8	-1.2	1.3	1.2	1.9
200	1.0	.5	.0	- .2	1.1	.9	.2
600	1.2	-2.0	2.1	.5	.7	-2.0	1.3
800	-1.6	-1.0	.1	-2.0	- .1	.3	-1.0
700	1.2	- .4	.8	.5	.7	- .1	- .6
100	.0	- .0	.0	1.0	-1.0	- .1	.1
300	- .2	.3	- .4	.4	-1.0	1.0	- .3

The Residuals as Per Cents

The Number of the Fit

Batch	1	2	3	4	5	6	7
400	-1.3	1.2	-2.6	- .1	- .6	-3.3	-2.4
500	-1.2	3.0	-4.2	1.3	-2.7	- .6	- .9
900	.2	3.1	-2.9	-1.5	2.3	3.3	3.5
200	1.5	1.3	.1	- .2	1.8	2.3	.3
600	1.7	-5.5	7.6	.6	1.2	-4.3	2.4
800	-2.3	-2.7	.3	-2.4	- .2	.6	-1.7
700	1.7	-1.3	2.9	.6	1.0	- .2	-1.0
100	.0	- .1	.1	1.2	-1.6	- .3	.2
300	- .3	1.0	-1.3	.5	-1.3	2.5	- .5

Table VI
(Continued)

The Residuals in Absolute Amounts

	The Number of the Fit						
Batch	1	2	3	4	5	6	7
400	-9.760+01	5.581+02	-4.228-03	-1.904+00	-1.723-03	-9.300-03	-6.716-03
500	-9.317+01	1.386+03	-6.946-03	3.771+01	-7.978-03	-1.882-03	-2.727-03
900	1.440+01	1.422+03	-4.779-03	-4.646+01	6.803-03	9.708-03	1.048-02
200	1.102+02	5.760+02	2.121-04	-7.008+00	5.945-03	7.463-03	1.041-03
600	-1.302+02	-2.522+03	1.248-02	1.958+01	3.819-03	-1.486-02	7.835-03
800	-1.750+02	-1.238+03	4.918-04	-7.702+01	-6.060-04	2.053-03	-5.630-03
700	1.270+02	-5.732+02	4.773-03	2.006+01	3.376-03	-5.507-04	-3.274-03
100	3.135+00	-4.432+01	9.555-05	3.926+01	-5.202-03	-9.098-04	8.144-04
300	-1.915+01	4.352+02	-2.097-03	1.577+01	-4.434-03	8.282-03	-1.819-03

Table VII

The Results of the Least-Squares Fits for Pu and Isotopic Data the CdN Reactor

Fit	Model	Correlation	Relative Standard Deviation
1	$y = \bar{y} = 1195.8$		0.037
2	$y = \bar{y} = 7719.9$		0.044
3	$y = \bar{y} = 0.1549$		0.013
4	$y = 1256.0 + 3766.1x$	0.82	0.014
5	$y = 0.02575 + 0.748x$	0.68	0.052
6	$y = 0.03161 + 0.4571x$	0.72	0.049
7	$y = 0.0512 + 0.9207x$	0.72	0.050

Legend

Fit	Dependent Variable	Independent Variable	Model
1	$\frac{\text{(Pu/U g/tonne)}}{{}^{235}D}$	----	$y = c$
2	$\frac{\text{(Pu/U g/tonne)}}{\Delta {}^{236}U \text{ in wt\%}}$	----	$y = c$
3	$\Delta {}^{236}U/{}^{235}D$	----	$y = c$
4	(Pu/U g/tonne)	$^{240}Pu/^{239}Pu$	$y = a + bx$
5	$^{240}Pu/^{239}Pu$	^{235}D	$y = a + bx$
6	$^{240}Pu/^{239}Pu$	$\Delta {}^{236}U$	$y = a + bx$
7	$^{240}Pu/^{239}Pu$	$^{236}U/^{235}U$	$y = a + bx$

Table VIII

Various Residual Forms Used to Check on the Internal Consistency of CdN Pu and Isotopic Data

Legend:

	Dependent	
1	$(Pu/U)/{}^{235}D$	
2	$(Pu/U/\Delta^{236}U$	
3	$\Delta^{236}U/{}^{235}D$	
4	Pu/U	$^{240}Pu/{}^{239}Pu$
5	$^{240}Pu/{}^{239}Pu$	^{235}D
6	$^{240}Pu/{}^{239}Pu$	$\Delta^{236}U$
7	$^{240}Pu/{}^{239}Pu$	$^{236}U/{}^{235}U$

The Residuals Normalized

The Number of the Fit

Batch	1	2	3	4	5	6	7
400	1.7	1.7	- .9	-1.2	1.1	1.7	1.6
100	- .0	- .4	1.2	.4	- .7	-1.0	- .9
300	- .3	- .0	- .6	1.5	- .5	- .4	- .4
500	-1.0	- .6	- .6	- .4	- .8	- .6	- .7
200	- .4	- .7	1.0	-1.3	1.7	1.7	1.7

The Resiaual as Per Cents

The Number of the Fit

Batch	1	2	3	4	5	6	7
400	6.3	7.6	-1.2	-1.4	1.8	2.4	2.4
100	- .1	-1.7	1.6	.5	-3.1	-4.3	-3.8
300	-1.0	- .1	- .8	1.9	-2.4	-1.6	-1.9
500	-3.6	-2.8	- .8	- .5	-3.4	-2.6	-2.9
200	-1.6	-2.9	1.3	- .5	7.0	6.1	6.2

he Residuals in Absolute Amounts

The Number of the Fit

atch	1	2	3	4	5	6	7
400	7.498+01	5.846+02	-1.918-03	-2.353+01	2.328-03	3.021-03	2.985-03
100	-1.337+00	-1.340+02	2.518-03	7.886+00	-4.201-03	-5.912-03	-5.189-03
300	-1.140+01	-1.132+01	-1.293-03	3.431+01	-3.293-03	-2.212-03	-2.634-03
500	-4.318+01	-2.175+02	-1.306-03	-8.852+00	-4.683-03	-3.593-03	-4.018-03
200	-1.906+01	-2.218+02	1.998-03	-9.814+00	9.849-03	8.697-03	8.855-03

Table IX

Summary of Results From Regression Analyses for CANDU Data

Legend: H - the possibility that the isotopic measurement is high
L - the possibility that the isotopic measurement is low
∿ - no apparent effect

Batch	Fit	Pu/U	^{235}U	^{236}U	^{240}Pu	^{239}Pu
400	7		L	H	L	H
600	2	L		H		
	3		L	H		
	6			H	L	H
	1		∿			
	5		∿			
	7		∿	∿		
800	1	L	H			
	4	L			H	L

The data from the CdN reactor did not, in general, give good regression relationships. Thus, the apparent absence of outliers from these data may not be due to the absence of defective measurements but due to the inability to detect them because of the lack of sensitivity of the fits.

In summary for this section it can be said that added tools are given, based on statistical methods, for isolating anomalous results and for characterizing the quality of the functional relationships between the constituent elements and their isotopes as reflected on a batch to batch basis from data obtained by sampling dissolver batches composed of entire fuel assemblies.

6.3.3.3. Consistency Versus Measurability

A basic experimental problem in evaluating the potential effectiveness of using isotopic correlations in safeguards applications is to determine the consistency of the relationships in the light of their measurability. The problem is to determine if the variation observed in the relationships between successive dissolution batches of the same fuel represent normal measurement error only or are they due to "true differences" in the relationships, e.g., are the conversion ratios for two dissolution batches of the same fuel type truly different? An effort to test this proposition was made with the CANDU fuel by comparing the between-batch variation to the within-batch measurement variation. The situation is somewhat complicated by the fact that "true ratios" are not observed because of the contribution of nuclear materials added by the recycle acid.

The between dissolution batch variations for the isotopic correlations which are related to the Pu content are shown in Table II The variations have been indicated by determining the mean and the standard deviation of the mean from the batch values and these results are listed in Table III The within-batch variation of the ratios is shown in Table X which treats the ratios as observed without correction for recycle and additions. The values of sigma listed at the bottom of the table are estimated standard deviations of individual ratio measurements. The combined standard deviation, σ_{a+b}, represents the fact that on each dissolution batch two ratio measurements were made. The apparent measurability of the relationships versus the observed total variation is shown in Table XI. The first column, listed as Relative Ratio Measurements, is the observed variation in the relationships found between duplicate measurements. The second column, titled Propagated Error is another estimate of the within-batch measurement variation obtained by combining the individual component of error. The first two columns included are estimates of the measurement error for the ratios, while the last column reflects the total variation in the observed relationship due to all effects. These include errors in 1) the jacket dissolution waste measurements 2) recycle acid measurements 3) the ratio measurements, and 4) possible differences in the relationship as a result of irradiation differences. Because of the estimated effects of recycle acid additions and the few degrees of freedom, it is concluded that the observed total variation is not significantly different from the total measurement error associated with the data. Also it should be noted that actual observed total variation is not large and corresponds favorably to results obtained under more favorable head end process conditions.

Table X

Relative (1) Measurability of Burnup Relationships - CANDU Fuel

Batch #1	Pu grams/TU	%R(2)	Wt. % ^{235}U	%R	Wt. % ^{236}U	%R	Pu g/TU / ^{235}D	%R	Pu g/TU / $\Delta^{236}U$	%R
1 a.	3314	1.6	0.2720	0.40	0.0730	2.8	7542	1.8	45397	1.2
b.	3261		0.2710		0.0710		7405		45930	
2 a.	3267	Same	0.2890	1.1	0.0690	5.6	7734	0.75	47348	5.6
b.	3267		0.2921		0.0730		7792		44753	
3 a.	3405	0.4	0.2540	0.5	0.0730	4.3	7444	1.1	46644	3.8
b.	3419		0.2526		0.0762		7452		44869	
4 a.	2790	1.1	0.3390	0.6	0.0610	3.3	7492	0.6	45738	2.2
b.	2758		0.3410		0.0590		7446		46746	
5 a.	2861	0.6	0.3090	0.6	0.0650	1.5	7110	0.06	44015	2.2
b.	2877		0.3070		0.0640		7114		44953	
6 a.	3268	0.9	0.2809	2.5	0.0780	5.3	7591	0.6	41897	6.2
b.	3299		0.2740		0.0740		7542		44581	
7 a.	3371	0.3	0.2710	Same	0.0750	2.7	7654	0.4	44947	2.4
b.	3360		0.2710		0.0730		7620		46027	
8 a.	3226	0.3	0.2750	1.5	0.0730	4.2	7392	0.6	44192	4.5
b.	3236		0.2710		0.0700		7347		46229	
9 a.	3083	0.3	0.3020	1.3	0.0660	4.7	7530	0.7	46712	4.4
b.	3075		0.3060		0.0630		7585		48810	
		σ_1 = 0.60%		σ_1 = 0.94%		σ_1 = 3.4%		σ_1 = 0.65%		σ_1 = 3.20%
		σ_{a+b} = 0.43%		σ_{a+b} = 0.66%		σ_{a+b} = 2.40%		σ_{a+b} = 0.46%		σ_{a+D} = 2.3%

---

(1) Relative ratios uncorrected for Recycle Acid and Jacket Dissolution

(2) Relative Percent Range

Table XI

Comparison of Measurability of Burnup Relationships Versus Observed Values - CANDU Fuel

	Percent Relative Standard Deviation, σ		
Burnup Relationship	Relative Ratio Measurements	Propagated Errors	Observed Between Dissolver Batches (RAR + JD)(1)
$\frac{\text{Pu grams/tonne}}{\Delta^{235}\text{D}}$	0.46%	0.79	1.45 (1.22)(2)
$\frac{\text{Pu grams/tonne}}{\Delta^{236}\text{U}}$	2.3	2.52	2.79
$\frac{\text{Pu grams/tonne}}{^{240}\text{Pu}/^{239}\text{Pu}}$	—(3)	—	1.69 (1.39)(2)

(1) Observed differences between dissolution batches includes Recycle Acid (RAR) and Jacket Dissolution (JD)

(2) Standard deviation without batch #8

(3) Duplicate Pu isotopic data not available.

6.4. A FURTHER DESCRIPTION OF THE DATA

The chemical plant measurement data in its original form are shown in Tables XII and XIII.

The batches listed in Table XII were ordered according to decreasing ^{235}U weight percent within a given single initial enrichment. Of particular interest are the isotopic values set apart by the dotted lines. These isotopes, along with ^{238}U, are the isotopes that have been used in the isotopic correlation analysis. The fact that functional relationships do exist between U and Pu isotopes is apparent from Table II by noting the general trends of each column of isotopic values. That is, while the ^{235}U weight percent decreases, the

- ^{236}U values increase,
- ^{239}Pu values decrease,
- ^{240}Pu values increase,
- ^{241}Pu values increase and
- ^{242}Pu values increase.

The Pu/U ratio also increases as seen from Table XIII where the data of Table XII have been converted to isotopic ratios and Pu/U ratios. The data tabulated in ratio form emphasize that functional relationships are apparent although various data forms are used.

TABLE XII

CHEMICAL PLANT MEASUREMENT DATA

INDIVIDUAL BATCHES

(ORDERED ACCORDING TO DECREASING 235U CONTENT)

BATCH NO.	234U W%	235U W%	236U W%	238U W%	TOTAL U(GM)*	238PU W%	239PU W%	240PU W%	241PU W%	242PU W%	TOTAL PU(GM)
					CANDU						
0	.0057	.7114		99.285							
400	.0050	.3362	.05986	99.599	1.04602	.1073	75.981	20.415	2.804	.692	2888.6
500	.0047	.3040	.06389	99.627	1.05830	.1196	74.250	21.662	3.131	.837	3177.5
900	.0050	.3032	.06490	99.627	1.11373	.1177	73.044	22.443	3.406	.989	3397.0
200	.0050	.2794	.07084	99.645	1.07061	.1371	71.438	23.436	3.894	1.094	3500.1
600	.0050	.2778	.07642	99.641	1.02545	.1275	71.622	23.448	3.711	1.091	3373.8
800	.0050	.2735	.07193	99.650	.99626	.1290	71.723	23.445	3.654	1.048	3177.2
700	.0040	.2708	.07426	99.651	.99853	.1289	71.216	23.738	3.806	1.112	3336.9
100	.0050	.2700	.07233	99.653	1.07578	.1411	71.714	23.341	3.734	1.070	3542.7
300	.0050	.2535	.07403	99.667	1.03066	.1396	70.560	24.079	4.042	1.179	3510.5
					CdN						
0	.0185	4.4800	.04800	95.453							
400	.0170	3.1271	.25502	96.601	.16799	.0693	87.327	11.288	1.177	.139	288.8
100	.0200	3.0065	.28001	96.693	.17889	.0635	86.929	11.453	1.364	.190	315.2
300	.0180	2.9570	.28200	96.743	.19847	.0559	86.648	11.816	1.341	.140	358.0
500	.0177	2.9570	.28198	96.743	.01071	.0000	86.702	11.702	1.596	.000	18.8
200	.0160	2.9379	.29001	96.756	.13138	.0839	85.319	12.878	1.510	.210	238.4

* $\times 10^6$

TABLE XII (Cont'd)

CHEMICAL PLANT MEASUREMENT DATA

INDIVIDUAL BATCHES

(ORDERED ACCORDING TO DECREASING 235U CONTENT).

BATCH NO.	234U W%	235U W%	236U W%	238U W%	TOTAL U(GM)*	238PU W%	239PU W%	240PU W%	241PU W%	242PU W%	TOTAL PU(GM)
VAK											
0	.0170	2.3300	.00700	97.646							
100	.0121	1.0666	.23031	98.691	.61169	.6173	67.566	22.115	7.689	2.013	2980.8
200	.0121	1.0289	.23651	98.723	.42666	.6535	65.742	22.980	8.267	2.357	2142.3
0	.0180	2.5100	.00900	97.463							
300	.0122	1.0623	.26690	98.659	.74240	.7706	64.996	23.345	8.400	2.486	4075.0
0	.0172	2.4000	.00770	97.575							
400	.0121	1.0922	.23542	98.660	.14680	.5327	68.278	21.641	7.764	1.785	750.9
TRINO											
0	.0193	2.9200	.01420	97.046							
100	.0140	1.8000	.24963	97.936	.56880	.4383	75.473	15.712	7.187	1.189	3559.0
0	.0200	3.3100	.01900	96.651							
200	.0140	2.3088	.22559	97.452	.60996	.3600	78.747	14.056	5.942	.895	3138.8

$^{*} \times 10^6$

TABLE XIII

ISOTOPIC RATIOS AND RATIO VALUES FOR TESTING INTERNAL CONSISTENCY AND MEASUREMENT ACCURACY OF U AND PU CHEMICAL PLANT DATA

CANDU

INDIVIDUAL BATCHES
ISOTOPIC RATIOS ARE FORMED USING WT. PERCENTS

BATCH NO.	235U/238U	236U/238U	236U/235U	240PU/239PU	241PU/239PU	241PU/240PU	242PU/239PU	242PU/240PU	242PU/241PU	PU/U
0	.71654-02									
400	.33755-02	.60101-03	.17805-00	.26868-00	.36904-01	.13735-00	.91075-02	.33897-01	.24679-00	.27615+04
500	.30514-02	.64129-03	.21016-00	.29174-00	.42168-01	.14454-00	.11273-01	.38639-01	.26733-00	.30025+04
900	.30434-02	.65143-03	.21405-00	.30725-00	.46629-01	.15176-00	.13540-01	.44067-01	.29037-00	.30501+04
200	.28040-02	.71092-03	.25354-00	.32806-00	.54509-01	.16615-00	.15314-01	.46680-01	.28095-00	.32693+04
600	.27880-02	.76695-03	.27509-00	.32739-00	.51814-01	.15827-00	.15233-01	.46528-01	.29399-00	.32901+04
800	.27446-02	.72183-03	.26300-00	.32688-00	.50946-01	.15585-00	.14612-01	.44700-01	.28681-00	.31691+04
700	.27175-02	.74520-03	.27422-00	.33332-00	.53443-01	.16033-00	.15615-01	.46845-01	.29217-00	.33418+04
100	.27094-02	.72582-03	.26789-00	.32547-00	.52068-01	.15998-00	.14920-01	.45842-01	.28656-00	.32932+04
300	.25435-02	.74277-03	.29203-00	.34126-00	.57285-01	.16786-00	.16709-01	.48964-01	.29169-00	.34061+04

CdN

BATCH NO.	235U/238U	236U/238U	236U/235U	240PU/239PU	241PU/239PU	241PU/240PU	242PU/239PU	242PU/240PU	242PU/241PU	PU/U
0	.46934-01	.50286-03	.10714-01							
400	.32371-01	.26390-02	.81552-01	.12926-00	.13481-01	.10429+00	.15860-02	.12270-01	.11765+00	.17192+04
100	.31093-01	.28959-02	.93135-01	.13175-00	.15693-01	.11911+00	.21898-02	.16620-01	.13953-00	.17620+04
300	.30565-01	.29150-02	.95369-01	.13636-00	.15474-01	.11348+00	.16119-02	.11820-01	.10417+00	.18038+04
500	.30566-01	.29147-02	.95358-01	.13497-00	.18405-01	.13636-00	.00000	.00000	.00000	.17554+04
200	.30364-01	.29973-02	.98712-01	.15093-00	.17699-01	.11726+00	.24582-02	.16287-01	.13889-00	.18146+04

TABLE XIII (Cont'd)

ISOTOPIC RATIOS AND RATIO VALUES FOR TESTING INTERNAL CONSISTENCY AND MEASUREMENT ACCURACY OF U AND PU CHEMICAL PLANT DATA

VAK
INDIVIDUAL BATCHES
ISOTOPIC RATIOS ARE FORMED USING WT. PERCENTS

BATCH NO.	235U/238U	236U/238U	236U/235U	240PU/239PU	241PU/239PU	241PU/240PU	242PU/239PU	242PU/240PU	242PU/241PU	PU/U
0	.23862-01	.71688-04	.30043-02							
100	.10808-01	.23337-02	.21593-00	.32731-00	.11380+00	.34769-00	.29791-01	.91019-01	.26178-00	.48730+04
200	.10422-01	.23957-02	.22987-00	.34955-00	.12575-00	.35974-00	.35856-01	.10258+00	.28515-00	.50211+04
0	.25753-01	.92343-04	.35857-02							
300	.10767-01	.27053-02	.25125-00	.35917-00	.12924-00	.35982-00	.38247-01	.10649+00	.29594-00	.54890+04
0	.24596-01	.78914-04	.32083-02							
400	.11070-01	.23862-02	.21556-00	.31695-00	.11371+00	.35877-00	.26136-01	.82462-01	.22985-00	.51151+04
TRINO										
0	.30089-01	.14632-03	.48630-02							
100	.18379-01	.25489-02	.13868-00	.20818-00	.95231-01	.45744-00	.15748-01	.75644-01	.16536-00	.62570+04
0	.34247-01	.19658-03	.57402-02							
200	.23692-01	.23149-02	.97708-01	.17850-00	.75454-01	.42271-00	.11369-01	.63690-01	.15067-00	.51459+04

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JEX - 70

Chapter 7

Analytical Interlaboratory Tests

Evaluated and reported
by

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The names of the analysts and the authors of special contributions are given with the title of the corresponding section.

1)EURATOM, delegated to GFK
2)Gesellschaft für Kernforschung (GFK), Karlsruhe, Germany
3)Bhabha Atomic Research Center, Bombay, India, delegated to GFK

Abstract

Within the framework of the safeguards experiment JEX-70, an analytical intercomparison program was carried out with the cooperation of eight international laboratories. Main objective was the acquisition of basic data on the errors involved in several analytical techniques applicable to safeguards measures.

In order to approach practical conditions as far as possible, the samples were taken from a reprocessing campaign at the EUROCHEMIC plant and analyzed according to routine procedures. The results were evaluated by statistical methods mainly in regard to the calculation of the estimates of the variances for the different error components contributing to the total error of the analytical techniques considered.

In particular, concentration and isotopic analyses of uranium and plutonium product solutions by wet-chemical methods and mass spectrometry, respectively, were investigated. Furthermore, a preliminary test on the isotopic dilution analysis of active feed solutions was performed.

Data on the efforts (manhours) of the analytical procedures used are compiled.

The following laboratories participated on the analytical tests reported in this Chapter:[1]

BCMN -

Bureau Central de Mesures Nucléaires, EURATOM, Geel, Belgium

CEN -

Centre d' Etude de l'Energie Nucléaire, Mol-Donc, Belgium

CCR -

Joint Research Center of EURATOM, Chemistry Division, Ispra, Italy

EUROCHEMIC -

European Company for Chemical Processing of Irradiated Fuels, Analytical Laboratory, Mol, Belgium

GFK -

Gesellschaft für Kernforschung, Institut für Radiochemie, Karlsruhe, Germany

IAEA -

International Atomic Energy Agency Laboratory, Seibersdorf, Austria

ORNL -

Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

TU -

European Institute of Transuranium Elements, EURATOM, Karlsruhe, Germany

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1)The laboratories are given in the alphabetic order of the abbreviations used in this report.

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Introduction

Knowledge about the capabilities of methods applicable to the analysis of nuclear fuels should be as complete as possible for the establishment of a most efficient safeguards system. For this reason, an extensive analytical intercomparison program was carried out within the framework of JEX-70 with the cooperation of many international laboratories. Main objective was the acquisition of basic data on the errors involved in different analytical techniques and on the effort required. Furthermore, experience should be gained on sampling, sample storage and transportation.

The following analytical procedures were the subject of this test program:

a) Determination of uranium and plutonium concentrations, respectively, in nitric solutions by wet-chemical methods and X-ray fluorescence spectrometry.

b) Determination of the isotopic composition of uranium and plutonium by thermionic mass spectrometry including α-spectrometric measurements of the plutonium isotope Pu-238.

c) Determination of uranium and plutonium concentrations by mass spectrometric isotope dilution analysis.

In order to approach practical conditions as far as possible, the samples were taken directly from active feed solutions and product material of a reprocessing campaign at the EUROCHEMIC plant and distributed to the laboratories without any purification prior to shipment. For the same reason, the laboratories were asked explicitely to perform the analyses according to their routine procedures and no common standards or reference materials were supplied. This should be emphasized, since it should be taken into account in the judging on the results obtained and because this way of performance is essentially different from those followed in other tests carried out in recent years (e.g. the umpire test program [7.-1]) using synthetic sample solutions.

A total of eight analytical laboratories participated in some or all of the tests performed. In case of the concentration measurements on nitric product solutions, the results of 75 single determinations were made available for uranium, 55 for plutonium. Investigations on the mass spectrometric analysis of isotopic compositions could be based on roughly 1000 single isotopic ratio determinations for uranium and about 1400 for plutonium. In regard to the mass spectrometric isotope dilution analysis of active feed samples, 15 independent concentration determinations each were reported for uranium and plutonium, respectively.

After preliminary compilation of the analytical data communicated, analysts of the participating laboratories discussed their experience and the results during a meeting held at Ispra from October 6 to 8, 1970. The conclusions and recommendations elaborated in these sessions (Appendix I) were used as the basis of the evaluation and interpretation presented in this Chapter.

The statistical methods applied are summarized in Appendix II. The calculations were related mainly to determination of the estimates of the variances for the different error components contributing to the total error of the analytical procedures investigated. However, no attempt was made to calculate "best estimates" for the true values of the quantities considered (concentrations, isotopic ratios etc.) because of the principal difficulties in their most appropriate definition and the unknown true compositions of the samples.

In this report, the names of the laboratories were codified differently for each test. In particular, there is no relation of the code numbers to the alphabetic order in which the names of the participating laboratories are given with the headline of each test.

7.1 Interlaboratory Test I:

Concentration and Density Determination of Uranium Product Samples

Participants:

- CEN:
  R. Boden, A. Demildt, F. Lievens and P. De Regge
- CCR:
  J. Collin and H. Muntau
- EUROCHEMIC:
  H. Bokelund and K.H. Henn
- GFK:
  A. von Baeckmann, E. Mainka and H. Ruf
- IAEA:
  J. Jirota, J. Malinowski and K. Russin
- TU:
  L. Angeletti and W. Bartscher

7.1.1 Planning and Performance of the Experiment

7.1.1.1 Objectives

Aim of this interlaboratory test was mainly to estimate the magnitude of the different error components involved in the uranium concentration determination of samples taken from the uranium product solution of a reprocessing plant. It was assumed that the existing sources of error could be described by the following three components:

a) The "sampling error" which includes inhomogeneity of the solution in the tank and possible cross contaminations in course of the sampling procedure.

b) The "interlaboratory deviation" caused by differences in the standards or reference materials used, errors in standardization and random components.

c) The "precision" (or reproducibility) by which the statistical error of the measurement itself is understood. This error component may also include contributions by sample preparation steps performed within the laboratories after the sample material was subdivided for the single repetition measurements.[1)]

Because of the stability of the sample material investigated in this test, the possibility of changes in sample composition during storage time between sampling and analysis was not considered in particular.

7.1.1.2 Sampling system

Figure 7.1-1 shows the scheme of the sampling system commonly used in reprocessing plants.

The samples were taken from two relatively small product receiver tanks (maximum capacity about 1500 l) installed in parallel and fed continuously

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1)Errors introduced by sample preparation steps before subdivision of the sample material for the single repetition measurements contribute to the interlaboratory deviation or the sampling error depending on the model used for the analysis of variances (7.1.4.2).

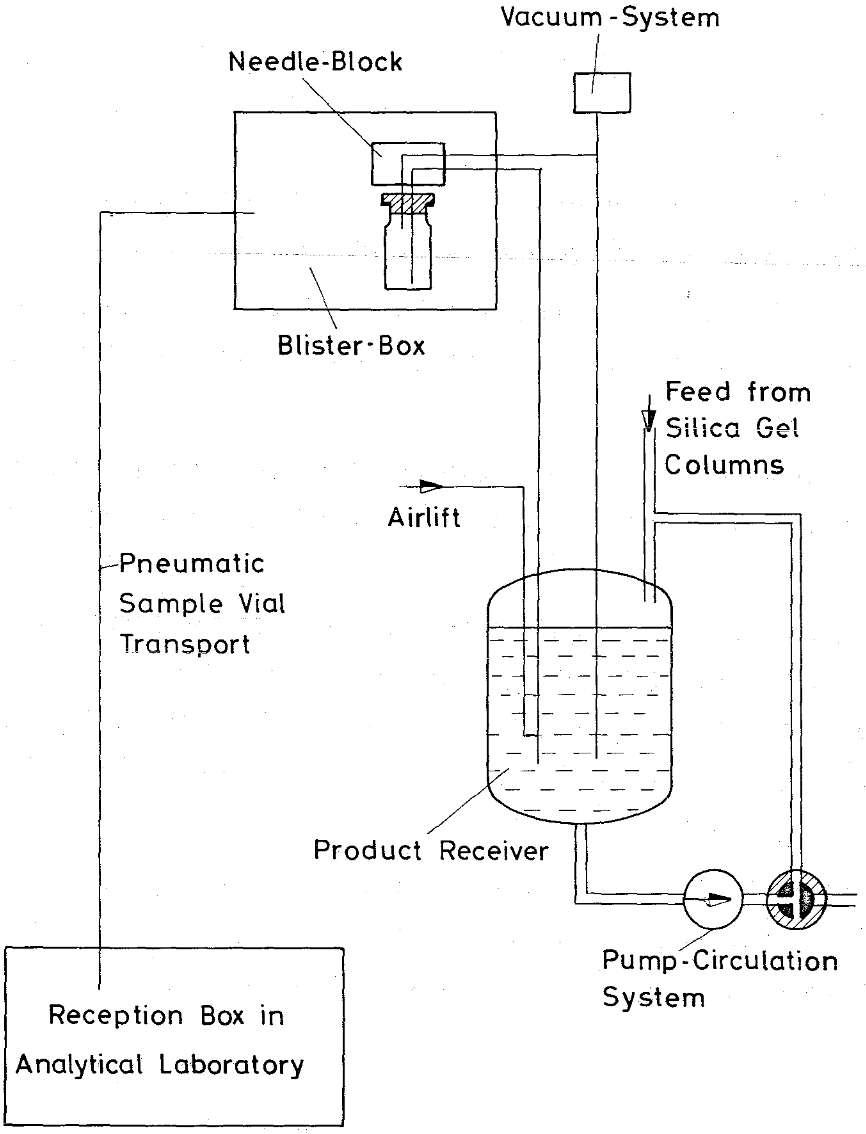

Fig. 7.1-1 Interlabtest I : Scheme of U-Product Sampling Tank and Sampling System

by the silica gel columns with uranium product from the third extraction cycle (3UP). During sampling and batch measurements the flow is switched over to the parallel tank.
In these particular product receiver tanks, homogenization of the solution is only possible by circulation maintained with a pump as shown in the scheme.

By means of an air lift and vacuum system the material can be circulated through the sample vial (Figure 7.1-2) back to the tank. This procedure is important in order to avoid cross contamination in the sample line.

After stopping circulation the sample vial is disconnected from the needle block, put into a plastic cartridge (Figure 7.1-2) and shot by a pneumatic post system to the reception box in the analytical laboratory.

In order to guarantee safe sample shipments to the laboratories, the plastic cartridges with the sample bottles were put into specially developed inserts (Figure 7.1-3) which fitted to BF-3 birdcages. No damages were reported on sample bottles packed in this way.

7.1.1.3 Sampling procedure

The sampling procedure followed in this particular test is shown schematically in Figure 7.1-4. Three sets of seven samples each (in the following indicated as A, B and C-samples) have to be distinguished. The A-samples were taken without previous homogenization of the tank solution, the B- and C-samples after circulation of the tank solution for thirty and (in total) sixty minutes, respectively.[1)]

Before sampling of each set, the sample line was flushed by means of the air lift and vacuum system mentioned above (7.1.1.2) to avoid cross con-

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1)Special attention is drawn to the fact that the A-samples were taken without preceding homogenization. As this sampling procedure is not used in normal plant operation, different concentrations of the A-samples compared to the others are of no practical interest and therefore not considered in the evaluation of this test. However, inhomogeneity indicated by concentration differences between the B- and C-samples would be of importance as these samples were taken according to routine procedures.

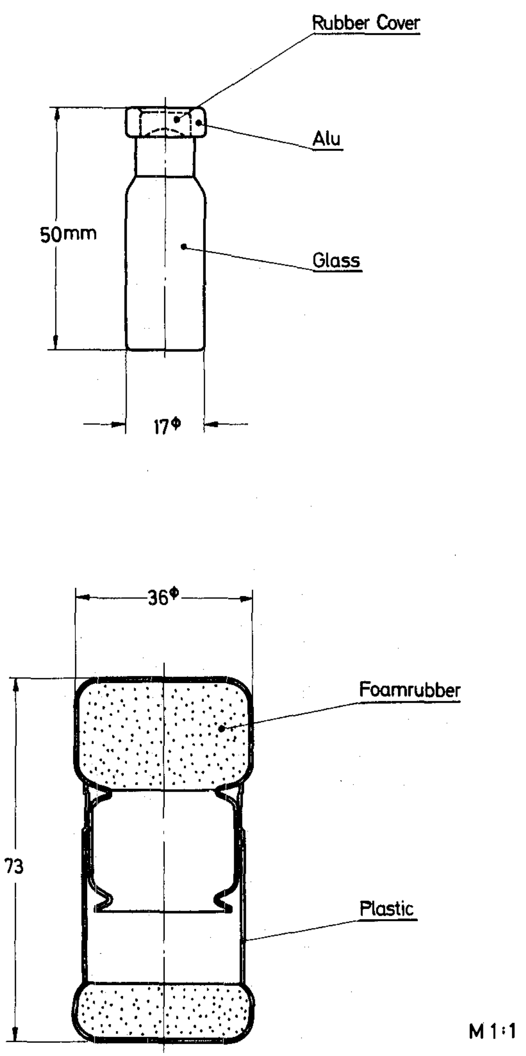

Fig. 7.1-2 Interlabtest I. Sample Vial and Plastic Cartridge

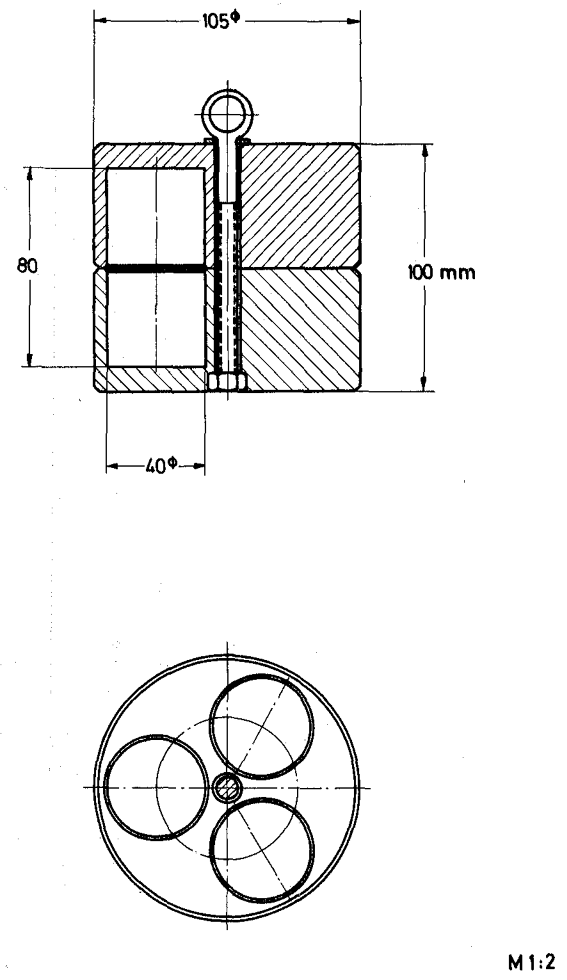

Fig. 7.1-3 Interlabtest I. Insert for Transportation of Sample Vials (Fig. 7.1-2) in BF-3 Birdcages

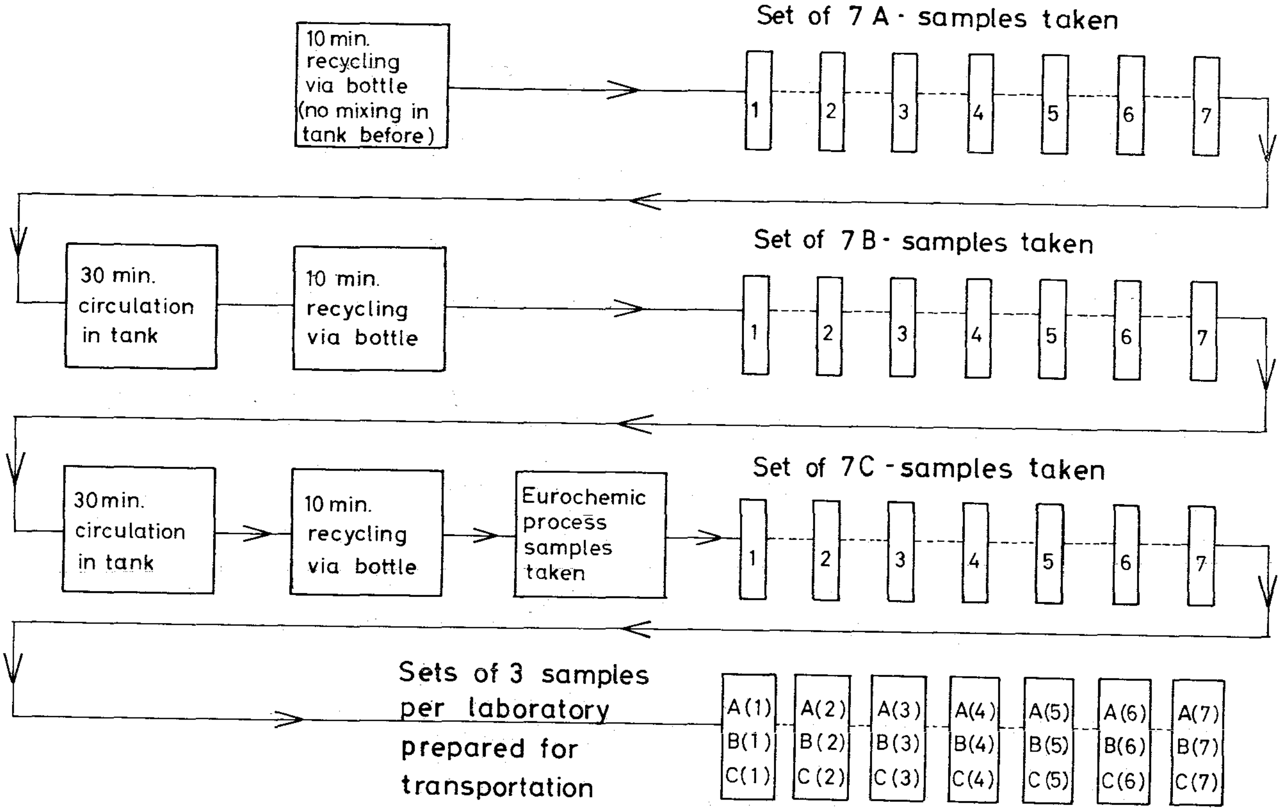

Fig.7.1-4 Interlabtest I: Sampling Procedure of U-Product Samples

tamination with residual material. However, the seven bottles belonging to the same group of samples were filled immediately one after the other. Therefore, within each set, the samples can be considered as homogeneous and with agreement of the participating laboratories no further homogenization steps were carried out.

All 21 samples for this interlaboratory test were taken on March 19, 1970 from CANDU batch 3UP-1000 and each sample bottle contained approximately 3 ml solution with a concentration of nearly 280 mg U/g solution, a density of about 1.6 g/ml and a nitric acidity of less than 0.5 M.

7.1.1.4 Request for analysis

Each of the six laboratories participating in this test received one A-, one B- and one C-sample with request for the determination of the uranium concentration using their routine method. As some laboratories used several analytical techniques, the results of eight independent analytical procedures became available. It was asked to perform the analysis on each sample at least in triplicate in order to allow the calculation of the precisions for the different methods applied.

Furthermore, density measurements on the samples were requested. Originally this was done only as an additional check on the representativeness of the samples in case extraordinary deviations in the concentration values would occur. However, because of the general interest in this method for the detection of sample inhomogeneity, the results obtained by the laboratories were included in this report and also evaluated to a certain extent.

7.1.2 Analytical Methods Applied by the Laboratories

The analytical methods applied were reported by the participating laboratories as follows:

7.1.2.1 Concentration determinations

Laboratory code I:

Method: After dilution with 3 M HNO_3, the sample is given into conc. phosphoric acid and reduced with an excess of Fe^{++}. The excess of Fe^{++} resp. U^{3+} is oxidised with air oxygen on nitric acid in the presence of a Molybdat-catalysator. After dilution and waiting for 15 minutes the sample is titrated with $K_2Cr_2O_7$. The endpoint is determined optically using Ba-Diphenylaminsulfonat as indicator.

Lit.: W. Davies and W. Gray, Talanta 11, 1203 (1964)

Reference material: U_3O_8 nuclear pure Merck

Remark: From each original sample solution one dilution was made and then split into 3 single samples. All samples were titrated with the same $Cr_2O_7^{--}$ solution.

Laboratory code II:

Method: The dissolved sample is first converted to the chloride and then the uranyl chloride is reduced in strong hydrochloric acid solution by metallic aluminium in the presence of cadmium chloride to trivalent uranium. Phosphoric acid is added and the U III is oxidized to U IV by hydrogen ions. After dilution excess Fe III is added and the resulting solution titrated by adding first a weighed amount of solid potassium dichromate and then titrating the remainder with a standard solution of potassium dichromate to a potentiometric endpoint using the platinum-calomel electrode pair.

Lit.: L. Pszonicki, Talanta 13, 403 (1966)

Standard: NBS standard dichromate was used as the primary titrant. The weighed amount was corrected to vacuum. All samples were run with standards and reagent blanks.

Reference Standard: NBS U_3O_8 950a.

NBS U standard recovery was 99.993 % and 99.979 % when run through the procedure.

Laboratory code III:

Method: The uranium determination is based on the potentiometric titration of U (IV) with 0.2 N dichromate. The uranium was previously reduced to U (IV) by Ti (III). Each titration was performed on about 100 mg uranium.

Laboratory code IV:

Method: About 2,9 g of sample solution was weighed in a dissolution flask, 30 ml of water, 5 ml 9 M H_2SO_4, and 300 mg $NaNO_2$ were added and the solution was heated to boiling for 40 min. After cooling the solution was made up to 100 ml in a volumetric flask.

An aliquot of 5 ml was taken, 0.1 ml of 1 M sulfamic acid solution was added and a pre-electrolysis was carried out of + 0.1 V vs.sat. AgCl electrode. Then the main-electrolysis was made at - 0.4 V vs. sat.AgCl electrode until the current had dropped to a constant value of 20-30 µa. The coulombs for the main-electrolysis were measured and after a correction for reagents blank and residual current the amount of uranium was calculated.

Laboratory code V:

Method: Gravimetric determination of U after conversion to U_3O_8.

Corrections of oxide weight for:

a) Isotopic composition of U,

b) Impurities forming non-volatile oxides via emission spectrographic impurity determination. In this particular case the impurities amounted to 398 ppm expressed as oxides.

Standard: NBS, U_3O_8 (not always used)

Laboratory code VI:

Method: A weighed aliquot of the sample is mixed with a defined amount of thorium nitrate solution. In the solution the ratio of the intensities of the uranium and the thorium $L\alpha_1$-lines are compared.

Lit.: P.A. Pella et al., Anal. Chim. Acta 47, 431 (1969)

Reference material: U_3O_8 Merck, nuclear pure

Remark: From each original sample solution one dilution was made and divided into three single samples. To each of these single samples a different amount of thorium has been given as internal standard and one analysis per single sample was performed.

Laboratory code VII:

Not reported as data codified under this number were given for orientation only and do not form an official part of the interlaboratory test.

Laboratory code VIII:

Method: The uranium has been prepared as a sulphate. The hexa-valent uranium is reduced in 0.5 M sulphuric acid after a pre-electrolysis step at + 0.1 V vs.sat.Calomel-electrode at a mercury pool cathode at -0.325 V. The coulomb is used as a primary standard.

Remark: U_3O_8 (Merck, nuclear pure), treated according to the NBS procedure has been carried through the complete analytical process and a constant systematic error of - 0.15 % has been found. Other laboratories are also observing similar effects and discussions were leading to the conviction that this error is due to certain characteristics of the ORNL coulometer. Therefore, it may be concluded that coulomb should be substituted by the NBS uranium oxide as a primary standard.

Laboratory code IX:

Method: Gravimetric determination of U after conversion to U_3O_8.

Corrections of oxide weight for:

a) Isotopic composition of U,

b) Impurities forming non-volatile oxides. 400 ppm were assumed.

7.1.2.2 Density determinations

Laboratory code I:

A H_2O-calibrated pipette (2 ml) was used and a correction for temperature has been applied.

Laboratory code II:

U-density: Obtained by weighing a calibrated dry 1 ml glass pipette. The value was corrected for temperature but not for air buoyancy.

Laboratory code III:

The measurements were made by picnometers; the room temperature was constant within 3° C and humidity about 60 %. However, density determinations and picnometer calibration were performed using a water bath of 20.0 ± 0.2° C.

Laboratory code IV:

No density measurements reported.

Laboratory code V:

Pipetting of 1 ml of solution using siliconized calibrated pipette at constant temperature, weighing.

Laboratory code VI:

A 2 ml pipette was used, calibrated with H_2O. Corrected for temperature.

Laboratory code VII:

No density measurements reported.

Laboratory code VIII:

The determination of density was made using a 1 ml-picnometer. The results have been corrected for temperature and air buoyancy.

Laboratory code IX:

No density measurements reported.

7.1.3 Reported Analytical Results

In Table 7.1-1, all single concentration determinations and in Table 7.1-2 all single density measurements which were reported are compiled in columns 5 and 4, respectively. The concentration values are given in mg U/g solution, the density values are corrected for 20° C in all cases.

For a first survey, these results are graphically presented in Figures 7.1-5 and 7.1-6. Figure 7.1-5 shows for each individual laboratory the relative deviation of the mean value per sample from the mean of all these means. The error bars correspond to the relative standard deviation of the mean value per sample, calculated from the reported data. For the laboratories V and IX this was not possible as only one measurement per sample was available. Therefore, the dashed bars shown were based on the communicated long term experience of these laboratories.

Figure 7.1-6 represents the results of the density determinations in the same manner.

7.1.4 Evaluation

7.1.4.1 Review of data

Review of the concentration determinations (Table 7.1-1, columm 5) shows in case of laboratory VIII, sample A, a distinct difference between the values obtained from the repetition measurements 1 to 3 and 4 to 6. The laboratory reported that malfunction of the electronic equipment was observed during the first three measurements.

In order to decide whether these values can be rejected from further calculations, the mean value of this first group of measurements on sample A (1 to 3) was compared with the mean value of the second group of determinations (4 to 6) of this same sample. By a test of significance (Appendix II,2) it could be shown that there exists a significant difference with a probability of error of less than 2.5 %. Therefore, on the basis of this test and the reported experimental difficulties, the first three values were considered as outliers and excluded from the further calculations. The value for sample A given in Figure 7.1-5 was calculated from the remaining three single determinations.

Furthermore the mean value of the concentration of sample A determined by laboratory VI using X-ray fluorescence spectrometry is relatively high compared to the values obtained on the samples B and C by the same laboratory. As it can be seen from Figure 7.1-5, the relative standard deviations of these mean values would allow to consider this deviation as strictly random. It should be noted, however, that the density of this sample (only one determination) has also been found very high compared to the values of the other samples (Figure 7.1-6). This indicates, that the explanation of the higher concentration by random errors only is very probably insufficient and that there exists a significant deviation in the composition of this specific sample because of evaporation or other reasons.

7.1.4.2 Estimation of error components

As already mentioned in 7.1.1.1, sampling errors, interlaboratory deviations and the precision of the measurements were considered as the main

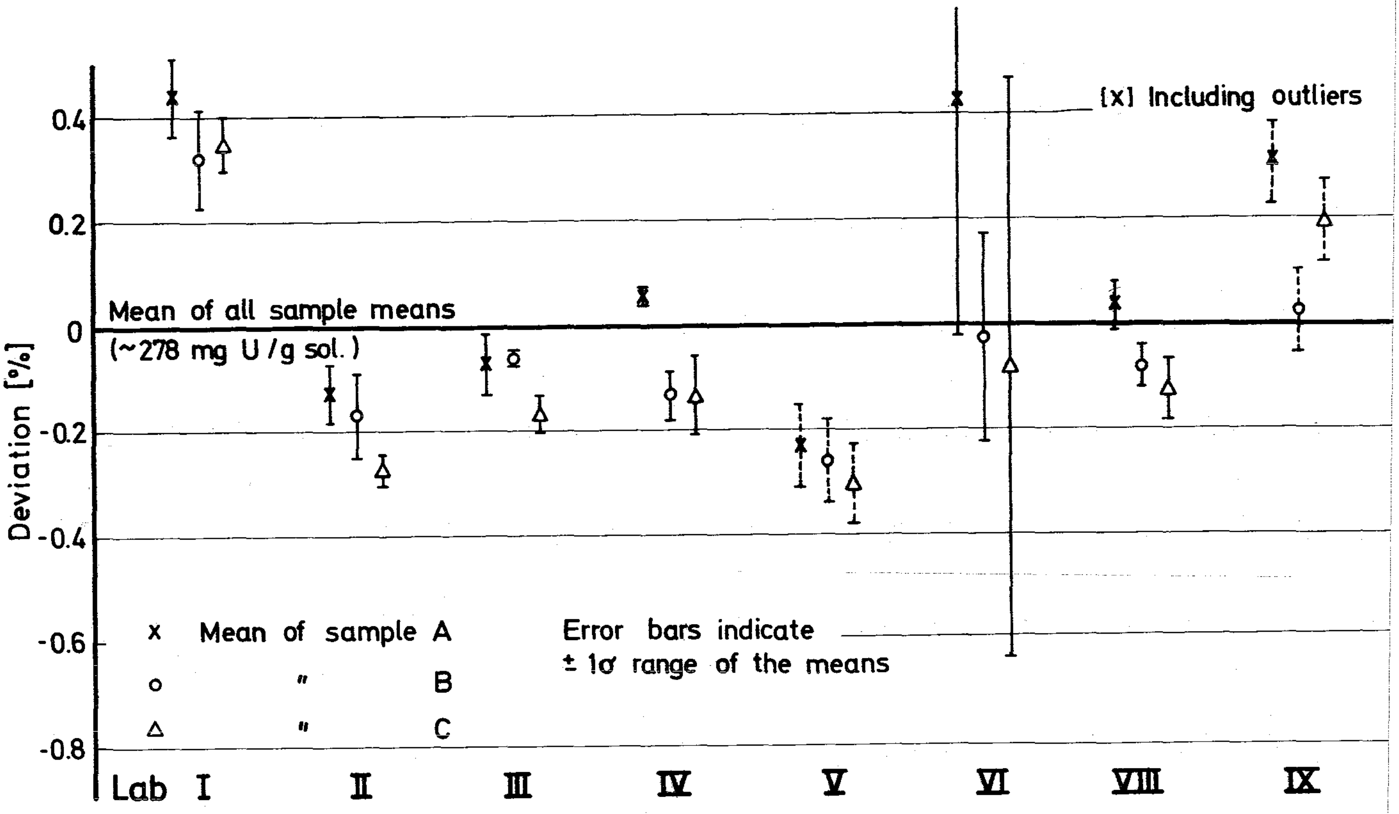

Fig.7.1-5 Interlabtest I: Concentration Determinations of U-Product Samples

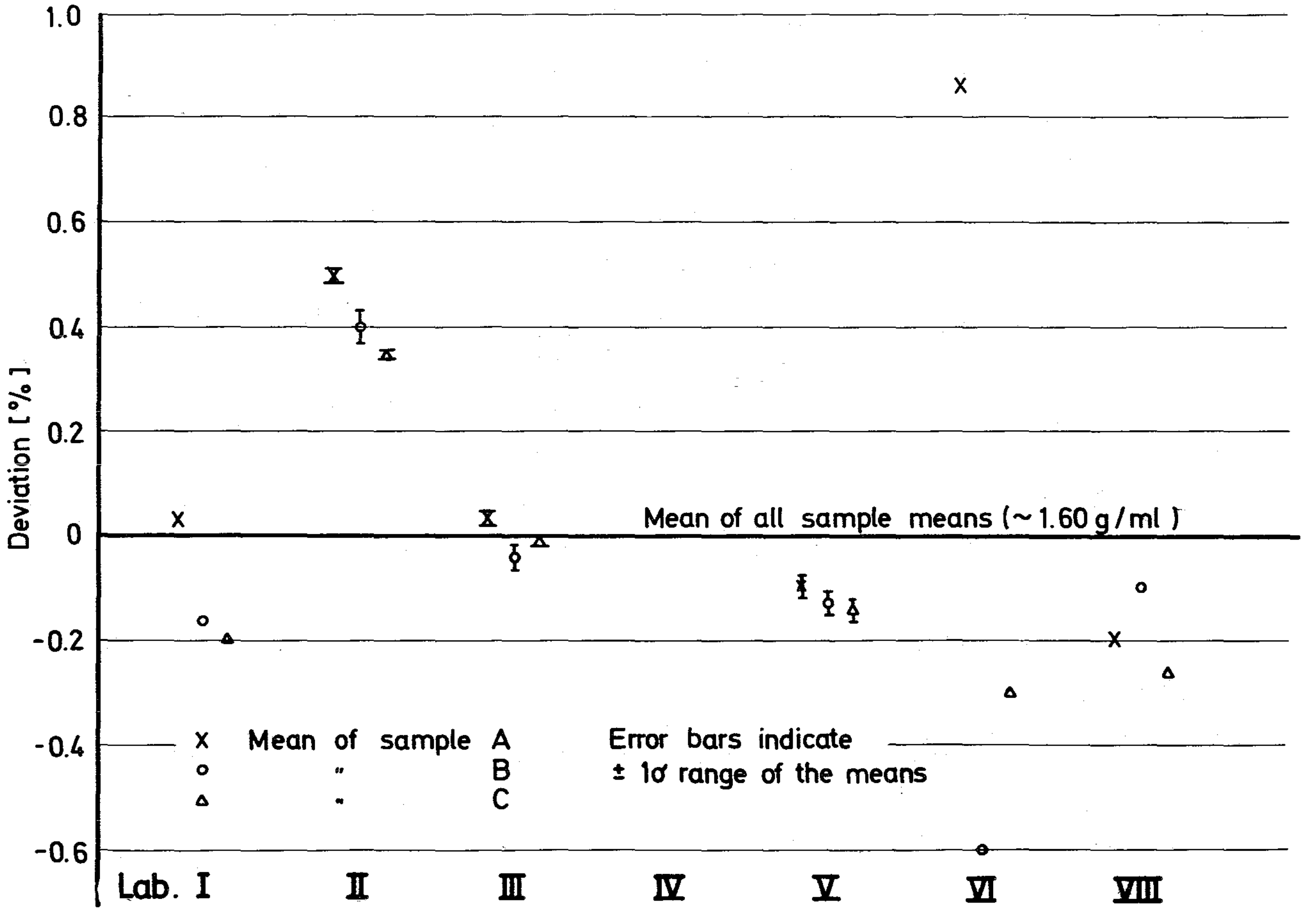

Fig.7.1-6 Interlabtest I: Density Determinations of U-Product Samples

Table 7.1.-1: Interlabtest I: Reported Concentration Determinations

Laboratory code	Analytical method	Sample description	Repetition measurement number	Reported single determination [mg U/g sol.]	Mean value per sample ± SD [mg U/g sol.]
1	2	3	4	5	6
I	Oxydimetry	A	1	278.39	
			2	278.77	278.76
			3	279.11	± 0.36
		B	1	278.30	
			2	278.92	278.43
			3	278.07	± 0.44
		C	1	278.37	
			2	278.81	278.50
			3	278.33	± 0.26
II	Oxydimetry	A	1	277.44	
			2	277.40	277.18
			3	277.05	± 0.29
			4	276.83	
		B	1	277.74	
			2	277.13	277.05
			3	277.09	± 0.46
			4	276.53	
			5	276.75	
		C	1	276.84	
			2	276.89	276.77
			3	276.88	± 0.16
			4	276.74	
			5	276.49	
III	Oxydimetry	A	1	277.57	
			2	277.03	277.34
			3	277.43	± 0.28
		B	1	277.42	
			2	277.36	277.37
			3	277.33	± 0.04
		C	1	277.21	
			2	277.11	277.06
			3	276.86	± 0.18
IV	Coulometry	A	1	277.8	
			2	277.7	277.70
			3	277.6	± 0.10
		B	1	277.4	
			2	277.0	277.17
			3	277.1	± 0.20
		C	1	277.2	
			2	276.8	277.17
			3	277.5	± 0.35

Table 7.1.-1 (continued)

1	2	3	4	5	6
V	Gravimetry	A	1	276.9	276.9
		B	1	276.8	276.8
		C	1	276.7	276.7
VI	X-ray fluorescence spectrometry	A	1	279.54	-
			2	276.24	278.72
			3	280.39	± 2.19
		B	1	277.11	
			2	276.77	277.47
			3	278.54	± 0.94
		C	1	277.38	
			2	279.98	277.32
			3	274.62	± 2.68
VII	Values codified under this number were given for orientation only				
VIII	Coulometry	A	1	(279.12) 1)	
			2	(281.02) 1)	
			3	(281.22) 1)	
			4	277.42	277.65
			5	277.72	± 0.20
			6	277.82	
		B	1	277.42	
			2	277.01	
			3	277.12	277.30
			4	277.72	± 0.26
			5	277.12	
			6	277.42	
		C	1	276.61	
			2	277.12	
			3	277.72	277.20
			4	277.32	± 0.38
			5	277.01	
			6	277.42	
IX	Gravimetry	A	1	278.4	278.4
		B	1	277.6	277.6
		C	1	278.1	278.1

---

1) Considered as outliers (see 7.1.4.1).

Table 7.1.-2: Interlabtest I: Reported Density Determinations

Laboratory code	Sample description	Repetition measurement number	Reported single determination [g/ml]	Mean value per sample ± SD [g/ml]
1	2	3	4	5
I	A	1	1.59693	1.59693
	B	1	1.59394	1.59394
	C	1	1.59347	1.59347
II	A	1	1.6045	1.60435
		2	1.6042	± 0.00067
	B	1	1.6032	
		2	1.6031	
		3	1.6014	1.60304
		4	1.6032	± 0.00104
		5	1.6043	
	C	1	1.6023	
		2	1.6021	
		3	1.6018	1.60182
		4	1.6010	± 0.00050
		5	1.6019	
III	A	1	1.59732	
		2	1.59715	1.59706
		3	1.59670	± 0.00032
	B	1	1.59639	
		2	1.59600	1.59592
		3	1.59538	± 0.00051
	C	1	1.59653	
		2	1.59644	1.59646
		3	1.59642	± 0.00006
V	A	1	1.5946	1.59495
		2	1.5953	± 0.00050
	B	1	1.5943	1.59465
		2	1.5950	± 0.00050
	C	1	1.5940	1.59425
		2	1.5945	± 0.00035
VI	1	1	1.6104	1.61040
	2	1	1.5869	1.58690
	3	1	1.5917	1.59170
VIII	1	1	1.59334	1.59334
	2	1	1.59577	1.59577
	3	1	1.59236	1.59236

Remark: Laboratories IV, VII and IX reported no density measurements.

sources of error in the concentration and density determinations. The structure of the experiment allows the calculation of the estimates of the variances of these three error components as described in detail in Appendix II, 4. According to the statistical model used (Figure 7.AII-1) errors introduced in course of sample preparation within the laboratories (before the material was subdivided for the single repetition measurements) contribute to the interlaboratory deviation which describes the difference between the true value of the concentration or density of the sample and the expectation values referring to the repetition measurements performed by the laboratories (Appendix II,1).

For these calculations, the concentration as well as the density measurements on sample A were excluded in order to avoid any simulation of inhomogeneity in the tank solution by this sample which was not taken according to routine procedures (7.1.1.3)

Furthermore, for the analysis of variance on the concentration determinations, the measurements carried out by X-ray fuorescence spectrometry (laboratory VI) had to be excluded. This was necessary as from the statistical point of view they are not comparable to those obtained by chemical methods in regard to their precision (7.1.5.3).

The estimates of the variances, standard deviations (SD) and relative standard deviations (RSD) of the different error components in the concentration determinations, based on the measurements of sample B and C by the laboratories I, II, III, IV, V, VIII and IX are given in the following Table 7.1-3.

Table 7.1-3: Interlabtest I: Calculated Variances and RSD of Error Components for the Concentration Determinations

(Only chemical methods, based on B and C samples.)

c = 280 $\frac{\text{mg U}}{\text{g sol.}}$	Sampling error	Interlab. deviation	Precision
Variance	not significant	0.309	0.092
SD	-	0.557	0.303
RSD /‾%_7	-	0.20	0.11

For the corresponding analysis of variances of the error components involved in the density measurements, the values reported by the laboratories I, II, III, V, VI and VIII could be used.[1] The results are summarized in the following Table 7.1-4.

Table 7.1-4: Interlabtest I: Calculated Variances and RSD of Error Components for the Density Determinations
(Based on B and C samples)

$d \simeq 1.6 \frac{g}{ml}$	Sampling error	Interlab. deviation	Precision
10^6 Variance	not significant	25.082	0.444
10^3 SD	-	5.008	0.667
RSD [%]	-	0.31	0.04

It should be noted that the results obtained by analysis of variances represent estimates (average values of measurement results) which have error bars themselves.

7.1.5 Discussion of the Results on the Concentration Determinations

7.1.5.1 Sampling error

As mentioned in 7.1.1.1, the sampling error describes inhomogenity of the tank solution and possible cross contamination during the sampling procedure. By analysis of variances based on the measurements of samples B and C performed by all laboratories using chemical methods, this error component was found as not significantly different from zero (Table 7.1-3).

For a more detailed investigation analyses of variances were carried out

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1)The laboratories IV and IX did not report density measurements.

in addition separately for the laboratories I, II, III, IV and VIII (Appendix II,3), again using the data of the B and C-samples. Applying this statistical model[1] also the errors of sample preparation steps performed within the individual laboratory (before subdivision of the sample material for the single repetition measurements) contribute to the sampling error component.

Only in case of the laboratories II and III, small positive variances for the sampling error corresponding to relative standard deviations of 0.04 % and 0.07 %, respectively, were calculated. Tests of significance (Appendix II, 2) confirmed the existence of a significant difference between the B and C sample in case of laboratory III with a probability of error of less than 5 %. For the results of laboratory II however, no significant difference between the B and C sample could be confirmed with a probability of error below 10 %.

Although there is no final proof it seems that these small positive values of the sampling error have to be considered more likely as caused by sample preparation in the laboratories than as an indication for inhomogeneity of the tank solution which should become visible also by the measurements of the other laboratories.

7.1.5.2 Interlaboratory deviation

According to the result of the variance analysis (Table 7.1-3), the interlaboratory deviation has a relative standard deviation of about 0.20 % and contributes the main part to the total variance of a single measurement in this experiment. As already mentioned (7.1.1.1), this error component is caused by differences in the standards and reference materials used, by errors in the standardization and random components. Significant contributions by sample preparation errors which are included in the interlaboratory deviation calculated in this way (7.1.4.2) do not exist as shown by the investigations discussed before (7.1.5.1).

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1) In this case the index "j" is attributed to the sample and the index "i", describing the laboratory, is fixed for each test.

In respect to the recommendations given at the Ispra Meeting (Appendix I), significance tests as described in Appendix II,2 were made for further confirmation on the existence of these interlaboratory deviations. In order to get results which are principally independent of concentration differences between the A, B and C-samples, the tests were performed for each type of sample separately. Based on the values obtained by the laboratories I, II, III, IV and VIII using chemical methods[1], these tests confirmed in each case (A, B and C-samples) the existence of significant differences between the measurements of the laboratories with a probability of error of less than 1 %.

7.1.5.3 Precision

The precisions calculated from the data of this experiment for the individual laboratories, partially using different analytical methods, are summarized in the following Table 7.1-5 together with the values reported by the laboratories for long term experience.

Table 7.1-5: Interlabtest I: Calculated and Reported Long Term Precision per Laboratory for Concentration Determinations

Method	Lab.code	Precision calculated from the data of this experiment (based on A, B and C samples) RSD [%]	Precision reported for long term experience RSD [%]
Gravimetric method	V	*)	0.08
	IX	*)	not reported
Oxidimetry and controlled potential coulometry	I	0.13	0.1 to 0.2
	II	0.12	(0.03 for 500 mg sample)
	III	0.07	not reported
	IV	0.08	0.25
	VIII	0.11	0.15
X-ray fluorescence spectrometry	VI	0.75	1.0

*)only one determination per sample available.

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[1] The measurements of the laboratories V and IX could not be included since only one single determination per sample was available.

According to the general opinion of the analysts expressed during the Ispra Meeting (Appendix I), the gravimetric method is the most precise one if the concentration determinations are performed on pure materials.

For oxidimetry and controlled potential coulometry a mean value of 0.11 % was calculated by analysis of variance (Table 7.1-3). This value seems to be somewhat better than it could be expected from the data reported on long term experience.

Concerning the higher value obtained by X-ray fluorescence spectrometry, it has to be taken into consideration that this technique is still in the development stage for this type of analysis.[1)]

7.1.6 Discussion of the Results on the Density Determinations

In discussing the results on the density determinations it has to be kept in mind that these measurements were requested only as an additional check on the representativeness of samples in case extraordinary deviations in the concentration values would be observed (7.1.1.4). Therefore, no exact specifications for the performance of these measurements had been given and for some of the laboratories the density determinations could not be considered as a well established routine procedure. As it can be seen from the description of the methods reported (7.1.2.2), some laboratories used picnometers, others pipettes calibrated in different ways and the corrections applied were not the same in all cases. Very probably these are the reasons for the relatively high interlaboratory deviation of 0.3 % calculated by analysis of variances (Table 7.1-4).

As recommended at the Ispra Meeting (Appendix I), significance tests were made (Appendix II,2) on the interlaboratory deviations separately for the A, B and C sample. They could be based only on the determinations of the laboratories II, III and V as only one measurement per sample was performed by the others. The results confirmed in each case the existence of

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1)In this connection it should be noted that the suitability of any analytical method for the application in safeguards depends not only on its precision but also on parameters like the feasibility of automating the process, tamperproofness, sample throughput per time unit, dependency on sample impurity, cost of equipment etc.

significant differences with a probability of error of less than 1 %.

As in the case of the concentration determinations, the sampling error calculated by analysis of variances as described in 7.1.4.2 was found as not significantly different from zero (Table 7.1-4). This means that also the density measurements gave no indication for inhomogeneity of the tank solution in this experiment.[1]

Concerning the precision for which an average value of 0.04 % was calculated by analysis of variances (Table 7.1-4), individual data could only be calculated for the laboratories II, III and V. They are compiled in the following Table 7.1-6.[2]

Table 7.1-6: Interlabtest I: Calculated Precision per Laboratory for Density Determinations

Laboratory code	Calculated precision (based on A, B and C samples) RSD [%]
II	0.045
III	0.022
V	0.028

These values are about one third of the precision obtained in average for concentration determinations by chemical methods (Table 7.1-3). Even taking into consideration that relative differences in density are only about one third of the corresponding differences in concentration for sample material as used in this experiment [7-2], this shows the usefulness of density measurements for checking the homogeneity of different uranium samples because of their lower effort compared to concentration determinations. However, from the results obtained in this experiment, this statement can only be made if the density measurements are performed within one individual laboratory and therefore independent of interlaboratory deviations.

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[1] It should be noted that this result is based on the investigation of samples taken from one single batch only.

[2] No information on the values for long term experience could be given by the laboratories.

7.1.7 Analytical Efforts

In respect to safeguards applications, the laboratories were asked to report the average value of manhours necessary for the analysis of one sample (including sample preparation, density measurement, calculation etc.) based on three independent determinations.

In the following Table 7.1-7 the reported values are summarized.

Table 7.2-7: Interlabtest I: Analytical Efforts (Manhours) Reported by Each Laboratory

Laboratory code	Analytical method	Manhours per analysis
VI	X-ray fluorescence	3
V	Gravimetry	3.5 *)
IX	Gravimetry	not reported
I	Oxidimetry	4
II	Oxidimetry	4
III	Oxidimetry	4
IV	Coulometry	6
VIII	Coulometry	6

*) In addition 4 to 6 manhours for emission spectroscopic determination of impurities forming non-volatile oxides necessary as correction for the gravimetric result.

7.2 Interlaboratory Test II:

Concentration Determination of Plutonium Product Samples

Participants:

- CEN:
  R. Boden, A. Demildt and P.De Regge

- EUROCHEMIC:
  R. Berg and R. Swennen

- GFK:
  A. von Baeckmann and E. Mainka

- IAEA:
  J. Jirota, K. Russin and V. Schuelein

- TU:
  L. Angeletti and W. Bartscher

7.2.1 Planning and Performance of the Experiment

7.2.1.1 Objectives

Aim of this interlaboratory test was to estimate the magnitude of the different error components involved in the determination of the plutonium concentration of samples taken from the plutonium product solution of a reprocessing campaign.[1)]

In comparison to the corresponding investigations on uranium product samples (Interlaboratory Test I), additional sources of error had to be taken into consideration:

Firstly, the possible instability of the sample material due to polymerisation of the plutonium, plating out or other "aging" effects. In order to minimize these effects as far as possible, it seemed advisable to dilute the samples with concentrated nitric acid immediately after they were taken. This dilution step itself, however, may introduce a second additional source of error.

For these reasons, somewhat different definitions of the main error components became necessary compared to those used in the case of Interlaboratory Test I:

a) "Sampling errors" due to possible inhomogeneity of the solution in the tank, errors in the dilution step after sampling mentioned above, and possible cross contamination during the sampling and dilution procedure. The layout of this experiment principally does not allow to distinguish between these sources of error.

b) "Sample errors" caused by aging effects of the sample material and errors which may be introduced by sample preparation steps within

---

1)Although until now the nitric plutonium solution is converted into plutonium oxide in the final stage of the EUROCHEMIC reprocessing plant, it was decided to take the samples for this experiment from the plutonium solution flow before the conversion step. This has been done as this material is more representative as product from reprocessing plants and as there is also a trend to deliver in future plutonium product as nitric solution to the fuel element fabrication plants which will convert it to plutonium oxide by themselves. Therefore, error analysis of the plutonium concentration determination on nitric solution may become of special interest for safeguards purposes in the future.

the laboratories before the material is subdivided for the single repetition measurements.

c) "Interlaboratory deviations" which are mainly due to differences in the standards or reference materials used, errors in standardization and random components.

d) The "precision" (or reproducibility), by which the statistical error of the measurement itself is understood. This error component may also include contributions by sample preparation steps performed after the subdivision of the sample material for the single repetition measurements.

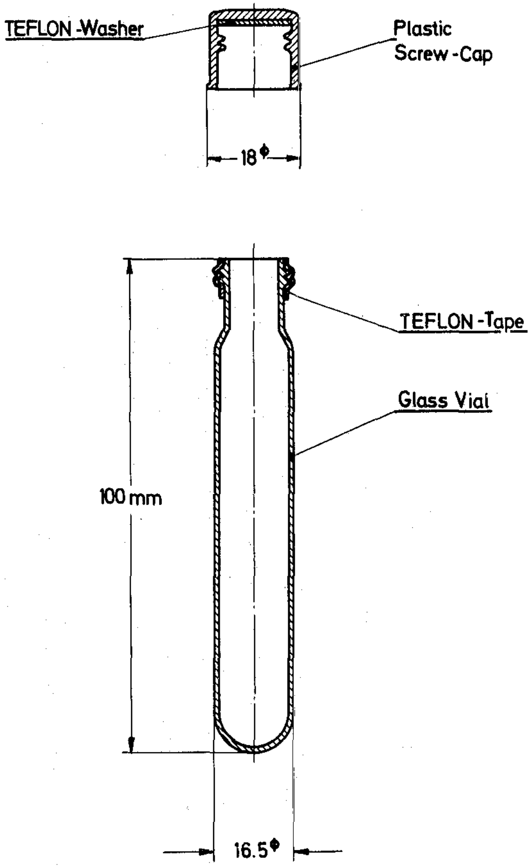
In principal, errors caused by aging effects may consist of two different components: Firstly, a random component varying from the sample solution in one individual sample bottle to the other, secondly, a systematic component depending only on the time interval between sampling and analysis. Only the random component, being specific for each individual sample, contributes to the sample error as defined above (b). A systematic component depending only on the time of analysis would be specific for the individual laboratories and therefore contribute to the "interlaboratory deviation" (c).

7.2.1.2 Sampling system

The samples were taken from a product receiver tank which is normally filled up to 150 l with plutonium product solution from the second extraction cycle (2BP).

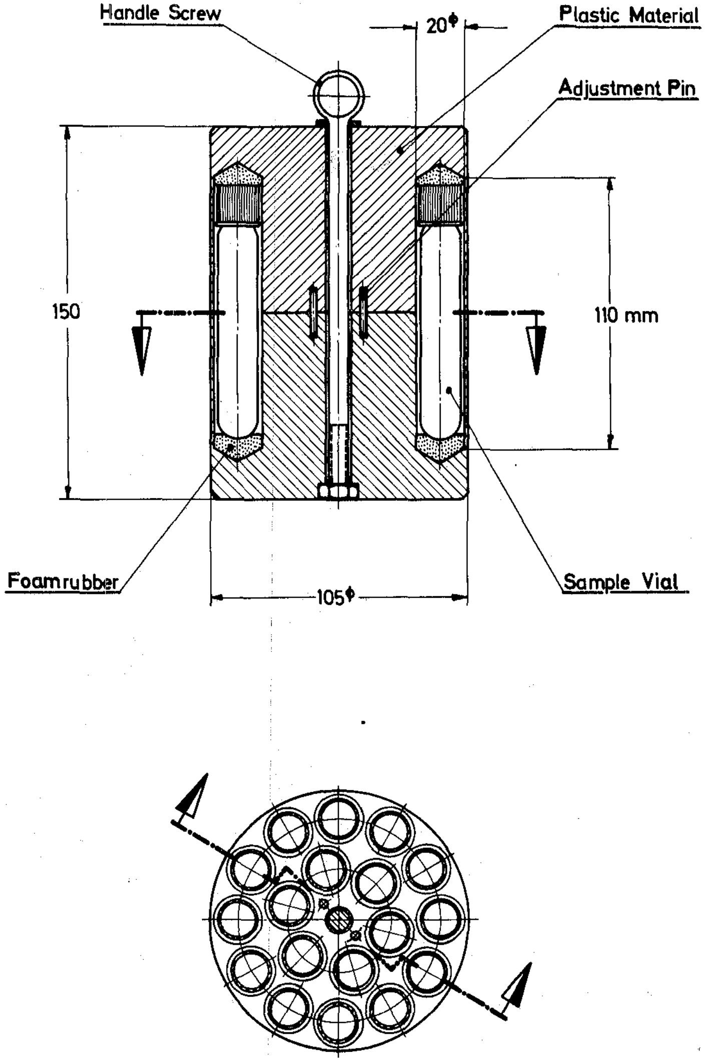
The sampling system connected to this vessel is analogous to that described in Interlaboratory Test I (7.1.1.2, schematically shown in Figure 7.1-1). However, homogenization before sampling was done by airsparging instead of pump circulation.

All sample bottles used within the EUROCHEMIC facility and the plastic cartridges for the pneumatic post system are of the type shown in Figure 7.1-2 (Interlaboratory Test I). In the course of special stabilization and



M 1:1

Fig. 7.2-1 Interlabtest II: Sample Vial



M 1:2

Fig. 7.2-2 Interlabtest II: Insert for Transportation of Sample Vials (Fig. 7.2-1) in BF-3 Birdcages homogenization procedures performed at the EUROCHEMIC plant before shipment to the laboratories (see next paragraph), the sample solutions were transferred into a second type of sample bottles (Figure 7.2-1)[1]. These glass vials were closed with a plastic screw cap and tightened with a TEFLON-washer. To avoid getting loose during transportation, the bottle threads were covered with thin TEFLON-tape which generated a close contact between the glass sample vial and the plastic screw cap.

For shipment of these sample bottles, special inserts were constructed (Figure 7.2-2). After welding with double plastic covers, these inserts were packed into BF-3 birdcages.

7.2.1.3 Sampling procedure

The sampling procedure followed in this particular test is shown schematically in Figure 7.2-3. Three sets of samples (in the following indicated as A, B and C-samples) have to be distinguished. The A-samples were taken without previous homogenization of the solution in the tank, the B- and C-samples after air sparging in the vessel for five and thirty minutes, respectively[2]. Before sampling of each set the sample line was flushed for ten minutes to avoid cross contamination with residual material.

In order to improve the stability of the sample solutions by reduction of the plutonium concentration and increase of their acidity, they were diluted with concentrated nitric acid within 24 hours after sampling. For this purpose, all samples belonging to the same set were given together in a glass beaker and 10 M HNO_3 was added in a ratio of approximately 1:1 by

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1)Two types of sample bottles were used:
  a) KIMAX Culture Tubes, Screw Cap with Teflon Liner 60828 354. Delivered by Van Waters & Rogers, P.O. Box 3200, Ringon Annex, San Francisco, Cal., 94119 USA
  b) Tubes à vis bouchés 4 611 51. Manufactured by SOVIREL, Paris, France, delivered by Bender & Hobein GmbH, Kaiserstr. 12, Karlsruhe, Germany.

2)Special attention is drawn to the fact that the A-samples were taken without preceding homogenization. As this sampling procedure is not used in normal plant operation, different concentrations of the A-samples compared to the others are of no practical interest and therefore not considered in the evaluation of this test. However, inhomogeneity indicated by concentration differences between the B- and C-samples would be of importance as these samples were taken according to routine procedures.

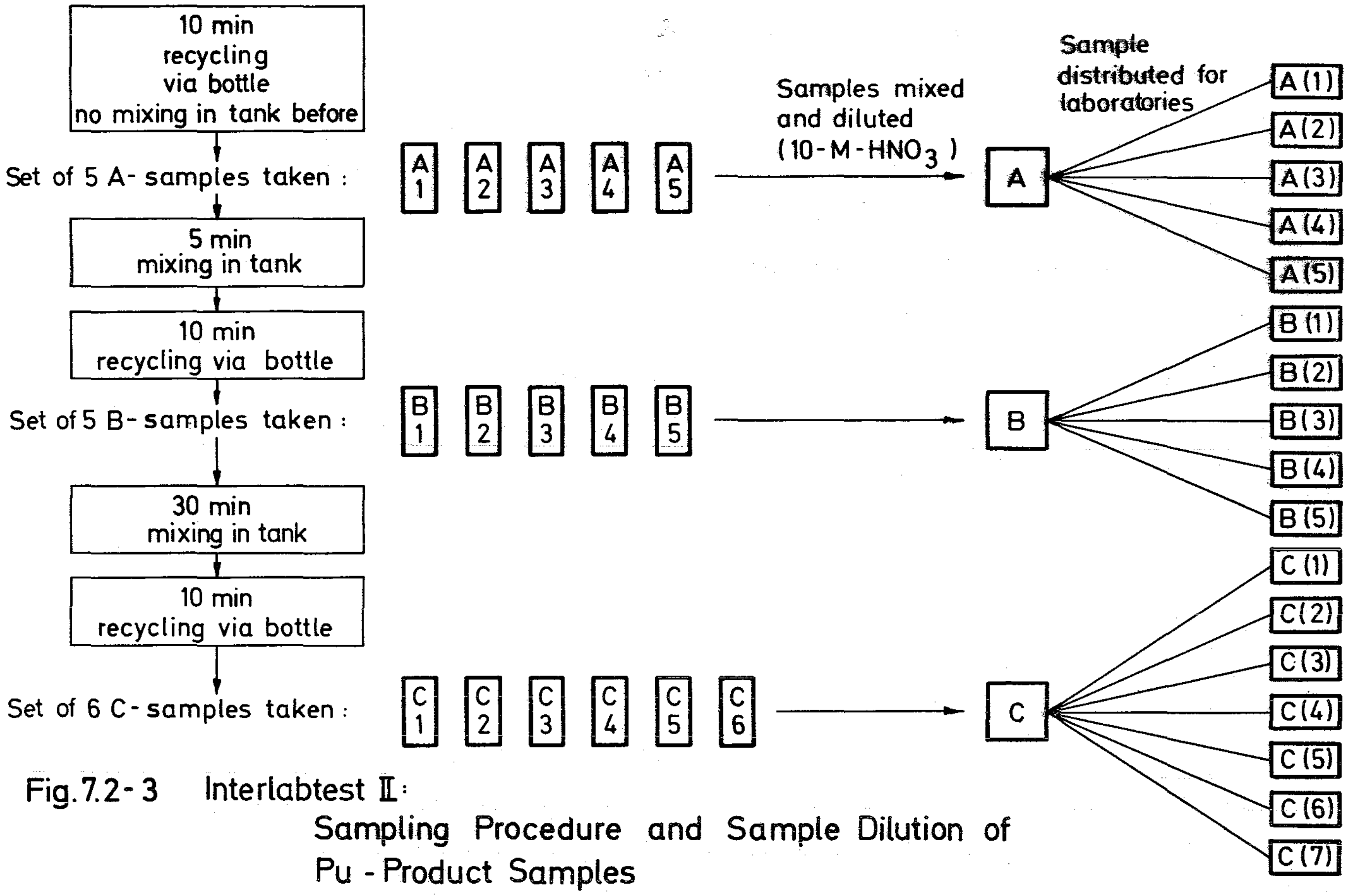

Fig.7.2-3 Interlabtest II: Sampling Procedure and Sample Dilution of Pu-Product Samples

weight[1]. After homogenization, the sample material was distributed on the bottles described before (Figure 7.2-1) for shipment to the laboratories.

In general, each sample bottle contained about 6 ml solution.

The concentration of the diluted sample material was approximately 19 mg Pu/g solution, the density about 1.22 g/ml and the nitric acidity about 6.5 M. Related to the plutonium content, the sample solutions contained approximately 3.5 % uranium.

All 16 original samples for this interlaboratory test were taken on April 25, 1970 from batch VAK 2BP-400.

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1)The exact dilution ratios are summarized in Table 7.2-3 (7.2.3.)

7.2.1.4 Request for analysis

Each of the five laboratories participating in this test received one A-, one B- and one C-sample with request for analysis of the plutonium-concentration using their standard methods. As some laboratories used several analytical techniques, the results of seven independent analytical procedures became available.

At least three repetition measurements should be carried out on each sample in order to allow the calculation of precisions for the different methods applied.

Furthermore, the density of each sample should be determined if possible as check on the representativeness of the samples in case extraordinary deviations of the concentration values should occur. Although these measurements were not considered as an official part of this test, the results communicated were included in this report for information.

7.2.2 Analytical Methods Applied by the Laboratories

The analytical methods applied were reported by the participating laboratories as follows:

7.2.2.1 Concentration determinations

Laboratory code I:

Method: Plutonium oxidised by silverperoxide to Pu (VI) is reduced by addition of Fe (II) in excess to Pu (IV). The excess Fe (II) is back-titrated against Ce (IV) potentiometrically. The Ce (IV) and Fe (II) are calibrated against each other and the Fe (II) is calibrated against dichromate (AERE-4975).

Calibration: $K_2Cr_2O_7$: Titrisol 0.1 N
Calibration of Fe (II) with $K_2Cr_2O_7$:
0.228340 ± 0.000090 ml Cr_2O_7/ml Fe (II)
(based on 4 determinations)

Calibration of Ce (IV) with Fe (II):
0.239220 ± 0.000088 ml Ce (IV)/ml Fe (II)
(based on 3 determinations)

Corrections: No corrections have been applied.

Remark: Some results have been rejected because in certain cases the titration equipment obviously produced erroneous results.

Laboratory code II:

Method: Plutonium oxidised by silverperoxide to Pu (VI) is reduced by addition of Fe (II) in excess to Pu (IV). The excess Fe (II) is back-titrated against Ce (IV) potentiometrically. The Ce (IV) and Fe (II) are calibrated against each other and the Fe (II) is calibrated against dichromate (AERE-4975).

Corrections: The value of the NBS-Pu standard has been corrected by 0.1 % for the Pu-241 decay. No correction has been applied for the difference of the isotopic composition of the NBS standard and the sample material.

Laboratory code III:

Method: About 2.5 g of sample solution were weighed in a 50 ml volumetric flask and made up to volume with 1 N HNO_3.

In an aliquot of 10 ml the Pu had been oxidised to the hexavalent state by AgO. The excess AgO had been destroyed by heating. After addition of sulphamic acid the Pu (VI) was reduced by excess iron (II). The excess iron (II) was titrated cerimetrically with amperometric end-point detection.

Lit.: J. Corpel, F. Regnaud: Anal. Chim. Acta 35, 508-513 (1966)

Remark: Control measurements using the NBS standard 949 b showed very good agreement. Atomic weight for sample: 239.16.

Laboratory code IV:

Method: In a nitric acid solution after addition of amidosulfonacid on a platinum net electrode at + 0.4 V versus saturated Calomel electrode Pu (IV) and Pu (VI) is reduced to Pu (III). Subsequently at + 0.9 V Pu (III) is oxidised to Pu (IV).

Corrections: A correction of 0.1 % for Pu-241 decay has been applied to the value of the NBS-standard. No correction concerning the different isotopic composition of sample and standard was made.

Laboratory code V:

Method: The method is based on a paper by Corpel and Regnaud. The principle of the method is as follows: The sample is first converted into sulfate by fuming with H_2SO_4. After dilution to a specific volume, aliquots containing 10-20 mg of Pu are taken for analysis. Plutonium is oxidized to hexavalent plutonium by stirring the aliquot with excess silver peroxide. The excess is then destroyed by heating. After cooling a measured excess of iron (II) is added and reduces plutonium to the trivalent state. The excess iron (II) is then titrated with potassium dichromate solution potentiometrically using a platinum tungsten electrode pair.

Manipulation of the sample: Each of the samples received was weighed 3 times for specific gravity determination. The remaining solution was then weighed in bulk and added to the flask. The average from these three weighings was taken for the specific gravity after a correction was made for temperature and pipette calibration.

After digesting with H_2SO_4 the solution was transferred to a volumetric flask and filled to a partial volume. On the day the sample is to be analysed, the flask is brought to the exact volume, the aliquots for analysis are taken and the temperature correction at this time applied.

The iron (II) solution was standardized against the potassium dichromate immediately before the titration.

The same Fe^{+2} and dichromate solution was used throughout the complete series of samples.

Corrections: Corrections applied to concentration were as follows:

Std. recovery of NBS Pu metal 949 C when run through the procedure

100.01
99.87
100.49
100.12 % avg. std. recovery using NBS 949 C

Pu metal standard with no isotopic correction and assuming 100 % 239. We realize this is slightly in error but since this standard is very new we do not have the necessary information to make the proper isotopic correction.

The three standards were run on three different days, each with a sample. The average recovery was used for the correction of each sample. The sample atomic weight was taken to be 239.44.

Laboratory code VI:

Method: Plutonium oxidized by silverperoxide to Pu (VI) is reduced by addition of Fe (II) in excess to Pu (IV). The excess Fe (II) is back-titrated directly by $K_2Cr_2O_7$. Fe (II) is standardized daily against $K_2Cr_2O_7$.

$$\mathrm{Pu} \xrightarrow{Ag_2O_2} \mathrm{Pu\ (VI)} \xrightarrow{Fe\ (II)} \mathrm{Pu\ (IV)}.$$

Calibration: Primary standard: $K_2Cr_2O_7$. NBS-949 standard is titrated at intervals for comparison. A secondary Pu-standard is used as a routine control.

Corrections: The isotopic composition of the samples is considered in the calculations (atomic weight is calculated for each individual sample).

Laboratory code VII:

Method: A weighed aliquot of the sample is mixed with a defined amount of thoriumnitrate solution. In the solution the ratio of the intensities of the plutonium and the thorium $L\alpha_1$-lines are compared.

Lit.: Pella e.a. Anal. Chim. Acta 47, 431 (1969)

Corrections: The plutonium content of the NBS-standard was corrected for Pu-241 decay.

Laboratory code VIII:

Not reported as these data were given for orientation only and do not form an official part of the interlaboratory test.

7.2.2.2 Density determinations[1]

Laboratory code I:

The measurements were made by picnometers. The room temperature was constant within 3° C and humidity about 60 %. However, density determinations and picnometer calibration were performed using a water bath of 20.0 ± 0.2° C.

Laboratory code II:

A 2 ml pipette calibrated with H_2O was used. Temperature correction has been applied.

Laboratory code V:

The density was obtained by weighing 1 ml pipette on a Mettler semimicro balance in an open hood. The specific gravity was only corrected by temperature and a balance calibration factor total correction was wt./. 99955 = specific gravity. Due to operating difficulties density for sample A was taken from only the first weighing. Sample B and C were determined from 3 weighings each.

No correction was made for air buoyancy.

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[1] Since the code numbers were assigned to each independent method of concentration determination, in some cases several code numbers are related to the same laboratory. The method of density determination used by those laboratories was given under one of these code numbers only.

The laboratories III and VI reported no density measurements.

7.2.3 Reported Analytical Results and Corrections Applied

In Table 7.2-1, all single concentration determinations and in Table 7.2-2 all single density measurements communicated are compiled in columns 5 and 4 respectively. In general, the concentration values were reported in mg Pu/g solution. The results of laboratory VI, given in mg Pu/ml solution were converted for further evaluation using the mean values of densities obtained by the other laboratories, as no density measurements were performed by laboratory VI itself.

All density values are corrected for 20° C.

In order to obtain comparable data, the reported concentration values had to be corrected for the dilution of the samples with concentrated nitric acid (7.2.1.3) and for the β-decay of the Pu-241 isotope since sample age was different at the time of analysis in the individual laboratories.

The corrected concentration value of a single determination was calculated according to

$$c_{corr.} = k \times (1+\alpha\Delta t) \times c_{uncorr.}$$

In this equation, k means the correction factor for the dilution of the sample, calculated from the data summarized in Table 7.2-3 which were reported by the EUROCHEMIC laboratory.

Table 7.2-3: Interlabtest II: Data on the Dilution of the Sample

Sample description	Weight of sample solution a [g]	Weight of added 10 M HNO_3 b [g]	Calculated correction factor $k = \frac{a+b}{a}$
A	17.21924	18.90285	2.09777
B	18.84407	18.89552	2.00273
C	21.28750	22.44445	2.05435

Table 7.2-1: Interlabtest II: Reported Concentration Determinations

Laboratory code	Analytical method	Sample description	Number of repetition measurement	Reported single determination [mg Pu/g sol.]	Time interval between sampling and analysis [days]	Single determination corrected for dilution and Pu-241 decay [mg Pu/g sol.]	Mean value per sample ± SD [mg Pu/g sol.]
1	2	3	4	5	6	7	8
I	Oxydimetry	A	1	19.01		39.918	
			2	19.01		39.918	39.946
			3	19.05		40.002	± 0.049
		B	1	20.01		40.115	
			2	19.87	95	39.834	40.068
			3	20.08		40.255	± 0.214
		C	1	19.40		39.894	
			2	19.43		39.956	39.942
			3	19.44		39.977	± 0.043
II	Oxydimetry	A	1	18.934		39.735	39.788
			2	18.984		39.840	± 0.074
		B	1	20.074	41	40.219	40.227
			2	20.082		40.235	± 0.011
		C	1	19.318		39.702	39.702
			2	19.318		39.702	± 0.000
III	Oxydimetry	A	1	18.899		39.674	
			2	18.921		39.720	39.689
			3	18.899		39.674	± 0.027
		B	1	19.698		39.477	
			2	19.698	66	39.477	39.460
			3	19.673		39.427	± 0.029
		C	1	19.363		39.806	
			2	19.337		39.753	39.788
			3	19.363		39.806	± 0.031
IV	Coulometry	A	1	19.016		39.907	
			2	19.050		39.979	39.969
			3	19.070		40.020	± 0.057
		B	1	19.934		39.938	
			2	19.930	38	39.930	39.953
			3	19.960		39.990	± 0.033
		C	1	19.252		39.566	
			2	19.360		39.788	39.728
			3	19.380		39.829	± 0.142

Table 7.2-1: (continued)

1	2	3	4	5	6	7	8
V	Oxydimetry	A	1	18.741	59	39.338	39.342 ± 0.128
			2	18.658		39.164	
			3	18.780		39.420	
			4	18.793		39.447	
		B	1	19.820		39.718	39.721 ± 0.005
			2	19.824		39.726	
			3	19.820		39.718	
		C	1	19.322		39.718	39.523 ± 0.135
			2	19.207		39.482	
			3	19.171		39.408	
			4	19.207		39.482	
VI	Oxydimetry	A	1	23.08 1)	84	39.653 2)	39.696 ± 0.061
			2	23.13 1)		39.739 2)	
		B	1	24.10 1)		39.643 2)	39.635 ± 0.011
			2	24.09 1)		39.627 2)	
		C	1	23.59 1)		39.827 2)	39.681 ± 0.048
			2	23.63 1)		39.895 2)	
VII	X-ray fluorescence spectrometry	A	1	18.593	31	39.016	39.372 ± 0.503
			2	18.932		39.727	
		B	1	19.810		39.686	39.573 ± 0.160
			2	19.697		39.460	
		C	1	19.256		39.570	39.769 ± 0.281
			2	19.449		39.967	
VIII	Values reported were given for orientation only.						

1) As reported by the laboratory, these values are given in mg Pu/ml solution.

2) Calculation of these values was based on the mean values of densities obtained by the other laboratories for the A, B and C-sample, respectively.

Table 7.2-2: Interlabtest II: Reported Density Determinations

Laboratory code	Sample description	Number of repetition measurement	Reported single determination [g/ml]	Mean value per sample ± SD [g/ml]
1	2	3	4	5
I	A	1	1.22565	
		2	1.22529	1.22545
		3	1.22540	± 0.00018
	B	1	1.22220	
		2	1.22194	1.22203
		3	1.22194	± 0.00015
	C	1	1.22411	
		2	1.22446	1.22443
		3	1.22471	± 0.00030
II	A	1	1.220	1.220
	B	1	1.215	1.215
	C	1	1.217	1.217
III	No density measurements reported			
IV 1)				
V	A	1 2)	1.2207 2)	1.2207
	B	1	1.2184	
		2	1.2192	1.2188
		3	1.2187	± 0.0004
	C	1	1.2131	
		2	1.2119	1.2124
		3	1.2123	± 0.0006
VI	No density measurements reported			
VII 1)				
VIII 1)				

1) Since the code numbers were assigned to each independent method of concentration determination, in some cases several code numbers are related to the same laboratory. For codification of the density determinations performed by those laboratories, only one of these numbers was used. Therefore, no specific data can be assigned to the code numbers IV, VII and VIII.

2) Two further determinations were rejected by the laboratory (7.2.2.2).

The factor $(1+\alpha\Delta t)$ gives the correction for the β-decay of the Pu-241 isotope. α is defined by

$$\alpha = \frac{A}{100} \times \frac{\ln 2}{H}$$

with

A = relative abundance of the Pu-241 isotope (7.8 %)
H = half life period of the Pu-241 isotope (5110 days).

Δt [days] is the time interval between sampling and analysis in the laboratory, given in column 6 of Table 7.2-1.

The corrected concentration values are compiled in column 7 of Table 7.2-1.

For a first survey these data are graphically presented in Figure 7.2-4. For each individual laboratory, the relative deviations of the mean values per sample from the mean of all these means are shown. The error bars indicate the relative standard deviation of the mean value per sample.

Figure 7.2-5 shows the results of the density determinations in the same manner. For laboratory II, no error bars could be calculated as only one determination per sample was made.

7.2.4 Evaluation

7.2.4.1 Review of data

A review of the data on the concentration as well as the density determinations gives no indication for outliers.

7.2.4.2 Estimation of error components

The following calculations of the different error components by analysis of variances were based on all data obtained by chemical methods for the B- and C-samples.
The measurements on sample A were excluded in order to avoid any simulation

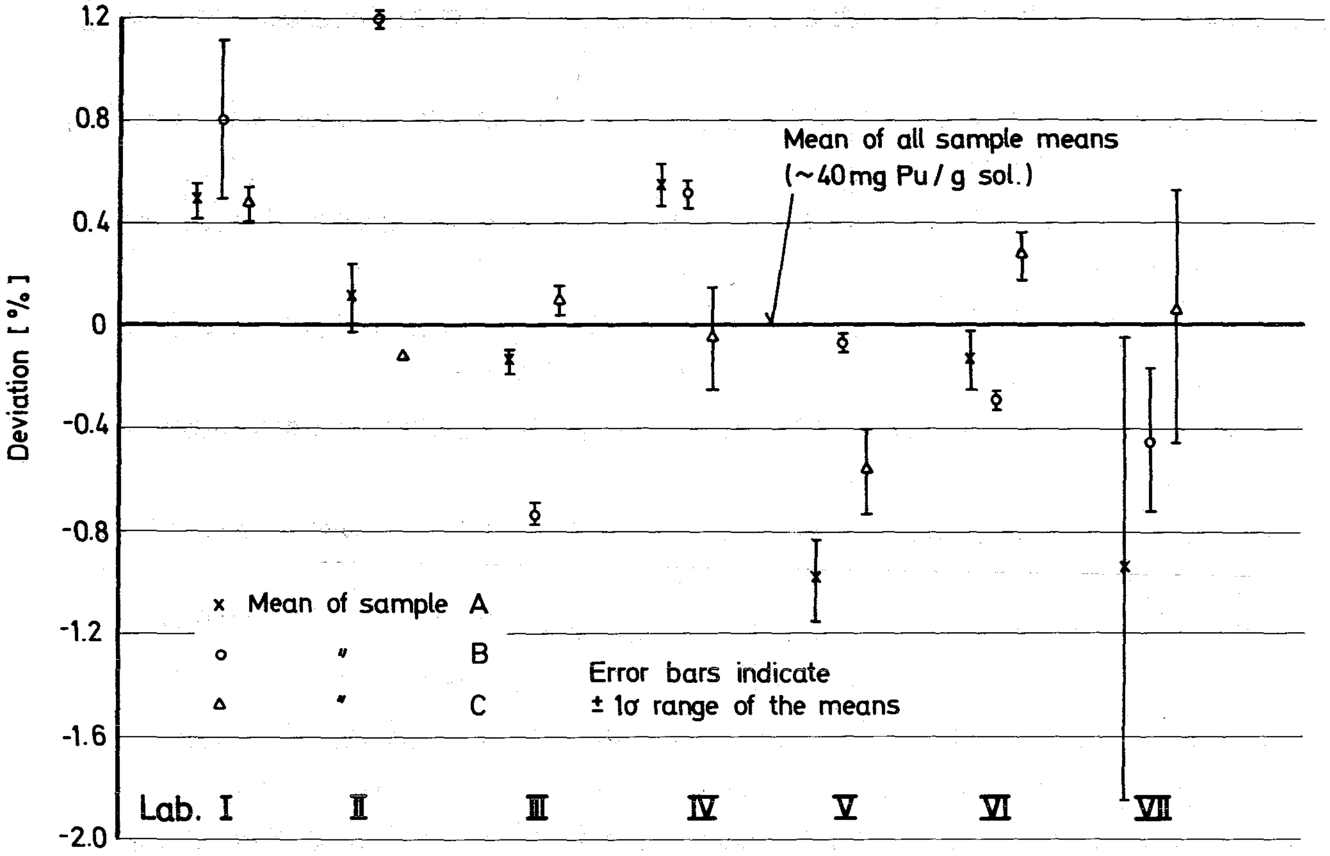

Fig. 7.2-4 Interlabtest II: Concentration Determinations of Pu-Product Samples

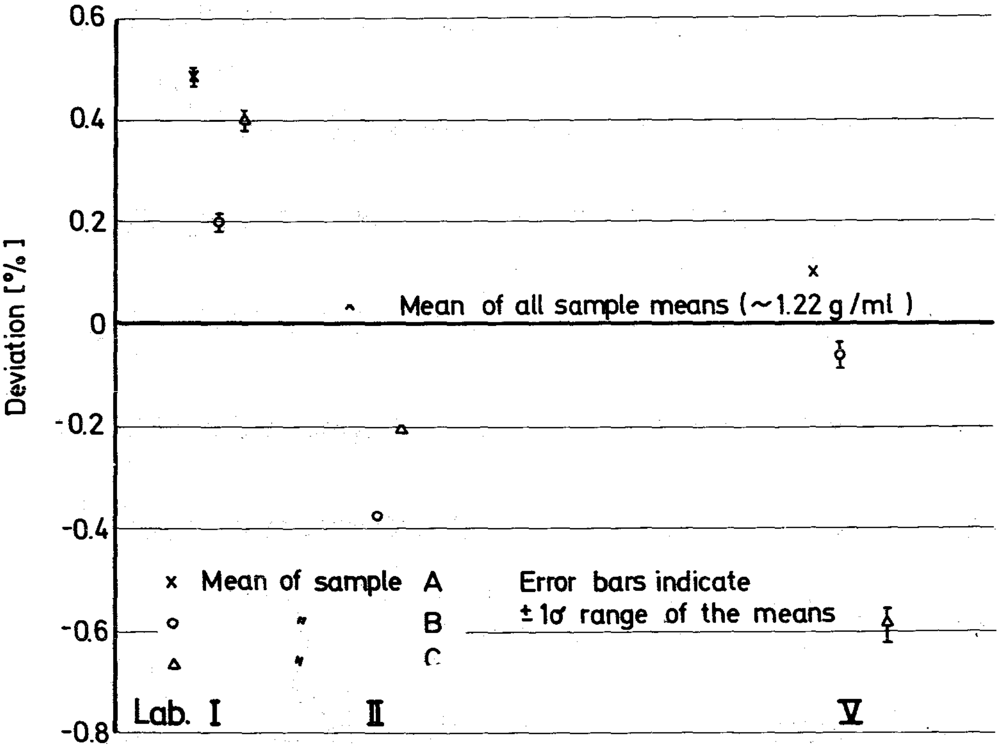

Fig. 7.2-5 Interlabtest II: Density Determinations of Pu-Product Samples

of inhomogeneity of the tank solution by this sample which was not taken according to routine procedures (7.2.1.3). The measurements carried out by X-ray fluorescence spectrometry (laboratory VII) had to be excluded as from the statistical point of view they are not comparable to those obtained by chemical methods in regard to their precision (7.2.5.4).

As mentioned in 7.2.1.1, there are four main error components which have to be considered in this interlaboratory test: Sampling error, sample error, interlaboratory deviation and precision.

By application of the variance analysis as described in Appendix II.4 and based on the model I schematically shown in Figure 7.2-6 1), it is possible to calculate the estimate for the variance of the precision, the estimate for the variance of the sampling error and the sum of the estimates for the variances of the sample error and the interlaboratory deviation.

As the result is obtained that there exists no significant sampling error, in this case the B- and C-samples can be considered as identical and the variances of the sample error and the interlaboratory deviation can be calculated separately by a second analysis of variance based on model II in Figure 7.2-6 in which the positions of laboratories and samples are interchanged.

Since by definition the different error components are considered as independent from each other, the variance of the sum of the sample error and the interlaboratory deviation calculated according to model I should be equal to the sum of the variances obtained on the basis of model II for the sample error and the interlaboratory deviation separately. This is well confirmed by the calculated values which are summarized in the following Table 7.2-4:

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1)This model is identical with that shown in Figure 7.AII-1.

Table 7.2-4: Interlabtest II: Calculated Variances and RSD of Error Components for the Concentration Determinations.

(Based on B- and C-samples measured by laboratories I to VI using chemical methods)

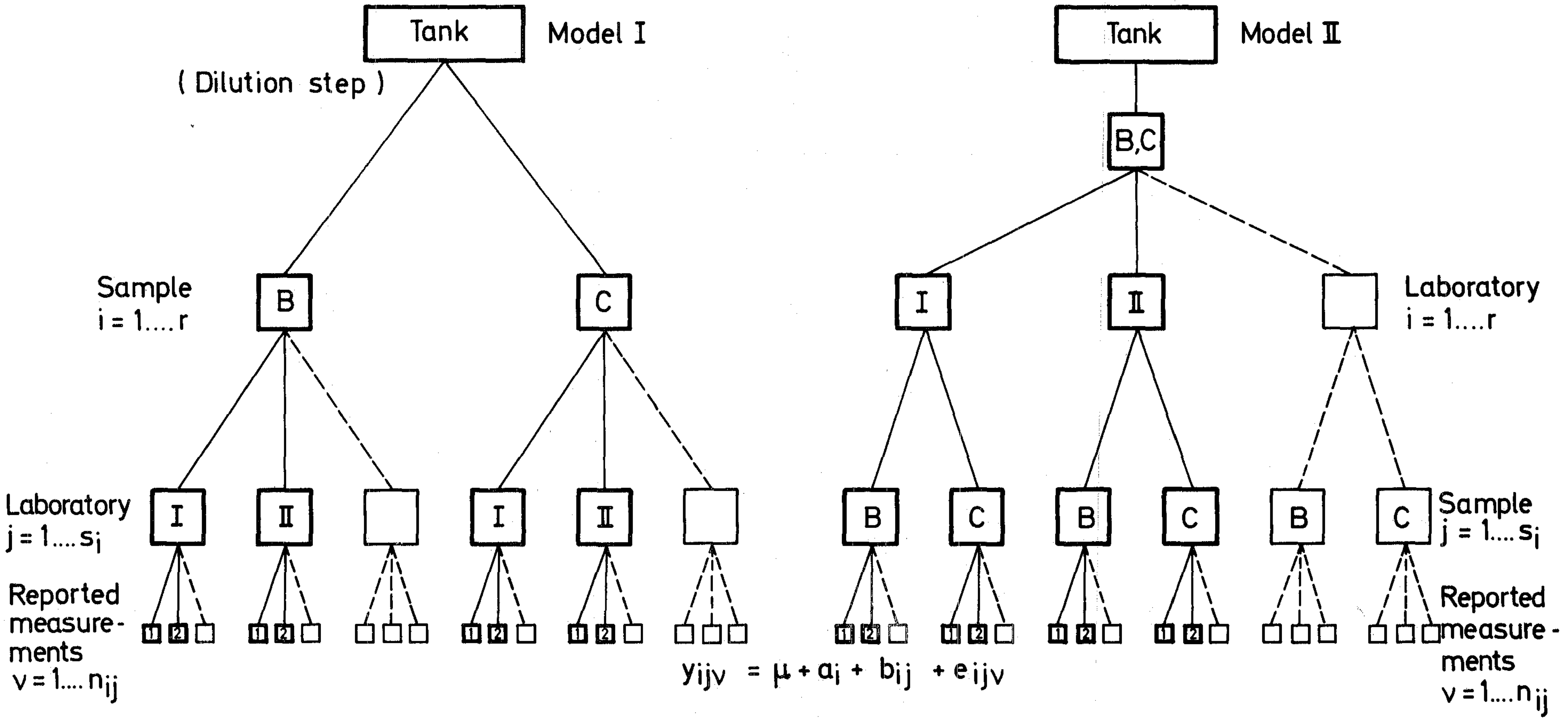
$c \sim 40 \frac{\text{mg Pu}}{\text{g sol.}}$		Sampling error	Sample error	Interlab. deviation	Precision
Model I (Fig. 7.2-6)	10^2 variance	not significant	4.80		0.946
Model II (Fig. 7.2-6)	10^2 variance	taken as not significant	3.64	1.00	0.946
Final results	10^2 variance	not significant	$3.72^{*)}$	1.00	0.946
	SD	-	0.193	0.100	0.0973
	RSD [%]	-	0.49	0.25	0.24

*) Mean of the values 3.64 obtained from the variance of sample error and 3.80 = 4.80-1.00, obtained from the variances of sample error and interlaboratory deviation.

Concerning the density measurements, the number of determinations reported was considered to be too small to allow a meaningful error analysis by statistical methods.

7.2.4.3 Complementary calculations.

During the Ispra Meeting (Appendix I) it was recommended to evaluate the measurements on the A, B and C-samples separately in order to avoid any



$$y_{ijv} = \mu + a_i + b_{ij} + e_{ijv}$$

$\hat{\sigma}_a^2 = \sigma^2_{\text{sampling}}$ (Dil., Inh.)

$\hat{\sigma}_b^2 = \sigma^2_{\text{interlab. dev.}} + \sigma^2_{\text{sample}}$ (Aging, Prep.)

$\hat{\sigma}_e^2 = \sigma^2_{\text{precision}}$

$\hat{\sigma}_a^2 = \sigma^2_{\text{interlab. dev.}}$

$\hat{\sigma}_b^2 = \sigma^2_{\text{sample}}$ (Aging, Prep.)

$\hat{\sigma}_e^2 = \sigma^2_{\text{precision}}$

Fig. 7.2-6 Interlabtest II : Models for the Analyses of Variances disturbances by possible errors due to the dilution step or sample inhomogeneity Although no indication was found for significant errors of this kind by the analyses of variances described before (7.2.4.2), the results of those calculati are given in the following as complementary information.

The analyses of variances for each type of sample (A, B and C) were carried out according to Appendix II,3 1). In this case, the estimate for the variance of the precision is obtained, but for the sample error and the interlaboratory deviation only the sum of the variances can be calculated.
The results, expressed in relative standard deviations of the error components are summarized in the following Table 7.2-5:

Table 7.2-5 Interlabtest II: RSD of Error Components for Concentration Determinations, Calculated per Sample. (Based on measurements of laboratories I to VI using chemical methods)

Sample	Precision RSD [%]	Sample error and interlab. deviation RSD [%]
A	0.20	0.64
B	0.25	0.69
C	0.24	0.37
Average value	0.23	0.57

The calculation of the average values is meaningful, as the number of single determinations per sample is equal within each individual laboratory with the only exception of laboratory V.

However, as the number of measurements per sample is different for the individual laboratories, in the statistical sense the system is not orthogonal and therefore, no confidence limits can be calculated for the estimates of the variances or relative standard deviations respectively. This

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1) In this case the index "j" is attributed to the laboratory and the index "i" describing the sample is fixed for each analysis of variances.

difficulty can be overcome to a certain extent by calculation of the standard deviations of the average values given in Table 7.2-5. About (0.23 ± 0.02) % are obtained for the relative standard deviation of the precision and (0.57 ± 0.10) % for the relative standard deviation of sample error and interlaboratory deviation together. The corresponding values of 0.24 % for the precision and 0.55 % for the sample error and interlaboratory deviation together[1] calculated by the variance analyses given in Table 7.2-4 are in good agreement with these results and show the consistency of these considerations.

7.2.5 Discussion of the Results on the Concentration Determinations

7.2.5.1 Sampling error.

By the result of the variance analysis given in Table 7.2-4, no significant value for the sampling error was indicated. According to the definition of this error component (7.1.1.1), this means that from the data obtained in this experiment there is no evidence for inhomogeneity of the tank solution or significant errors introduced by the dilution step.[2]

7.2.5.2 Sample error

The sample error component with a relative standard deviation of about 0.5 % in average (Table 7.2-4) represents the main contribution to the total error of a single concentration determination.

As described in 7.2.1.1, instability of the sample material as well as errors introduced in course of sample preparation within the laboratories may contribute to this component.
From the structure of the experiment, it is not possible to distinguish between these two error sources. However, comparison with the results

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[1] Calculated from the relative standard deviations 0.49 % and 0.25 % for the sample error and the interlaboratory deviation, respectively (Table 7.2-4).

[2] It should be noted that this result is based on two dilutions only performed on samples taken from one single batch.

obtained in Interlaboratory Test I (7.1.5.1) for the concentration determination of uranium product samples gives some indication. In that case it could be shown that in average no significant error contributions due to sample preparation exist. Only for two laboratories small values were found, being one order of magnitude lower than the value of about 0.5 % calculated in this experiment. Therefore, the assumption seems to be justified that the high value of the sample error in case of the concentration determinations of plutonium is mainly caused by instability of the sample material and not by sample preparation within the laboratories, even if the impeded manipulation in glove boxes is taken into consideration.1)

7.2.5.3 Interlaboratory deviation

According to the result of the variance analyses (Table 7.2-4), this error component has a relative standard deviation of 0.25 % which is very close to the corresponding value of 0.20 % calculated in the case of uranium concentration determinations (Interlaboratory Test I, Table 7.1-3 and 7.1.5.2). However, whereas in the case of uranium product analysis this error component contributes the main part to the total error of a single measurement, it amounts in the case of plutonium product analysis only to about one half of the value found for the sample error component.

As already mentioned (7.2.1.1), the main contributions to the interlaboratory deviation are probably differences in the standards and reference materials used as well as calibration errors. Furthermore, it was pointed out that any systematic component of aging effects depending only on the storage time of the sample material would also contribute to this error component. However, from the data obtained in this experiment, no indication could be found for the existence of such an effect.

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1)Measures for improving the stability of plutonium samples were recommended at the Ispra Meeting (Appendix I).

7.2.5.4 Precision

Nearly all laboratories used oxidimetric methods with slight modifications and different endpoint determinations (7.2.2). Only laboratory IV used coulometry and laborabory VII X-ray fluorescence spectrometry.

As an average value for all laboratories applying chemical methods (laboratory I to VI) a precision for the single determination of 0.24 % was calculated by the variance analyses (Table 7.2-4). This is about twice as much as the corresponding value obtained in the case of uranium concentration determinations (Interlaboratory Test I, Table 7.1-3).

The precisions obtained by the individual laboratories are summarized together with the reported values for long term experience in the following Table 7.2-6:

Table 7.2-6 Interlabtest II: Calculated and Reported Long Term Precision per Laboratory

Method	Laboratory code	Precision calculated from the data of this experiment RSD [%]	Precision reported for long term experience RSD [%]
Oxidimetry and coulometry	I	0.32	not reported
	II	0.11	0.3
	III	0.07	not reported
	IV	0.23	0.3
	V	0.29	0.2 to 0.3
	VI	0.11	0.1
X-ray fluorescence spectrometry	VII	0.87	1.0

There is good agreement between the values for the precisions obtained in this experiment and those reported on the basis of long term experience.

Concerning the higher values obtained by X-ray fluorescence spectrometry, reference is made to the remarks given in Interlaboratory Test I (7.1.5.3).

7.2.6 Discussion of the Results on the Density Determinations

It should be emphasized that density measurements were no official part of this interlaboratory test (7.1.1.4) and the number of determinations reported was insufficient for a detailed error analysis.

From the data obtained by the laboratories I and V (Table 7.2-2), a precision of 0.018 % and 0.043 %, respectively, could be calculated for the single repetition measurement. These values are of the same order of magnitude as those found for the density determinations on uranium product samples (Interlaboratory Test I, Table 7.1-6).

As indicated by the results shown in Figure 7.2-5, also the interlaboratory deviation seems to be of the same order of magnitude as in the case of density determinations on uranium product samples for which a relative standard deviation of 0.3 % was calculated (Interlaboratory Test I, Table 7.1-4).

7.2.7 Analytical Efforts

In respect to safeguard considerations, the laboratories were asked to report the average value of manhours necessary for the analysis of one sample (including sample preparation, density measurement, calculation etc.) based on three independent determinations.

The reported values are summarized in the following Table 7.2-7:

Table 7.2-7: Interlabtest II: Analytical Efforts (Manhours) Reported by Each Laboratory

Laboratory code	Analytical method	Manhours per analysis
I	Oxidimetry	20
II	"	2
III	"	6
V	"	12
VI	"	2
IV	Coulometry	2
VII	X-ray fluorescence spectrometry	2

The considerable differences in the reported values are mainly caused by the fact that some laboratories based their estimation on large series of routine measurements, other laboratories on the relatively small number of determinations performed for this test.

7.3 Interlaboratory Test III:

Isotopic Analysis of Uranium Product Samples by Mass Spectrometry

Participants:

- CCR:

  J. Evans, S. Facchetti, A. Marrel and S. Zierfuss

- EUROCHEMIC:

  H. Bokelund and J. van Roon

- GFK:

  A. von Baeckmann and E. Gantner

- ORNL:

  A.E. Cameron, L.T. Corbin, R.E. Eby and C.E. Lamb

- TU:

  K. Kammerichs, L. Koch and C. Rijkeboer

7.3.1 Planning and Performance of the Experiment

7.3.1.1 Objectives

The aim of this interlaboratory test was chiefly to estimate the magnitude of the different error components involved in the determination of the isotopic composition of uranium product samples by mass spectrometry.[1]

The following error components were considered:

a) "Scan[2] errors", by which the precision (or reproducibility) of the single isotopic ratios is understood and which is obtained from the repeated scans with the same filament loading (run). These are the statistical errors caused by the overall instability of the instrumental conditions.

b) "Run[2] errors", introduced by measurement on different filaments loaded with the same sample.

c) "Interlaboratory deviations" which may be caused e.g. by differences in the standards used, errors in standardization or other random components.

In respect to the isotopic correlation studies [7-3], it was of special interest to estimate these errors for low abundant isotopes. Therefore, samples of depleted uranium were used as specified in the next paragraph.

7.3.1.2 Sample material

The sample material for this experiment was identical with that used for the determination of the uranium concentration in Interlaboratory Test I (7.1.1.3) from CANDU batch 3UP-1000. The concentration of this solution was nearly 280 mg U/g solution, the density about 1.6 g/ml and the nitric

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1) For other sample material, e.g. active feed solutions, additional sources of error may exist which are not covered by this experiment.

2) One "scan" is defined as the single measurement of the peaks of all isotopes considered. One "run" is defined as the total of all repeated scans performed with the same filament loading.

acidity below 0.5 M. The approximate isotopic composition was as follows:

U-234	U-235	U-236	U-238	
0.004	0.35	0.06	> 99	[wt. %]

In order to enable the detection of possible inhomogeneity of the tank solution in respect to the isotopic composition, three sets of samples (A, B and C) were taken after zero, thirty and sixty minutes circulation of the tank solution1).

7.3.1.3 Request for analysis

Each of the five laboratories participating in this test received one A-, one B- and one C-sample with request for analysis of the uranium isotopic composition by mass spectrometry using their standard methods.

At least two runs per sample should be carried out, each run consisting of at least six scans. In case of insufficient ion current intensity for the rare isotopes using routine conditions, attempts should be made for their determination by increase of the filament current or other means.

The laboratories were asked to report all individual isotopic ratios determined as well as the isotopic compositions in weight percent including mass discrimination factors or other corrections applied.

7.3.2 Instruments and Measurement Techniques Used by the Laboratories

Four of the five participating laboratories performed the measurements with commercial single stage mass spectrometers of the type MS52), CH43) and CH53), one laboratory (ORNL)4) with a tandem magnetic instrument of special

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1)For the description of the sampling system and the sampling procedure see Interlaboratory Test I (7.1.1.2 and 7.1.1.3).

2)Associated Electrical Industries Ltd., Manchester, Great Britain.

3)Varian MAT, Bremen, Germany.

4)The permission for the revelation of the code was kindly given by the laboratory.

design which is described in detail in Appendix III together with the measurement technique applied.

All laboratories used thermion sources with rhenium filaments but different filament arrangements.

In all cases, the measurements were made on the U^+-ions and instrument calibration was performed by all laboratories with NBS uranium standards (U 005, U 010, U 020 and U 500).

Applying routine measurement procedures, ion yields of about 10^{-12} amps/μg U were obtained with the commercial instruments and 0.1 to 2 μg U were reported as usual sample quantities per filament loading. These conditions were satisfactory for the determination of the U-235/U-238 and U-236/U-238 ratios. For the peak of the rare isotope U-234 however, a signal to noise ratio of about 10:1 only could be achieved. Therefore, additional runs with higher ion current intensities - obtained by increased heating of the sample filament - were carried out by the laboratories II and V. From these spectra, the ratios U-234/U-235 were determined1).

In evaluating the spectra, the laboratories rejected data on the basis of different statistical and empirical criteria or by visual inspection.

7.3.3 Reported Analytical Results

In Table 7.3-1, the isotopic ratio determinations are summarized. Because of the high number of scans in total (about 1000), only the mean values per run are given together with the relative standard deviation for the single scan and the number of scans used for their calculation. As recommended at the Ispra Meeting (Appendix I), no attempt was made to apply common or further rejection criteria to the basic data of the individual scans which were reported by the laboratories.

According to the information of the laboratories, all data were corrected for mass discrimination.

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1) Laboratory V applied this method also to some determinations of the isotope U-236.

Table 7.3-1: Interlabtest III: Reported Isotopic Ratio Determinations and Calculated Scan Precision per Run
(All values corrected for mass discrimination)

Laboratory code	Sample	Run	$\frac{\text{U-234}}{\text{U-238}}$ or $\frac{\text{U-234}}{\text{U-235}}$ (*)			U-235/U-238			$\frac{\text{U-236}}{\text{U-238}}$ or $\frac{\text{U-236}}{\text{U-235}}$ (§)		
			Mean value of isotopic ratio per run × 10^4	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run × 10^4	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run × 10^4	RSD of single scan [%]	Used number of scans
1	2	3	4	5	6	7	8	9	10	11	12
I	A	1	0.4661	5.42	11	35.565	1.03	11	6.1059	2.04	11
		2	0.3763	17.40	11	35.179	0.88	11	5.9800	2.31	12
	B	1	0.4424	6.16	12	35.370	0.92	12	6.0523	3.68	12
		2	0.4472	11.93	12	34.954	0.57	12	6.0444	2.36	12
	C	1	0.4294	6.78	11	35.214	1.21	10	6.0655	2.39	11
		2	0.4604	13.42	12	35.283	0.70	12	6.1579	1.64	11
II	A	1	140.25 *	1.38	7	34.691	0.43	8	5.9826	1.05	6
		2	152.78 *	0.99	6	34.768	0.22	6	6.2857	0.87	6
		3	138.47 *	4.80	5	34.914	0.42	6	5.7781	4.03	5
		4	157.31 *	0.59	5	34.463	0.79	6	6.0492	2.75	6
		5	141.89 *	2.28	7	34.475	1.02	8	5.9422	2.21	8
	B	1	161.45 *	2.99	5	34.944	0.70	5	6.0539	0.66	5
		2	142.56 *	0.56	7	34.720	0.70	7	6.0725	1.41	6
		3	142.40 *	2.05	6	34.923	0.53	6	5.7594	1.49	6
		4	153.67 *	3.04	5	34.533	0.29	7	5.7275	0.47	7
		5	149.39 *	2.25	5	34.606	0.63	7	5.9909	1.09	8
	C	1	147.07 *	1.81	5	34.419	0.79	7	6.0909	2.01	8
		2	180.62 *	3.57	5	34.638	1.28	6	5.9576	2.01	6
		3	133.01 *	0.99	7	35.137	1.10	9	6.0203	2.07	9
		4	138.77 *	3.40	5	34.729	1.67	7	5.8627	1.90	6
		5	-	-	-	34.968	1.04	6	5.8018	1.93	7

Table 7.3-1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
III	A	1	0.4252	7.31	9	34.444	0.85	9	5.6847	3.39	9
		2	0.3835	5.92	9	34.196	0.17	9	5.4650	0.64	9
	B	1	0.4057	3.66	9	34.153	1.11	9	5.6191	1.06	9
		2	0.3918	6.22	9	34.072	1.29	9	5.6244	0.61	9
	C	1	0.4548	2.22	9	34.382	0.42	9	5.8783	0.35	9
		2	0.4604	1.84	8	34.503	1.21	8	5.8846	0.85	8
IV	A	1	0.4595	8.43	10	34.246	1.24	10	5.8320	2.96	10
		2	0.4594	7.73	10	34.165	0.76	10	5.7611	1.83	10
	B	1	0.4595	6.32	10	34.226	1.39	10	5.9130	2.22	10
		2	0.4595	6.32	10	34.175	0.95	10	5.8725	1.47	10
	C	1	0.4595	6.32	10	34.308	1.01	10	5.9030	1.79	10
		2	0.4595	9.14	10	34.247	1.31	10	5.9536	1.34	10
V	A	1	155.51 *	0.65	9	34.419	1.07	8	1728.7 §	0.21	9
		2	154.57 *	1.99	10	35.070	0.46	8	1717.9 §	1.99	10
	B	1	0.4858	1.28	10	33.958	0.23	10	5.9946	0.45	10
		2	140.76 *	3.04	10	34.342	0.38	10	1737.3 §	0.84	10
	C	1	0.4871	5.37	10	34.283	0.63	10	5.8100	1.37	10
		2	0.5856	3.51	10	34.406	0.66	10	6.1026	1.76	10

Table 7.3-2: Interlabtest III: Reported Isotopic Composition Determinations [wt %]

Laboratory code	Sample	Run	Relative isotopic abundance [wt %]			
			U-234	U-235	U-236	U-238
1	2	3	4	5	6	7
I	A	1	0.0046	0.350	0.060	99.59
		2	0.0039	0.346	0.059	99.59
	B	1	0.0043	0.348	0.060	99.59
		2	0.0044	0.344	0.060	99.59
	C	1	0.0042	0.346	0.060	99.59
		2	0.0045	0.347	0.061	99.59
II	A	1	0.0047	0.3411	0.0592	99.595
		2	0.0051	0.3421	0.0621	99.590
		3	0.0048	0.3431	0.0572	99.595
		4	0.0048	0.3391	0.0601	99.596
		5	0.0047	0.3391	0.0582	99.598
	B	1	0.0055	0.3441	0.0601	99.590
		2	0.0048	0.3411	0.0601	99.594
		3	0.0048	0.3431	0.0572	99.595
		4	0.0051	0.3401	0.0562	99.598
		5	0.0050	0.3401	0.0592	99.596
	C	1	0.0049	0.3382	0.0601	99.597
		2	0.0059	0.3411	0.0592	99.594
		3	0.0045	0.3460	0.0592	99.590
		4	0.0046	0.3421	0.0582	99.595
		5	0.0043	0.3441	0.0572	99.594
III	A	1	0.0041	0.337	0.0562	99.602
		2	0.0037	0.336	0.0535	99.607
	B	1	0.0039	0.336	0.0555	99.605
		2	0.0039	0.336	0.0555	99.604
	C	1	0.0044	0.338	0.0575	99.599
		2	0.0044	0.339	0.0585	99.598
IV	A	1	0.0045	0.3368	0.0576	99.6011
		2	0.0045	0.3360	0.0569	99.6026
	B	1	0.0045	0.3366	0.0584	99.6005
		2	0.0045	0.3361	0.0580	99.6014
	C	1	0.0045	0.3374	0.0583	99.5998
		2	0.0045	0.3368	0.0588	99.5999
V	A	1	0.0052	0.3393	0.0589	99.5966
		2	0.0053	0.3452	0.0595	99.5900
	B	1	0.0048	0.3344	0.0590	99.6018
		2	0.0047	0.3383	0.0590	99.5980
	C	1	0.0048	0.3371	0.0574	99.6007
		2	0.0057	0.3383	0.0603	99.5957

In general, the ratios of the rare isotopes to the isotope U-238 are given. Only in the case of laboratory II, the ratio U-234/U-235 and for some measurements of laboratory V the ratios U-234/U-235 and U-236/U-235 are reported in the table, as they were the primary data obtained because of the special method of measurement applied (7.3.2).

The isotopic compositions in weight percent as reported by the laboratories are compiled in Table 7.3-2.

7.3.4 Evaluation

7.3.4.1 Review of data

For each individual laboratory, the relative deviation of the mean value per sample from the mean of all these means are shown in the Figures 7.3-1, 7.3-2 and 7.3-3 for the isotopic ratios U-235/U-238, U-236/U-238 and U-234/U-238 respectively[1]. In addition, for each laboratory the mean value calculated from the means of the three samples (A, B and C) is given. The indicated error bars represent the relative standard deviation of the mean values and contain contributions by the scan errors as well as the run errors.

Comparison of the mean values taken over all sample mean values per laboratory (solid points) gives no indication that the results of any individual laboratory have to be considered as outliers in total.

As far as the mean values per sample are concerned, the values obtained by laboratory III on sample C (compared to those of sample A and B), represent the most evident irregularity especially for the isotopic ratios U-236/U-238 and U-234/U-238. By statistical tests (Appendix II,2) the significance of the deviation is confirmed for both isotopic ratios with

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1)The isotopic ratios U-234/U-238 and U-236/U-238 which could be calculated from the measurements of the isotopic ratios U-234/U-235, U-236/U-235 and U-235/U-238 performed by the laboratories II and V were not included in these figures, as they are not directly comparable.

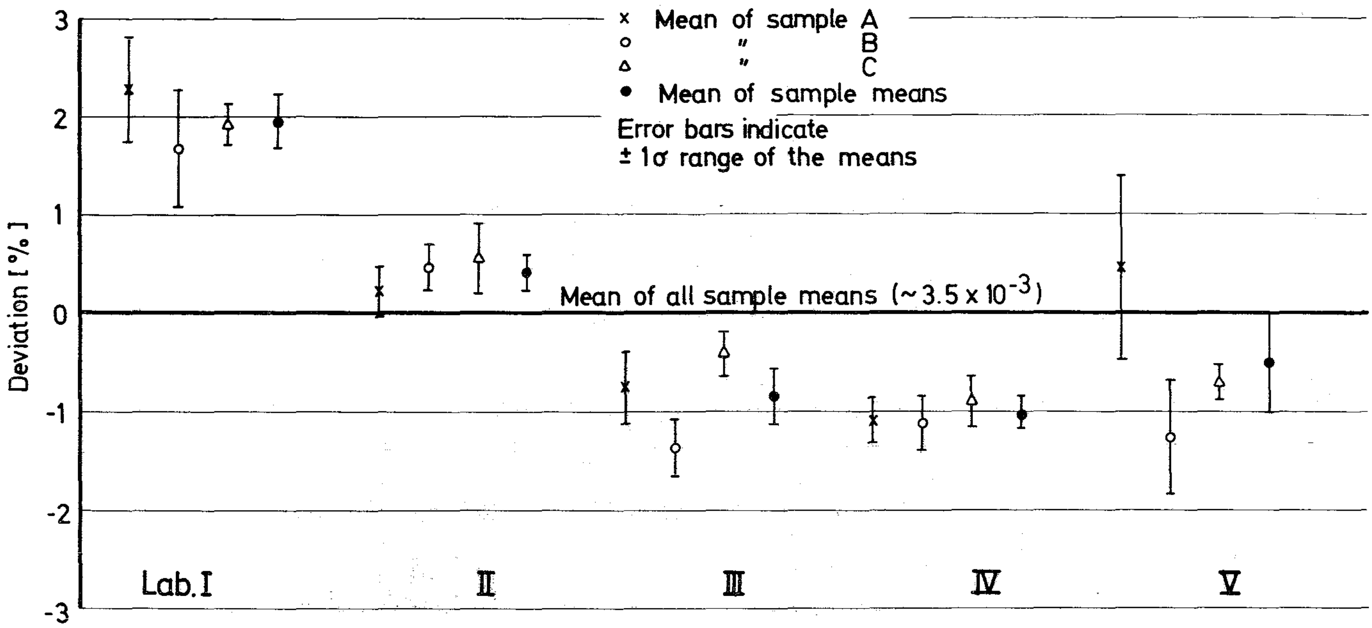

Fig. 7.3-1 Interlabtest III: Mass Spectrometric Determinations of the Isotopic Ratio U235/U238

a probability of error of less than 10 %. Although in principle this effect may be caused by small cross contaminations during sampling or sample preparation, memory effects in the mass spectrometer or similar sources of error, it seems more likely that the significance of this deviation is only simulated because of the specific measurement technique applied by this laboratory: The two repetition measurements per sample were performed by subsequent heating of two sample filaments introduced into the ion source simultaneously. Therefore, the two runs on which the mean values per sample are based can not be considered as independent from each other to the same extent as if the measurement technique used by the other laboratories (subsequent introduction of single sample filaments into the ion source) is applied. This may result in the suppression of a part of the run error component for the repetition measurements per sample, leading to small limits of error for the calculated sample mean value and simulating significant differences between the samples which, in fact, represent a part of the run error component.

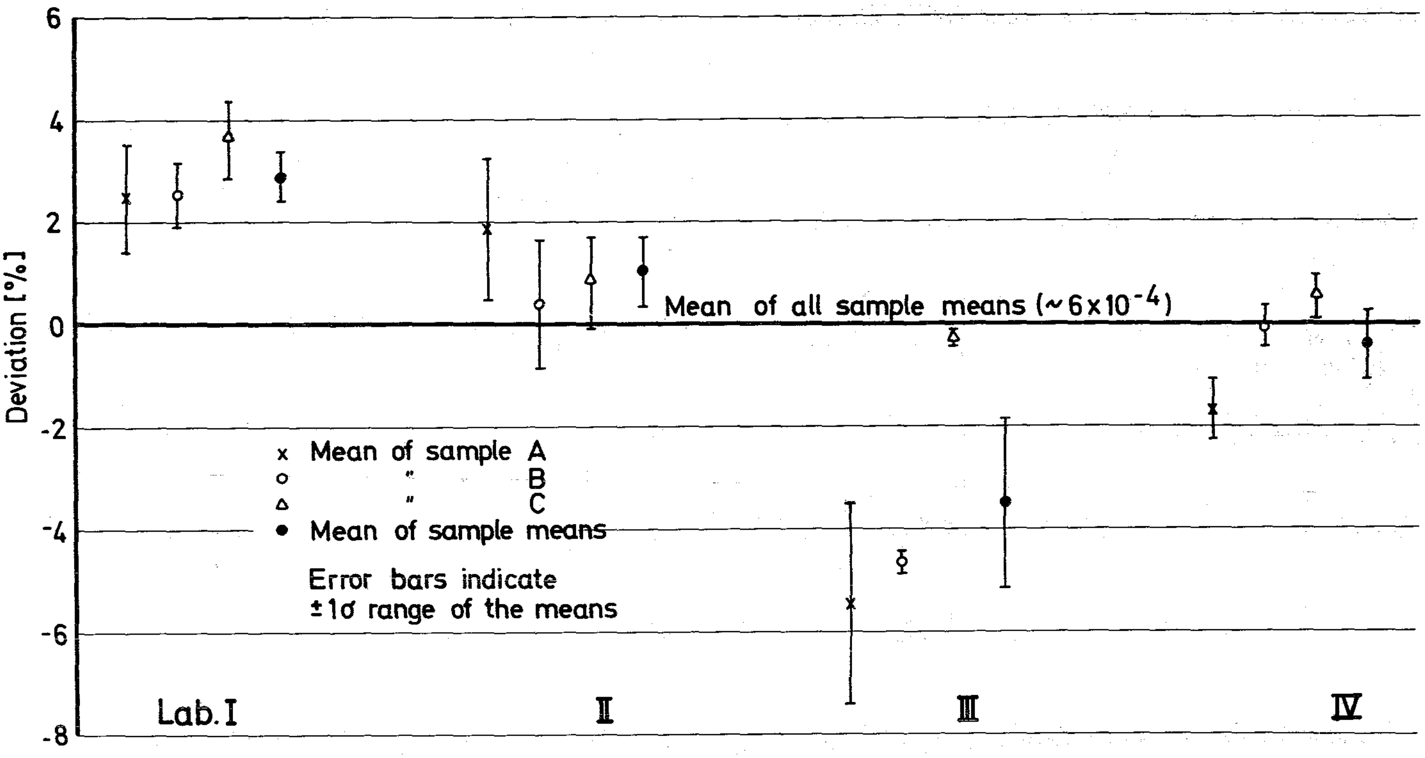

Fig. 7.3-2 Interlabtest III: Mass Spectrometric Determinations of the Isotopic Ratio U236 / U238

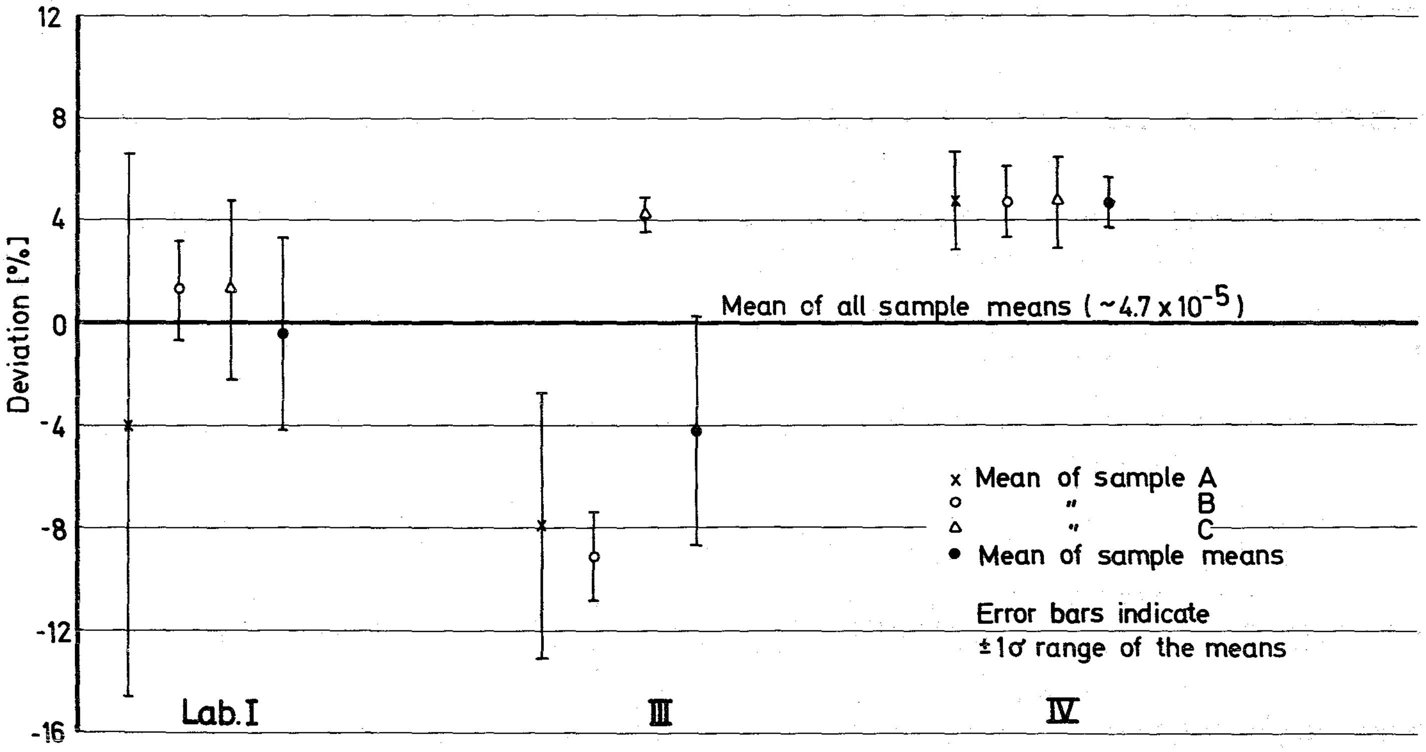

Fig. 7.3-3 Interlabtest III: Mass Spectrometric Determinations of the Isotopic Ratio U234 / U 238

Because of the possible isotopic inhomogeneity of the tank solution, tests on the significance of the deviations between the A, B and C-samples were carried out for each individual laboratory separately (Appendix II,2).

Besides the results obtained by laboratory III discussed above, only in case of the isotopic ratios U-236/U-238 determined by laboratory IV the existence of significant deviations between the mean values of the A, B and C samples was confirmed with a probability of error of less than 10 % by these tests. Although a more detailed investigation of these data excludes to a far extent that this result was obtained "by chance", this single case can not be considered as an essential indication for the existence of an isotopic inhomogeneity of the tank solution because of the many other possible sources of error1).

From these considerations it was concluded that there is no justification for the rejection of any data as outliers and that there is no need to distinguish between the results obtained on the A, B and C-samples per laboratory since no significant isotopic inhomogeneity of the tank solution is indicated.

7.3.4.2 Estimation of error components

As mentioned in 7.3.1.1., scan errors, run errors and interlaboratory deviations were considered as main error components of the mass spectrometric measurements.

For each isotopic ratio of interest, the estimates for the variances of these error components were calculated by analyses of variances (Appendix II,4) based on the model schematically shown in Figure 7.AII-1.

For the isotopic ratio U-235/U-238, the values of all five laboratories were available for these calculations (Table 7.3-1). In case of the

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1) It should be noted that in this case the A-sample deviates from the others, whereas the measurements of laboratory III show the main deviation for the C-sample. This excludes with high probability inhomogeneity of the tank solution as the common reason in both cases.

isotopic ratio U-234/U-238 however, the analysis of variances was based on the data of the laboratories I, II and IV only since this isotopic ratio was not directly measured by the laboratories II and V (for a part of the determinations) because of the special procedure applied (7.3.2). For the same reason, the measurements of laboratory V were excluded from the corresponding calculations concerning the isotopic ratio U-236/U-238.

The results of the analyses of variances expressed as the relative standard deviations of the error components are summarized in the following Table 7.3-3 for the different isotopic ratios considered. 1)

Table 7.3-3: Interlabtest III: Calculated RSD of Error Components for the Isotopic Ratio Determinations

Error component	RSD [%] of error component for isotopic ratio		
	U-234/U-238 1) ($\sim 0.4 \times 10^{-4}$)	U-236/U-238 2) ($\sim 0.6 \times 10^{-3}$)	U-235/U-238 3) ($\sim 0.35 \times 10^{-2}$)
Scan	8.53	2.04	0.90
Run	6.68	2.21	0.63
Interlab. deviation	(3.39) ~ 8.0 4)	2.56	1.20

1) Based on the data of laboratories I, III and IV
2) " " " " " " I, II, III and IV
3) " " " " " all 5 laboratories
4) Value calculated from the isotopic abundances of all 5 laboratories

The value of 3.39 % calculated for the interlaboratory deviation in case of the isotopic ratio U-234/U-238 has been put in brackets as it is based on the data of three laboratories only.

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1) In order to reduce the rather extensive numerical treatment of the data necessary according to the formulas given in Appendix II, a somewhat simplified way of calculation was followed. This may result in deviations in the second decimal figure for the calculated relative standard deviations of the error components which can be considered as negligible.

However, a more reliable value based on the measurements of all five laboratories can be obtained from the relative isotopic abundances given in Table 7.3-1: The relative standard deviation of the mean values per laboratory from the mean of these means represents in a good approximation the relative standard deviation of the interlaboratory component alone, as the contributions of the scan and run errors are small due to the relatively high number of repetition measurements performed by each laboratory. In the following Table 7.3-4, the corresponding data are compiled.

Table 7.3-4: Interlabtest III: Calculated Laboratory Mean Values of the Isotopic Composition /‾wt %_7

Laboratory code	Number of analyses (runs)	Mean value of relative isotopic abundances per laboratory /‾wt %_7			
		U-234	U-235	U-236	U-238
I	6	0.00432	0.3468	0.0600	99.590
II	15	0.00490	0.3416	0.0589	99.594
III	6	0.00407	0.3370	0.0561	99.602
IV	6	0.00450	0.3366	0.0580	99.601
V	6	0.00490	0.3387	0.0590	99.597
Mean of means		0.00454	0.3401	0.0584	99.597
SD		0.00036	0.0042	0.0015	-
RSD /‾%_7		8.02	1.24	2.51	-

Comparison of the values obtained for the relative standard deviations of the laboratory mean values calculated from the relative isotopic abundances (last line of Table 7.3-4) with the relative standard deviations calculated for the interlaboratory deviation on the basis of the isotopic ratios (Table 7.3-3) shows very good agreement in respect to the isotopes U-235 (1.24 % and 1.20 %, respectively) and U-236 (2.51 % and 2.56 %, respective-

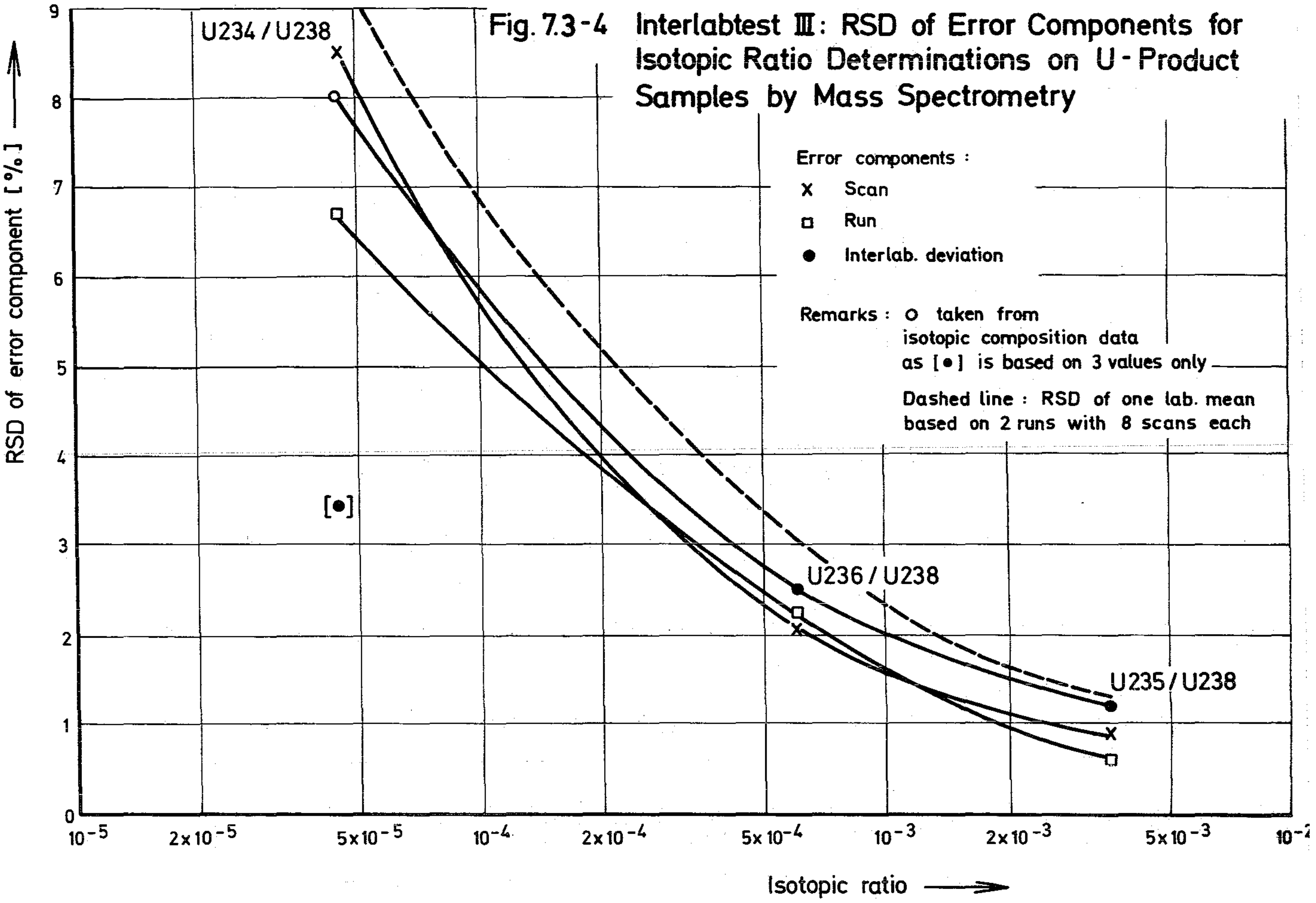

Fig. 7.3-4 Interlabtest III: RSD of Error Components for Isotopic Ratio Determinations on U-Product Samples by Mass Spectrometry

Error components :
X Scan
□ Run
● Interlab. deviation

Remarks : o taken from isotopic composition data as [•] is based on 3 values only

Dashed line : RSD of one lab. mean based on 2 runs with 8 scans each

ly)[1]. For the isotope U-234 however, 8.02 % compared to 3.39 % are found. As this higher value of about 8 % is considered as the more reliable one, it has been added in Table 7.3-3.

These results are plotted in Figure 7.3-4, showing clearly the dependence of the different error components on the magnitude of the isotopic ratio.[2]

---

1) In this connection it should be noted that for the special isotopic composition of this sample material (depleted uranium) the numerical values for the relative isotopic abundances of the rare isotopes are nearly equal to the numerical values of their ratios to the reference isotope U-238. As far as the errors of these quantities (relative isotopic abundance and corresponding ratio to the reference isotope U-238) are concerned, the same statement can be made.

2) It should be noted that these curves are only valid if the most abundant isotope (U-238) is used as reference and do not apply e.g. for the U-234/U-235 and U-236/U-235 ratios determined by the laboratories II and V (7.3.2).

Because of its usefulness in practice the dashed curve shown in Figure 7.3-4 has been calculated from the data obtained for the individual error components in this experiment: It represents the relative standard deviation δ associated in average to the result of an isotopic ratio or isotopic abundance determination performed in one laboratory on the basis of 2 runs, each one consisting of 8 scans. The calculation was carried out according to the formula[1)]

$$\delta^2 = \delta^2_{\mathrm{I.D.}} + \frac{1}{s}\,\delta^2_{\mathrm{Run}} + \frac{1}{sn}\,\delta^2_{\mathrm{Scan}}$$

with $s = 2$ = number of runs,
$n = 8$ = number of scans per run
and $\delta_{\mathrm{I.D.}}$, δ_{Run} and δ_{Scan} being the relative standard deviations for the error components as given in Table 7.3-3.

7.3.5 Discussion

Within the isotopic ratio range of about 0.005 % to 0.5 % investigated in this experiment, all three error components considered are of the same order of magnitude. By extrapolation of the curves shown in Figure 7.3-4, a value of 0.5 % to 1 % for an isotopic ratio of 10^{-2} can be assumed as a good approximation for all error components, which increases roughly by a factor of 10 with a decrease of the isotopic ratio by 2 orders of magnitude.

It should be kept in mind however, that the data calculated for the error components (7.3.4.2) are average values which have error bars themselves. Therefore, to get a more detailed picture, the scan and run error components were also calculated for each laboratory separately. The results are compiled in the following Table 7.3-5.

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1)Please refer in this connection to Appendix II,5.

Table 7.3-5: Interlabtest III: RSD of Scan and Run Errors Calculated per Laboratory

Laboratory code	U-234/U-238 RSD [%]		U-235/U-238 RSD [%]		U-236/U-238 RSD [%]		U-234/U-235 RSD [%]		U-236/U-235 RSD [%]	
	Scan	Run	Scan	Run	Scan	Run	Scan	Run	Scan	Run
I	11.09	7.31	0.90	0.57	2.50	0.94	-	-	-	-
II	-	-	0.87	0.61	1.90	2.53	2.38	8.65	-	-
III	5.03	7.64	0.93	0.49	1.55	2.86	-	-	-	-
IV	7.46	n.s. 3)	1.13	0.05	2.01	1.13	-	-	-	-
V	4.54 1)	12.91 1)	0.61	1.05	1.58 1)	3.43 1)	1.52 2)	n.s. 2,3)	0.31 2)	0.43 2)

1) Based on measurements of C-sample only
2) " " " " A-sample only
3) n.s. = "not significant"

As far as the scan error (precision) is concerned, the mean values per laboratory are different by a factor of about two at maximum. For the same laboratory, it may even change by a factor of five between different runs as it can be seen from the data compiled in Table 7.3-1 (columns 5,8 and 11).

In Table 7.3-5, also the relative standard deviations calculated for the error components in the determination of the isotopic ratios U-234/U-235 and U-236/U-235 by the laboratories II and V are given which applied the special measurement technique described before (7.3.2). From the values 2.38 % and 0.87 % obtained by laboratory II for the scan error of the isotopic ratios U-234/U-235 and U-235/U-238, respectively, a precision of 2.54 % for the isotopic ratio U-234/U-238 can be calculated. This value is about one half of the best values obtained by the other laboratories which measured the isotopic ratio U-234/U-238 directly. A corresponding comparison of the scan errors for the isotopic ratios U-234/U-238 and U-236/U-238 on the basis of the data obtained by laboratory V which used both methods of measurement leads also to the result that in case of direct determination of the isotopic ratios U-234/U-238 and U-236/U-238 the scan error is about twice as much as if the special measurement technique is applied. However, this advantage of an improved precision for the isotopic ratio U-234/U-238 (or U-236/U-238) by the determination of the ratios U-234/U-235 (or U-236/U-235) and U-235/U-238 in practically two different runs should not be overestimated as its effect on the total error of the isotopic analysis may be compensated by additional terms contributing to the run error component.

As far as the run error is concerned, comparison of the values shows clearly the advantage of the tandem mass spectrometer (Appendix III) used by laboratory IV compared to the single stage instruments.

The reasons for the smaller run errors obtained are certainly the much better abundance sensitivity of the tandem instrument along with generally better vacuum conditions. As reported by the laboratory the residual difficulties are in the positioning of the filament and in the placement of the sample in the "V" of rhenium.

7.3.6 Analytical Efforts

The laboratories were asked to report the average value of manhours necessary for the isotopic analysis of one sample in duplicate (2 runs), subdivided into

a) sample preparation including loading of two filaments,

b) mass spectrometric measurement (from filament introduction until termination of run, twice),

c) evaluation of the mass spectra and calculations.

The reported values are summarized in the following Table 7.3-6:

Table 7.3-6: Interlabtest III: Analytical Efforts (Manhours) Reported by Each Laboratory

(All values based on one analysis in duplicate)

Laboratory code	Reported manhours for sample preparation	mass spectrometric measurement	evaluation	total analysis
I	1	1.5	2	4.5
II	1.5	3.5	2	7.0
III	2	3	1.5	6.5
IV	2	2	-	4.0
V	not reported	not reported	not reported	4.5

The differences in the reported data are mainly due to the fact that the laboratories differently accounted for unavoidable dead time between analyses, instrument maintenance and calibration procedures.

7.4 Interlaboratory Test IV:

Isotopic Analysis of Plutonium Product Samples by Mass Spectrometry and α-Spectrometry

Participants:

- BCMN:
  G.H. Debus, Y. Le Duigou and K. Lauer

- CCR:
  P. Barbero, C. Cerutti, S. Facchetti, F. Mannone,
  A. Marell and A. Peil

- CEN:
  R. Boden, A. Demildt and P. De Regge

- EUROCHEMIC:
  H. Bokelund and J. van Roon

- GFK:
  A. von Baeckmann and E. Gantner

- ORNL:
  A.E. Cameron, L.T. Corbin, R.E. Eby and C.E. Lamb

- TU:
  K. Kammerichs, L. Koch and C. Rijkeboer

7.4.1 Planning and Performance of the Experiment

7.4.1.1 Objectives

The aim of this interlaboratory test was mainly to estimate the magnitude of the different error components involved in the determination of the isotopic composition of plutonium product samples by mass spectrometry.[1]

The following error components were considered:

a) "Scan[2] errors", by which the precision (or reproducibility) of the single isotopic ratios is understood and which is obtained from the repeated scans with the same filament loading (run). These are the statistical errors caused by the overall instability of the instrumental conditions.

b) "Run[2] errors", introduced by measurement on different filaments loaded with the same sample.

c) "Interlaboratory deviation" which may be caused e.g. by differences in the standards used, errors in standardization or other random components.

Furthermore, the capabilities of mass spectrometry and α-spectrometry for the determination of the isotope Pu-238 should be compared. Exact measurement of this isotope is of special interest in the application of calorimetry for safeguards purposes because of its high contribution to the total amount of heat generated by the decay of plutonium [7-4].

7.4.1.2 Sample material

Two different samples of plutonium product material were used for this experiment: One was taken from batch 2BP-400 of the VAK-campaign and is identical with sample C used in Interlaboratory Test II (7.2.1.3), the

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[1] For other sample material, e.g. active feed solutions, additional sources of error may exist which are not covered by this experiment.

[2] One "scan" is defined as the single measurement of the peaks of all isotopes considered. One "run" is defined as the total of all repeated scans with the same filament loading.

other from CANDU batch 2BP-1600 in the same manner[1]. The concentration of these plutonium solutions as shipped to the laboratories was nearly 20 mg Pu/g solution[2], the density roughly 1.2 g/ml and the nitric acidity about 6.5 M. The approximate isotopic composition was as follows:

	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	
Sample 2BP-400:	0.7	> 66	23	7.7	2.3	[wt %]
Sample 2BP-1600:	0.1	> 72	23	3.6	1.0	[wt %]

The sample material contained about 3.5 % (2BP-400) and 1.8 % (2BP-1600) uranium.

7.4.1.3 Request for analysis

Each laboratory participating in this test[3] received one sample 2BP-400 and one sample 2BP-1600 with request for analysis of the plutonium isotopic composition by mass spectrometry using their standard methods. In addition, the Pu-238 content should be determined by α-spectrometry if possible.

Chemical separation of the americium content should be carried out within two weeks before analysis. From each sample, a minimum of three mass spectrometer runs (i.e. three different filament loadings) should be made, each run consisting of at least six scans.

The laboratories were asked to report all individual isotopic ratios determined as well as the isotopic compositions in weight percent including mass discrimination factors or other corrections applied. The α-spectrometric results were demanded as activity ratios Pu-238/(Pu-239 + Pu-240). In addition, the half life values used for the calculation of the isotopic compositions should be communicated.

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1)For the description of the sampling system and the sampling procedure please refer to "Interlaboratory Test II" (7.2.1.2 and 7.2.1.3).

2)On special request, the samples for laboratory V were diluted to a concentration of about 0.2 mg Pu/g solution.

3)A total of seven laboratories participated in this experiment. However, as BCMN and CEN cooperated, they were covered by one common code number.

7.4.2 Instruments and Measurement Techniques Used by the Laboratories

With the exception of one laboratory, commercial single stage mass spectrometers of the type MS5[1], CH4[2] and CH5[2] were used. Laboratory V (ORNL)[3] used a tandem magnetic instrument of special design which is described in detail in Appendix III together with the measurement technique applied.

In all cases, the measurements were made on the Pu^+-ions and instrument calibration was performed by all laboratories with NBS uranium standards assuming this procedure gives correct results for the plutonium measurements too. Laboratory IV reported that a NBS Pu-standard was used for calibration additionally.

All laboratories used rhenium filaments but different filament arrangements. This may be one of the reasons for the wide variations of ion yields reported between 2×10^{-15} and 5×10^{-12} amps./µg Pu for the main isotope[4]. Using different amounts of sample material, all laboratories operated their instruments with ion current intensities of 10^{-13} to 10^{-12} amps. on routine conditions.

In evaluating the spectra, the individual laboratories rejected data on the basis of different statistical and empirical criteria or by visual inspection.

Concerning the methods used for the separation of americium and other α-emitters as well as for the α-determination of Pu-238, no information was requested in this interlaboratory test. All laboratories reported that americium separation was made within two weeks before mass spectrometric and α-spectrometric analyses.

In case of laboratory IV the series of mass spectrometric measurements following the americium separation were obviously hampered by loss of resolution due to mercury vapour at the collector end of the mass spectro-

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1)Associated Electrical Industries Ltd., Manchester, Great Britain.

2)Varian MAT, Bremen, Germany.

3)The permission for the revelation of the code was kindly given by the laboratory.

4)Because of its special features, the tandem mass spectrometer is not included in this consideration.

meter. Therefore, this laboratory performed a second series of isotopic ratio determinations six months later but without repeated americium separation prior to the mass spectrometric analysis. For this reason, the ratios Pu-241/Pu-239 reported by laboratory IV could not be used for the evaluation of this experiment and were given for information only.

Although the Pu-238 content was relatively high at least for sample 2BP-400 (about 0.7 %), all laboratories preferred α-spectrometry for its determination. Mass spectrometric values were reported additionally by laboratories IV and VI only.

7.4.3 Reported Analytical Results and Corrections Applied

The α-activity ratios Pu-238/(Pu-239 + Pu-240) as reported by the laboratories are summarized in Table 7.4-1 for both samples 2BP-400 and 2BP-1600.

The isotopic ratios obtained by mass spectrometry are compiled in the Tables 7.4-2 and 7.4-3 for the samples 2BP-400 and 2BP-1600, respectively.

In order to obtain comparable data for the evaluation, the values reported for the isotopic ratio Pu-241/Pu-239 had to be corrected for the β-decay of the Pu-241 isotope, as sample age was different at the time of analysis in the individual laboratories. As reference date, April 1st, 1970 was chosen and 14 years were used as half life period.

The data are also corrected for mass discrimination according to the information of the laboratories.

Because of the high number of scans in total (about 1400), only the mean values per run were given together with the relative standard deviation of the ratio for the single scan and the number of scans used for the calculation. As recommended at the Ispra Meeting (Appendix I), no attempt was made to apply common or further rejection criteria to the basic date of the individual scans which were reported by the laboratories.

Table 7.4-1: Interlabtest IV: Reported α-Activity Ratios Pu-238/(Pu-239 + Pu-240)

Laboratory code	Repetition measurement number	Sample 2BP-400		Sample 2BP-1600	
		Reported single determination of α-activity ratio	Laboratory mean value ± SD	Reported single determination of α-activity ratio	Laboratory mean value ± SD
1	2	3	4	5	6
I	1	1.24	1.26 ±0.02	0.234	0.2408 ±0.0070
	2	1.27		0.249	
	3	1.28		0.244	
	4	1.25		0.233	
	5	-		0.244	
II	1	1.208	1.2085 ±0.0007	0.2187	0.2212 ±0.0040
	2	1.209		0.2191	
	3	-		0.2258	
III	1	1.2999	1.2880 ±0.0136	0.2203	0.2201 ±0.0022
	2	1.2987		0.2176	
	3	1.2722		0.2229	
	4	1.2810		0.2196	
IV	1	1.3041	1.3041	0.2225	0.2225
V	1	1.2862	1.2784 ±0.0110	0.2180	0.2190 ±0.0014
	2	1.2706		0.2201	
VI	1	1.3016	1.3043 ±0.0062	0.2207	0.2219 ±0.0015
	2	1.2980		0.2234	
	3	1.3020		0.2196	
	4	1.3160		0.2225	
	5	1.3040		0.2235	
	6	1.3042		0.2217	

Table 7.4-2: Interlabtest IV: Reported Isotopic Ratios of Pu-sample 2BP-400 and Calculated Scan Precision per Run

(All values corrected for mass discrimination. Pu-241/Pu-239 ratio normalised for Pu-241 decay to reference date April 1, 1970)

Laboratory code	Run	Pu-238/Pu-239			Pu-240/Pu-239			Pu-241/Pu-239			Pu-242/Pu-239		
		Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans
1	2	3	4	5	6	7	8	9	10	11	12	13	14
I	1				0.3461	0.34	8	0.1154	0.45	7	0.03379	0.56	7
	2				0.3479	0.13	7	0.1157	0.26	9	0.03468	0.37	9
	3				0.3450	0.18	8	0.1151	0.29	8	0.03411	0.68	10
	4				0.3468	0.42	8	0.1161	0.28	8	0.03425	0.35	7
II	1				0.3482	0.54	11	0.1184	0.67	12	0.03630	0.51	11
	2				0.3477	0.37	12	0.1171	0.67	12	0.03587	0.75	11
III	1				0.3477	0.23	9	0.1169	0.42	9	0.03481	0.64	9
	2				0.3481	0.28	9	0.1172	0.46	9	0.03490	0.45	9
	3				0.3467	0.29	9	0.1166	0.21	9	0.03467	0.44	9
	4				0.3487	0.30	9	0.1170	0.36	9	0.03492	0.26	9
	5				0.3475	0.27	9	0.1167	0.25	9	0.03470	0.24	9
	6				0.3462	0.14	9	0.1168	0.15	9	0.03462	0.17	9
IV	1	0.0108	0.93	8	0.3484	0.32	8	0.1172 1)	2.73	8	0.03448	0.32	8
	2	0.0108	0.93	8	0.3481	0.34	8	0.1181 1)	1.35	8	0.03427	0.29	8
	3	0.0107	0.93	8	0.3478	0.17	8	0.1192 1)	1.17	8	0.03427	0.32	8
	4	0.0107	0.93	8	0.3470	0.29	8	0.1149 1)	0.35	8	0.03435	0.26	8
V	1				0.3492	0.17	10	0.1180	0.16	10	0.03476	0.26	10
	2				0.3485	0.05	10	0.1173	0.22	10	0.03449	0.31	10
VI	1	0.01072	0.90	10	0.3499	0.17	10	0.1165	0.48	10	0.03488	0.25	10
	2	0.01083	1.40	8	0.3486	0.32	8	0.1181	0.48	8	0.03522	0.97	8
	3	0.01102	1.36	10	0.3480	0.58	10	0.1169	0.65	10	0.03515	0.98	10

1) No Am-Pu separation was made. Values given are for information only and were not used for further evaluation.

Table 7.4-3: Interlabtest IV: Reported Isotopic Ratios of Pu-Sample 2BP-1600 and Calculated Scan Precision per Run

(All values corrected for mass discrimination. Pu-241/Pu-239 ratio normalised for Pu-241 decay to reference data April 1, 1970)

Laboratory code	Run	Pu-238/Pu-239			Pu-240/Pu-239			Pu-241/Pu-239			Pu-242/Pu-239		
		Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans	Mean value of isotopic ratio per run	RSD of single scan [%]	Used number of scans
1	2	3	4	5	6	7	8	9	10	11	12	13	14
I	1				0.3140	0.14	10	0.0492	0.22	8	0.0136	0.58	10
	2				0.3139	0.32	9	0.0495	0.99	7	0.0137	1.37	7
	3				0.3151	0.50	7	0.0493	0.49	7	0.0139	0.40	7
	4				0.3148	0.18	9	0.0488	0.40	8	0.0134	1.10	8
	5				0.3147	0.16	10	0.0493	0.23	6	0.0136	0.59	8
II	1				0.3140	0.45	12	0.04907	(2.45)	11	0.01391	0.68	12
	2				0.3145	0.18	12	0.04901	0.80	12	0.01372	0.90	12
	3				0.3149	0.25	12	0.04929	0.63	12	0.01390	0.60	12
III	1				0.3147	0.37	9	0.04938	0.21	9	0.01369	0.68	9
	2				0.3143	0.19	9	0.04937	0.15	9	0.01368	0.67	9
	3				0.3137	0.17	9	0.04920	0.18	9	0.01370	0.16	9
	4				0.3130	0.29	9	0.04924	0.53	9	0.01374	0.25	9
	5				0.3136	0.18	9	0.04935	0.24	9	0.01379	0.49	9
	6				0.3131	0.10	9	0.04933	0.22	9	0.01372	0.19	9
IV	1	0.00176	1.14	10	0.3148	0.22	10	0.04925 1)	0.45	10	0.01371	0.80	10
	2	0.00174	1.72	11	0.3147	0.41	11	0.04850 1)	0.72	11	0.01361	0.73	11
	3	0.00186	2.69	8	0.3142	0.35	8	0.04905 1)	0.18	8	0.01366	0.66	8
	4	0.00170	1.18	10	0.3153	0.35	10	0.04797 1)	0.33	10	0.01362	0.59	10
V	1				0.3153	0.13	10	0.04966	0.09	10	0.01362	0.41	10
	2				0.3154	0.22	10	0.04974	0.44	10	0.01365	0.79	10
VI	1	0.00176	2.20	11	0.3163	0.36	11	0.0494	0.84	11	0.01374	1.40	11
	2	0.00171	1.20	7	0.3142	0.60	7	0.0495	0.48	7	0.01395	1.20	7
	3	0.00184	4.60	12	0.3138	0.42	12	0.0494	1.05	12	0.01425	2.20	12

1) No Am-Pu separation was made. Values given are for information only and were not used for further evaluation.

According to the request for analysis (7 4.1.3) the laboratories reported also the isotopic compositions of the two samples in weight percent. Since no common reference date in respect to the Pu-241 decay and no common values for the half life periods of the different isotopes were stated in the planning of the experiment, these data, as reported by the laboratories, were not directly comparable. For this reason, the isotopic compositions were recalculated on the basis of the laboratory mean values of the corrected isotopic ratios obtained from the data compiled in Table 7.4-2 and 7.4-3, respectively. In particular, the isotopic ratios R (238/239) were calculated using the laboratory mean values of the α-activity ratios α(238/(239 + 240)) given in columns 4 and 6 of Table 7.4-1 according to

$$R(238/239) = H(238) \times \alpha(238/(239 + 240)) \times \left(\frac{1}{H(239)} + \frac{R(240/239)}{H(240)}\right)$$

with the half life values

$H(238) = 86.4$ years

$H(239) = 2.44 \times 10^{4}$ years

$H(240) = 6.58 \times 10^{3}$ years

For conversion of atom percent to weight percent the following values for the nuclidic masses were used [7-5]:

Pu-238 : 238.0495

Pu-239 : 239.0522

Pu-240 : 240.0540

Pu-241 : 241.0567

Pu-242 : 242.0587

The results of these calculations, representing the mean values of the isotopic compositions obtained per laboratory on a comparable basis, are summarized in Table 7.4-4 for both samples[1].

---

[1] For the reasons given in 7.4.2, the data obtained by laboratory IV were excluded from these calculations.

Table 7.4-4: Interlabtest IV: Laboratory Mean Values of the Isotopic Composition [wt %] Calculated from the Reported Isotopic Ratio Determinations

(All values corrected for mass discrimination and normalised for Pu-241 decay to reference date April 1, 1970. For half-life periods and nuclidic masses used see 7.4.3)

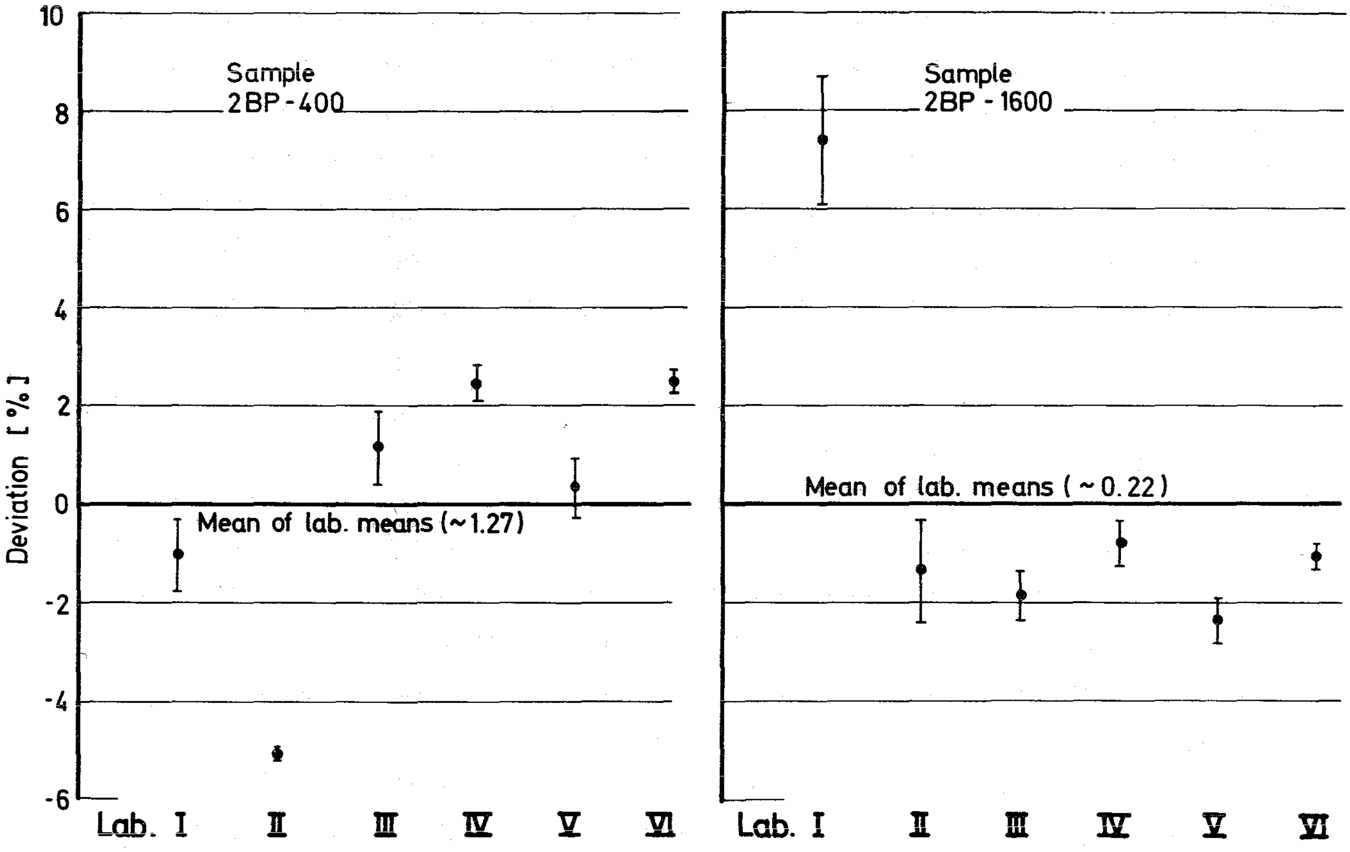
Laboratory code	Number of runs	Mean value of relative isotopic abundances per laboratory [wt %]				
		Pu-238	Pu-239	Pu-240	Pu-241	Pu-242
1	2	3	4	5	6	7
		Sample 2BP-400				
I	4	0.6714	66.2596	23.0517	7.7220	2.2953
II	2	0.6434	66.0311	23.0717	7.8404	2.4134
III	6	0.6861	66.1217	23.0723	7.7923	2.3276
V	2	0.6815	66.0353	23.1332	7.8345	2.3155
VI	3	0.6954	66.0283	23.1292	7.8013	2.3458
		0.7162*)	66.2292*)	23.0414*)	7.7189*)	2.2943*)
		Sample 2BP-1600				
I	5	0.1330	72.4061	22.8671	3.5937	1.0001
II	3	0.1221	72.4105	22.8661	3.5866	1.0147
III	6	0.1214	72.4460	22.8240	3.6022	1.0064
V	2	0.1210	72.3449	22.9092	3.6257	0.9992
VI	3	0.1225	72.3707	22.8751	3.6073	1.0244
		0.1276*)	72.3668*)	22.8741*)	3.6071*)	1.0244*)

*) Based on mass spectrometric determinations of the Pu-238 content.

7.4.4 Evaluation and Discussion of α-Spectrometric Measurements

7.4.4.1 Review of data

In Figure 7.4-1, for each laboratory the relative deviation of the mean value from the mean of these means are shown for the α-activity ratios Pu-238/(Pu-239 + Pu-240) determined on the two samples 2BP-400 and 2BP-1600. The indicated error bars represent the relative standard deviation of the mean values per laboratory[1].



(Mean values per laboratory ; error bars indicate ± 1σ range of these means)

Fig. 7.4-1 Interlabtest IV : α-Spectrometric Determinations of the Activity Ratio Pu 238 / (Pu 239 + Pu 240)

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[1] For laboratory IV, the error bars were calculated on the basis of eight values obtained from repetition measurements on samples of batch 2BP-400 and 2BP-1600 performed before Am-separation. These data were not included in Table 7.4-1.

In case of sample 2BP-400, the result of laboratory II and in case of sample 2BP-1600, the result of laboratory I is suspect. Application of the Dixon criterium [7-6] allows the rejection of these data with a probability of error of less than 10 % and less than 1 %, respectively. However, the application of outlier criteria to mean values is problematic, since the error bars of these mean values remain disregarded. Therefore, the deviations between the laboratory mean values were also checked for their significance using the statistical method described in Appendix II.2. By those tests, the existence of significant differences was confirmed for both samples with a probability of error of less than 1 %.

Based on these considerations, the measurements of laboratory II on sample 2BP-400 and those of laboratory I on sample 2BP-1600 were rejected as outliers for the further evaluation in respect to the interlaboratory deviations. Cross contamination or, in case of the analysis of sample 2BP-1600 by laboratory I, insufficient separation of americium contributing to the peak measured for the Pu-238 activity are the most probable causes for these effects.

7.4.4.2 Estimation and discussion of error components

The estimates of the variances for the precision and the interlaboratory deviation of the α-activity determinations were calculated by analysis of variances for the two samples separately (Appendix II,3). For the reasons discussed before (7.4.4.1), the measurements of laboratory II on sample 2BP-400 and of laboratory I on sample 2BP-1600 were excluded from the calculation of the interlaboratory deviations, whereas the calculations of the precision were based on the data of all laboratories.

The calculated values for the relative standard deviations of these error components are given in the following Table 7.4-5.

Table 7.4-5: Interlabtest IV: Calculated RSD of Error Components for the α-Spectrometric Determinations of the Activity Ratio Pu-238/(Pu-239 + Pu-240)

Sample	2BP-400	2BP-1600
Approximate relative Pu-238 abundance [%]:	0.7	0.1
Approximate α-activity ratio Pu-238/(Pu-239 + Pu-240):	1.27	0.22
Precision: RSD [%]	0.91	1.78
Interlaboratory deviation: RSD [%]	1.46	not significant

According to these results, no significant interlaboratory deviation was found in case of sample 2BP-1600, whereas a relative standard deviation of about 1.5 % was calculated for this error component in case of sample 2BP-400. This may be an indication for errors introduced with increasing α-activity ratios due to insufficient resolution.

Concerning the precision, a somewhat better value seems to be indicated for sample 2BP-400 than for sample 2BP-1600. In order to decide whether or not the difference of these two values is significant, a statistical test according to Appendix II,2 was performed on the basis of the precisions calculated for the individual laboratories which are summarized in the following Table 7.4-6. The significance of this effect could not be confirmed with a probability of error below 10 %.

Table 7.4-6: Interlabtest IV: Calculated and Reported Long Term Precision per Laboratory for α-Spectrometric Determinations of the Activity Ratio Pu-238/(Pu-239 + Pu-240)

Laboratory code	RSD [%] of calculated precision for approximate α-activity ratio*) ~ 1.27 (2BP-400)	 ~ 0.22 (2BP-1600)	Reported long term precision RSD [%]
I	1.45 (4)	2.90 (5)	5.0
II	0.06 (2)	1.80 (3)	3.0
III	1.06 (4)	0.99 (4)	1.0
IV	0.48 (6)	0.63 (2)	not reported
V	0.86 (2)	0.64 (2)	not reported
VI	0.47 (6)	0.69 (6)	not reported

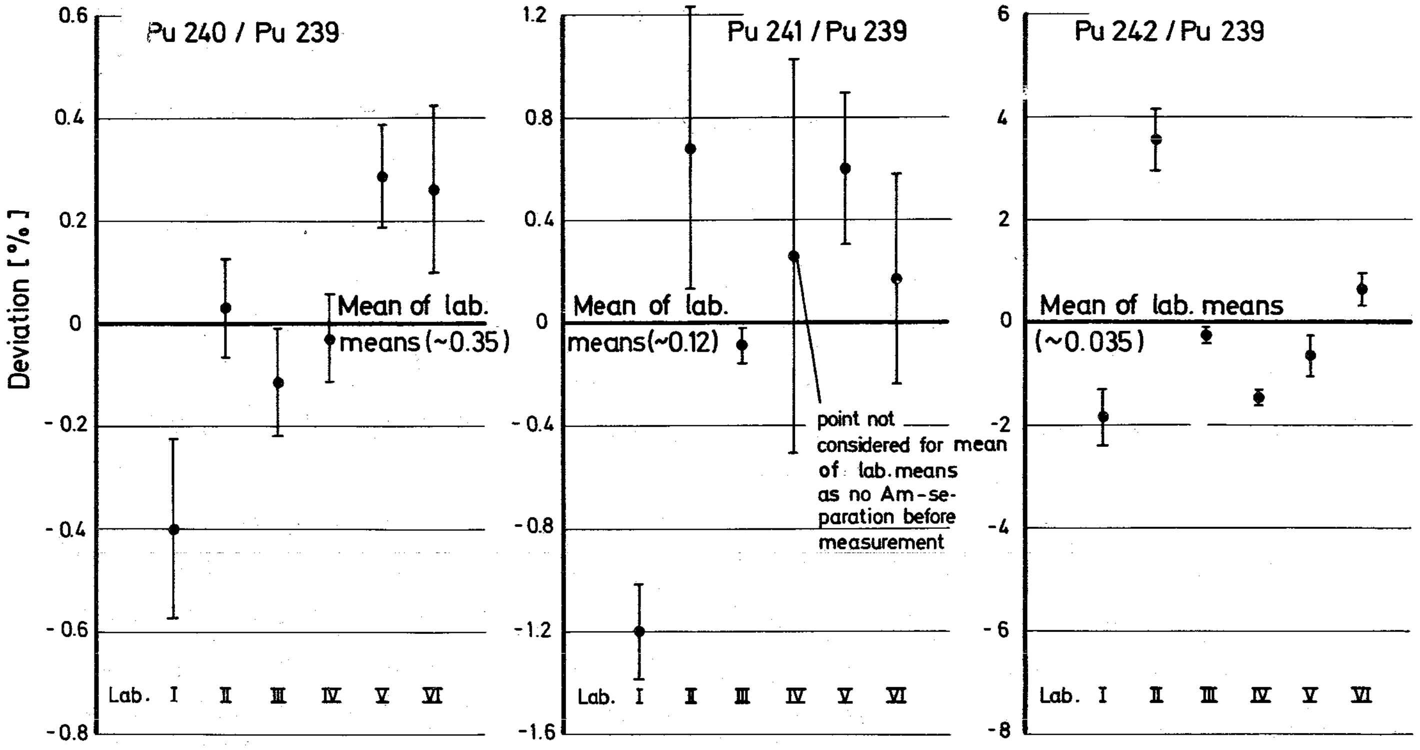
*) In brackets the number of determinations are given on which the calculations were based.

In Table 7.4-6 also the values reported for long term experience are given. Comparison of these figures indicates that the precisions calculated from the data of this experiment are in general probably somewhat better than it could be expected from long term experience on routine conditions.

7.4.5 Evaluation and Discussion of the Isotopic Ratio Determinations by Mass Spectrometry

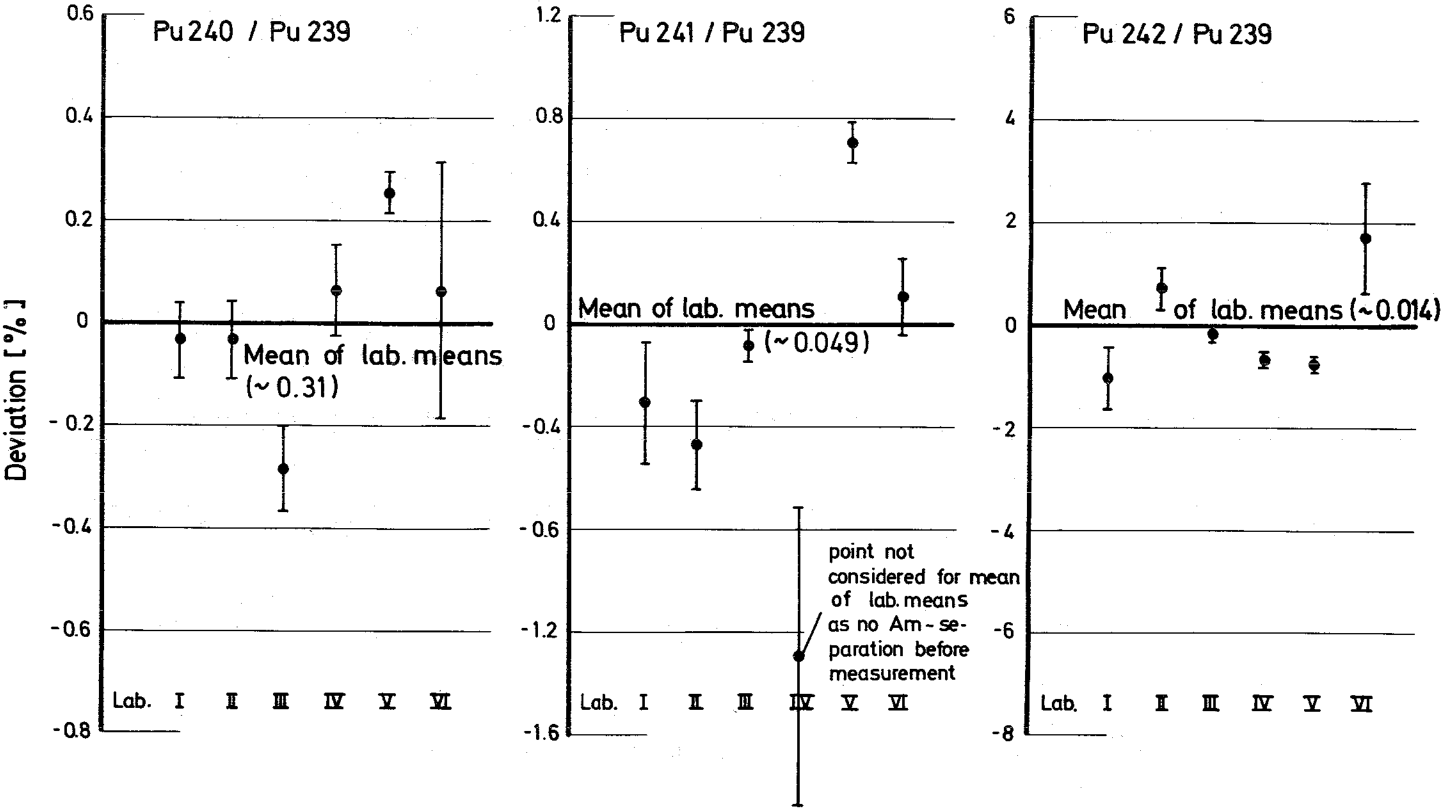
7.4.5.1 Review of data

In Figures 7.4-2 and 7.4-3, for each laboratory the relative deviations of the mean value from the mean of these means are shown for the isotopic ratios Pu-240/Pu-239, Pu-241/Pu-239 and Pu-242/Pu-239 of the two samples 2BP-400 and 2BP-1600, respectively. The indicated error bars represent the relative standard deviation of the mean values per laboratory and contain contributions by the scan error as well as the run error.



(Mean values per laboratory; error bars indicate ± 1σ range of these means)

Fig. 7.4-2 Interlabtest IV : Isotopic Ratio Determinations of Pu-Sample 2BP-400 by Mass Spectrometry



(Mean values per laboratory; error bars indicate ± 1σ range of these means)

Fig. 7.4-3 Interlabtest IV : Isotopic Ratio Determinations of Pu-Sample 2BP-1600 by Mass Spectrometry

The most evident irregularities are observed for the determinations of the Pu-241/Pu-239 ratio by laboratory I and the Pu-242/Pu-239 ratio by laboratory II, in both cases on sample 2BP-400 (Figure 7.4-2).

Application of the Dixon outlier criterium [7-6] allows their rejection with a probability of error below 10 %. However, as already mentioned before (7.4.4.1), the rejection of mean values on the basis of outlier criteria alone is problematic since the error bars of these mean values are not taken into consideration. Therefore, the existence of significant differences between the laboratory mean values was proved in addition by application of the statistical test according to Appendix II,2. They were confirmed with a probability of error below 1 % in both cases. Based on these results, rejection of the isotopic ratio Pu-241/Pu-239, determined by laboratory I, and Pu-242/Pu-239, determined by laboratory II,was considered as justified for the further evaluation in respect to the interlaboratory deviations.

As discussed at the Ispra Meeting (Appendix I), there are different possible reasons for the appearance of these outliers: Cross contamination, especially in the case of Pu-242, since this isotope is used in the laboratories in high concentration as spike for isotopic dilution analyses. Furthermore, there is the risk of interference from organic material which would influence particularly the low abundant isotopes. In the case of Pu-241, errors can be introduced by insufficient americium separation. In this connection it was suggested to eliminate the interferences from Am-241 by measuring the oxide ions of plutonium as americium oxide ions do not appear.

Concerning the measurements of sample 2BP-1600 (Figure 7.4-3), a further irregularity is indicated for the data obtained by laboratory V on the isotopic ratio Pu-241/Pu-239. However, compared to the cases discussed before, corresponding tests lead to less distinct results: the probabilities of errors for the rejection on the basis of the Dixon criterium as well as for the existence of significant differences are twice as large. For this reason these measurements were not excluded from the further evaluation.

7.4.5.2 Estimation and discussion of error components

As mentioned in 7.4.1.1, scan errors, run errors and interlaboratory deviations were considered as main error components of the mass spectrometric measurements. The estimates for the variances of these error components were calculated for all isotopic ratios of both samples by analyses of variances as described in Appendix II.4 and based on the model schematically shown in Figure 7.AII-1.

For the calculation of the scan and run error components all data reported were used with the exception of the values obtained by laboratory IV for the isotopic ratio Pu-241/Pu-239, as there was no americium separation made within a short time before mass spectrometric measurement (7.4.2).

For the calculation of the interlaboratory deviation, the measurements of laboratory I on the isotopic ratio Pu-241/Pu-239 and those of laboratory II on the isotopic ratio Pu-242/Pu-239 (in both cases sample 2BP-400) were rejected in respect to the considerations given before (7.4.5.1). Furthermore, the calculation of the interlaboratory deviation for the isotopic ratio Pu-238/Pu-239 was not meaningful, as it could only be based on the data of the two laboratories IV and VI (see Tables 7.4-2 and 7.4-3).

The results of the analyses of variances expressed as the relative standard deviations of the error components are summarized in the following Table 7.4-7 1).

Table 7.4-7: Interlabtest IV: Calculated RSD of Error Components for the Isotopic Ratio Determinations

Error component	RSD [%] of error component for isotopic ratio							
	Pu-240/Pu-239		Pu-241/Pu-239		Pu-242/Pu-239		Pu-238/Pu-239	
	~0.35 (2BP-400)	~0.31 (2BP-1600)	~0.12 (2BP-400)	~0.049 (2BP-1600)	~0.035 (2BP-400)	~0.014 (2BP-1600)	~0.011 (2BP-400)	~0.0018 (2BP-1600)
Scan	0.32	0.31	0.43	0.56	0.57	0.89	1.08	2.38
Run	0.24	0.20	0.42	0.29	0.60	0.92	0.92	3.85
Interlab. deviation	0.21	0.14	0.35 1)	0.42	1.00 2)	0.94	-	-

1) Calculated without data of laboratory I (including lab.I: 0.72 %)
2) " II (including lab. II: 1.92 %)

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1) In order to reduce the rather extensive numerical treatment of the data necessary according to the formulas given in Appendix II, a somewhat simplified way of calculation was followed. This may result in deviations in the second decimal figure for the calculated relative standard deviations of the error components which can be considered as negligible.

A graphical presentation of these results is given in Figure 7.4-4. Within the isotopic ratio range covered, all three error components considered are of the same order of magnitude and show a clear increase with decreasing isotopic ratio. Their values are about 1 % for an isotopic ratio of 10^{-2}. This corresponds to the results obtained in Interlaboratory Test III for the mass spectrometric measurements on uranium (7.3.5) and indicates that the curves found there can be considered approximately as extensions of those obtained in this test. This would mean that the errors of the isotopic ratio determinations are very similar for uranium and plutonium in principle and that the higher degree of uncertainty in the measurements on plutonium generally observed in practice is probably caused by the specific sources of error discussed before (7.4.5.1) which easily lead to outliers. Because such deviations are difficult to detect if the data of one single laboratory only are available, the error curves presented are a certain idealization from the practical point of view. This also concerns their application to the mass

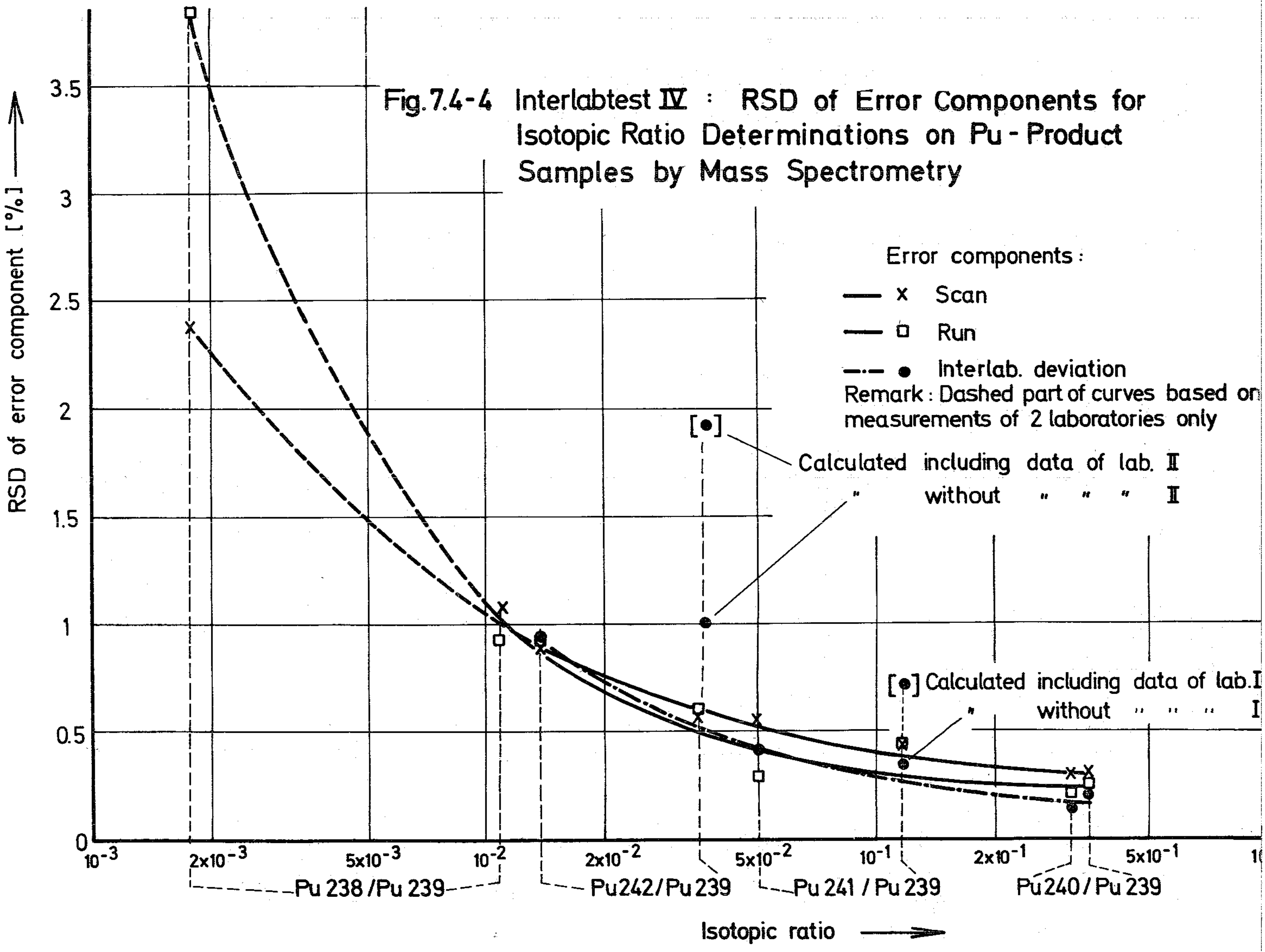

Fig.7.4-4 Interlabtest IV : RSD of Error Components for Isotopic Ratio Determinations on Pu - Product Samples by Mass Spectrometry

spectrometric determination of the isotopic ratio Pu-238/Pu-239 because of the possible interference by the isotope U-238 in the mass spectrum.

Furthermore, since the data for the error components given in Table 7.4-7 are estimates which have error bars themselves, a more detailed picture on the scan and run error components can be obtained if they are calculated for each laboratory separately. The corresponding results are summarized in Table 7.4-8.

As far as the scan error (precision) is concerned, the mean values per laboratory obtained using commerical instruments (laboratories I, II, III, IV and VI) are different by a factor of about two at maximum for high isotopic ratios and increase up to a factor of four for the lower ones[1]. For the same laboratory, it may even change by a factor of five between different runs as it can be seen from the data compiled in Tables 7.4-2 and 7.4-3. This was also found in case of the uranium measurements (Interlaboratory Test III, 7.3.5).

For the tandem mass spectrometer (laboratory V) the precision observed is better than that obtained in average by the commercial instruments. This may be due to the different ion detection system used (Appendix III)

Also the values calculated for the run error component vary considerably between the laboratories as well as for the different isotopic ratios determined by the same laboratory.

Comparison of the data shows the advantage of the tandem instrument as in the case of the uranium measurements (Interlaboratory Test III, 7.3.5) but less pronounced. However, since only two runs per sample were performed in this test, the data may not be overestimated.

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[1] This spread of the laboratory mean values is higher than it was found in the case of uranium determinations (Interlaboratory Test III, 7.3.5).

Table 7.4-8: Interlabtest IV: RSD of Scan and Run Errors Calculated per Laboratory

Laboratory code	Number of runs performed		Pu-240/Pu-239				Pu-241/Pu-239				Pu-242/Pu-239				Pu-238/Pu-239			
			~0.35 (2BP-400) RSD [%]		~0.31 (2BP-1600) RSD [%]		~0.12 (2BP-400) RSD [%]		~0.049 (2BP-1600) RSD [%]		~ 0.035 (2BP-400) RSD [%]		~0.014 (2BP-1600) RSD [%]		~ 0.011 (2BP-400) RSD [%]		~ 0.0018 (2BP-1600) RSD [%]	
	2BP-400	2BP-1600	Scan	Run	Scan	Run	Scan	Run	Scan	Run	Scan	Run	Scan	Run	Scan	Run	Scan	Run
I	4	5	0.29	0.33	0.29	0.14	0.32	0.35	0.54	0.50	0.52	1.06	0.89	1.30	-	-	-	-
II	2	3	0.46	n.s.[1]	0.31	0.11	0.67	0.76	0.72	0.21	0.64	0.82	0.74	0.71	-	-	-	-
III	6	6	0.26	0.25	0.23	0.19	0.33	0.13	0.28	0.12	0.40	0.33	0.46	0.25	-	-	-	-
IV	4	4	0.29	0.14	0.34	0.12	1.64[2]	1.42[2]	0.48[2]	1.16[2]	0.30	0.20	0.70	0.18	0.93	0.45	1.73	3.94
V	2	2	0.13	0.13	0.18	n.s.[1]	0.19	0.42	0.32	0.04	0.29	0.54	0.63	n.s.[1]	-	-	-	-
VI	3	3	0.40	0.25	0.47	0.41	0.55	0.69	0.82	n.s.[1]	0.79	0.44	1.66	1.77	1.23	1.35	3,02	3.70

1)n.s. = "not significant"

2)These data are given for information only as no Am-separation was made before mass spectrometric measurement.

7.4.6 Remarks on the Relative Isotopic Abundances

For some applications in safeguards (e.g. physical inventory, calorimetry) knowledge of the isotopic ratios is insufficient and the calculation of the isotopic composition (relative isotopic abundances), usually in weight percent, becomes necessary.

The errors of the relative isotopic abundances can be calculated by error propagation from the data on the different error components of the mass spectrometric isotopic ratio determinations and the α-spectrometric activity ratio measurements.

In the following, the relative standard deviation of the laboratory mean values obtained for the relative isotopic abundances are considered[1].

The data necessary for this calculation are compiled in Table 7.4-9 together with the results obtained. In general, the laboratory mean values for the relative isotopic abundances are identical with those already given in Table 7.4-4. However, in case of sample 2BP-400, analysed by laboratory I and II, and sample 2BP-1600, analysed by laboratory II, the values considered as outliers (7.4.4.1 and 7.4.5.1) were replaced before calculation of the isotopic compositions by the mean values of the corresponding data obtained by the other laboratories[2].

A graphical presentation of these results is given in Figure 7.4-5. The solid curve applies to the isotopes determined by mass spectrometry. Below a relative isotopic abundance of 1 % it is extrapolated in consideration of the results obtained in Interlaboratory Test III on uranium (Figure 7.3-4). The dashed line gives an approximation for the error in the determination of the Pu-238 content if α-spectrometry is used.

In addition, the relative standard deviations calculated on the basis of the relative isotopic abundances obtained without rejection of outliers[3]

---

[1] This is approximately the relative standard deviation associated in average to the result obtained by one laboratory on the basis of about three runs with more than six scans each and three α-activity determinations.

[2] The measurements of laboratory IV, performed without americium separation before analysis, were excluded from these considerations.

[3] These are the values as given in Table 7.4-4.

Table 7.4-9: Interlabtest IV: Laboratory Mean Values of the Isotopic Composition [wt %] after Rejection of Outliers

Laboratory code	Number of runs	Mean value of relative isotopic abundances per laboratory [wt %]				
		Pu-238	Pu-239	Pu-240	Pu-241	Pu-242
1	2	3	4	5	6	7
			Sample 2BP-400			
I	4	0.6706	66.1809	23.0245	7.8317	2.2923
II	2	0.6865	66.0684	23.0850	7.8446	2.3155
III	6	0.6861	66.1217	23.0723	7.7923	2.3276
V	2	0.6815	66.0353	23.1332	7.8345	2.3155
VI	3	0.6954	66.0283	23.1292	7.8013	2.3458
Mean of means		0.6840	66.0869	23.0888	7.8209	2.3193
SD		0.0090	0.0642	0.0447	0.0227	0.0195
RSD [%]		1.32	0.10	0.19	0.29	0.84
			Sample 2BP-1600			
I	5	0.1220	72.4140	22.8699	3.5939	1.0002
II	3	0.1221	72.4102	22.8661	3.5869	1.0147
III	6	0.1214	72.4460	22.8240	3.6022	1.0064
V	2	0.1210	72.3449	22.9092	3.6257	0.9992
VI	3	0.1225	72.3707	22.8751	3.6073	1.0244
Mean of means		0.1218	72.3977	22.8689	3.6032	1.0090
SD		0.0006	0.0396	0.0304	0.0148	0.0106
RSD [%]		0.49	0.05	0.13	0.41	1.05

Remark:

The following measurements were excluded as outliers and substituted by the mean values of the other laboratories:

Sample 2BP-400: Lab. I: isotopic ratio Pu-241/Pu-239
Lab.II: isotopic ratio Pu-242/Pu-239 and
α-activity ratio Pu-238/(Pu-239 + Pu-240)

Sample 2BP-1600: Lab. I: α-activity ratio Pu-238/(Pu-239 + Pu-240)

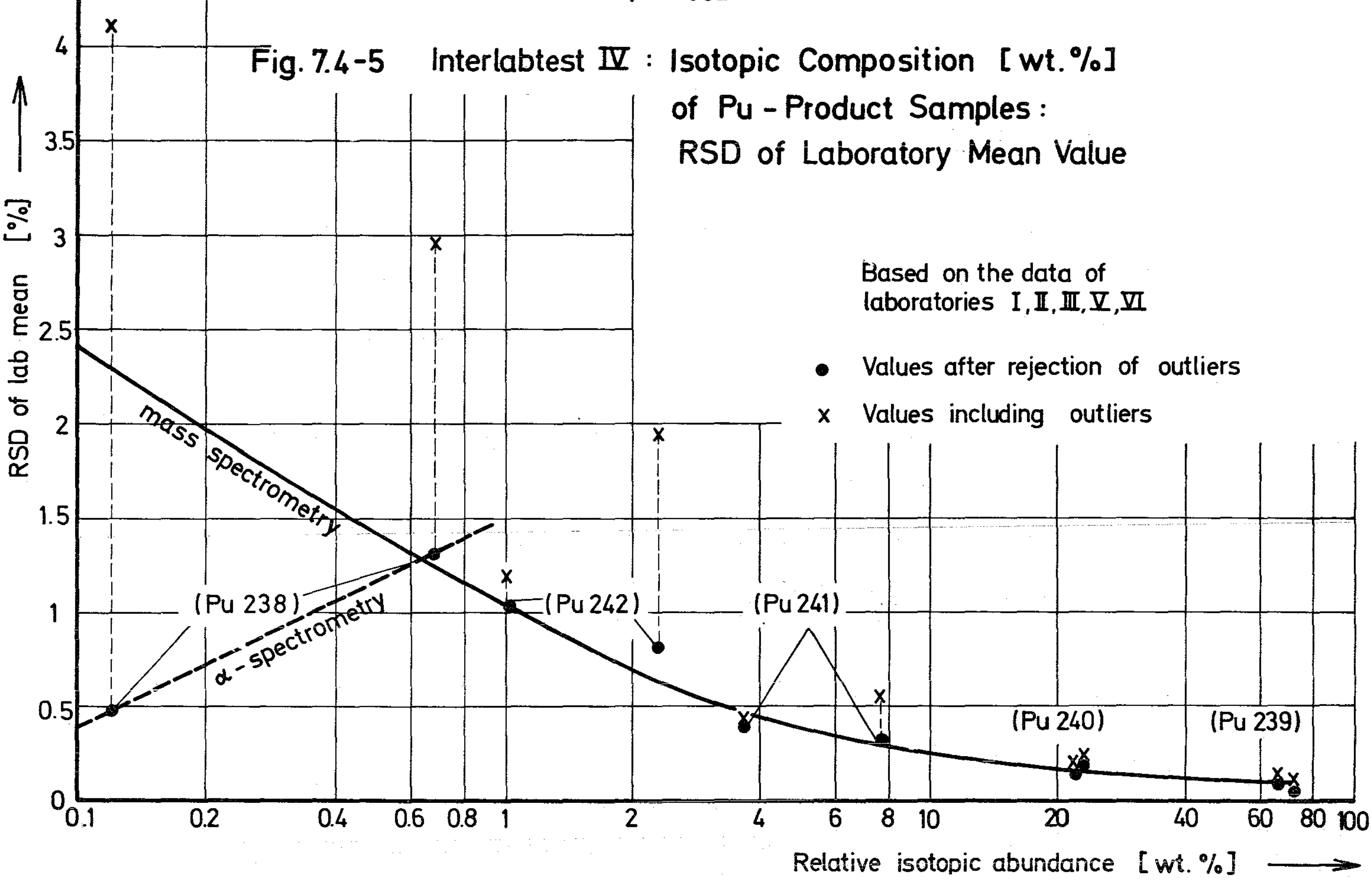

Fig. 7.4-5 Interlabtest IV : Isotopic Composition [wt.%] of Pu - Product Samples : RSD of Laboratory Mean Value

are also indicated in Figure 7.4-5. It shows again the unfavorable influence of outliers and the necessity of caution in the estimation of error limits for isotopic analyses of plutonium.

Concerning the determination of the isotope Pu-238, the shape of the curves confirms the advantage of α-spectrometry compared to mass spectrometry at least for a relative abundance below 0.7 %. But because of the difficulties in the mass spectrometric determination of Pu-238 due to the superimposed uranium isotope, α-spectrometry will be preferable even at higher concentrations[1]. However, the uncertainty introduced by outliers also in the α-spectrometric results should not be overseen.

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[1] Only laboratory VI determined the Pu-238 content by mass spectrometry and α-spectrometry for comparison (see Table 7.4-4). The values obtained by mass spectrometry were 3 % (sample 2BP-400) and 4 % (sample 2BP-1600) higher.

7.4.7 Analytical Efforts

The laboratories were asked to report the average value of manhours necessary for the isotopic analysis of one sample in duplicate (2 runs) subdivided into

a) sample preparation including americium separation and loading of two filaments,

b) mass spectrometric measurement (from filament introduction until termination of run, twice)

c) evaluation of mass spectra and calculation

d) α-spectrometric determination of Pu-238.

The reported values are compiled in the following Table 7.4-10:

Table 7.4-10: Interlabtest IV: Analytical Efforts (Manhours) Reported by Each Laboratory
(All values based on one analysis in duplicate.)

Laboratory code	Reported manhours for				
	Sample preparation including Am-separation	Mass spectrometric measurement	Evaluation	α-Spectrometric determination of Pu-238	Total analysis
I	1.5	3.5	2	1	8
II	2	2	2	0.7	6.7
III	2 1)	2	2	5 2)	11
IV	0.75 1)	5	2.75	4 2)	12.5
V	2 3)	2	- 4)	not reported	4 (+2)
VI	not reported	not reported	not reported	10 2)	10 +

1) Excluding Am-separation
2) Including separation of α-emitters (Am,Np,Cm)
3) 4 manhours if Pu were to be separated uranium free to enable Pu-238 determination by mass spectrometry
4) Computer printout

The differences in the reported data are mainly due to the fact that the laboratories differently accounted for unavoidable dead time between analyses, instrument maintenance and calibration procedures.

7.5 Interlaboratory Test V:

Determination of Uranium and Plutonium Concentrations in Active Feed Solutions by Mass Spectrometric Isotope Dilution Analysis

Participants:

- BCMN:
  G.H. Debus

- EUROCHEMIC:
  H. Bokelund, K. Koch and J. van Roon

- GFK:
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- TU:
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7.5.1 Planning and Performance of the Experiment

7.5.1.1 Objectives

By contrast to the other interlaboratory tests performed on relatively pure product samples of the reprocessing plant, this experiment was related to the determination of plutonium and uranium concentrations of the greatly contaminated active feed solutions by mass spectrometric isotope dilution analysis.

The number of error sources involved in this analytical technique is particularly high. Therefore, a detailed and separate investigation of the different error components would necessitate a rather extensive layout of the experiment and, consequently, the performance of very many expensive and time consuming isotopic dilution analyses.

Because of the many other analytical demands for JEX-70, such considerable additional requirements would have exceeded the capacities of the participating laboratories.

For these reasons, the scope of this interlaboratory test was restricted to preliminary investigations of the two main error components: The precision of the single analysis and the interlaboratory deviation.

Based on a very limited number of data, the results of these studies and their interpretation should not be considered as final statements but as a first approach useful for the design of further, more elaborated experiments.

7.5.1.2 Sampling procedure and sample material

Two composite samples (in the following indicated as A- and B-samples) were used for this interlaboratory test prepared within the framework of JEX-70 for verification purposes [7-7].

The basic samples for their preparation were taken from two dissolver tanks installed in parallel at the head end of the EUROCHEMIC plant and fed by active nitric solutions of dissolved CANDU fuel elements.

During the whole sampling procedure airsparging was maintained in the tanks for homogenization. Before taking the samples, the solution was recycled through the sample bottle for 10 minutes in order to avoid crosscontamination with residual material in the sample lines (Interlaboratory Test I, 7.1.1.2 and Figure 7.1-1).

From each of six dissolver batches[1], two samples were taken (a_1, a_2.....a_6 and b_1, b_2.....b_6). Immediately after sampling, each single sample was diluted separately with 5 N HNO_3 in a constant ratio of 1:248.2 by volume to increase their stability. Until preparation of the composite samples, these diluted sample solutions were stored in glass vials as described in Interlaboratory Test II (Figure 7.2-1).

The two composite samples A and B were prepared from the basic samples a_1 to a_6 and b_1 to b_6, respectively[2]. After careful homogenization in a glass flask, the sample solutions were distributed on several glass vials of the type mentioned before and packed for shipment to the laboratories as described in Interlaboratory Test II (7.2.1.3).

According to the procedures followed, concentration differences between the composite samples A and B could be caused by inhomogeneity of the solution in the dissolver tanks, instability of the sample material during storage time and failures in course of their preparation.

The approximate data of the samples were as follows:

Pu-concentration:	∿ 3 μg/ml
U-concentration:	∿ 1 mg/ml
β-activity:	∿ 180 μCi/ml
γ-activity:	∿ 60 μCi/ml
nitric acidity:	∿ 5 M

The basic samples were taken during the last week of March and the composite samples were prepared in the first days of April, 1970.

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[1] AFU-700, 710, 800, 810, 900 and 910 of CANDU campaign.

[2] The preparation of these composite samples was performed analogous to the procedure described in [7-8].

7.5.2 Information on the Analytical Procedures Reported by the Laboratories

Americium separation was made by all laboratories less than three weeks before analysis.

The isotope Pu-238 was determined in all cases by α-spectrometry with the exception of laboratory V which used mass spectrometry.

Further information on the analytical procedures is given in the following as reported by the laboratories:

Laboratory code I:

Sample preparation:

Uranium: Anion exchange separation (8 M HNO_3)
Plutonium: Redox cycle: NH_2OH; $NaNO_2$: anion exchange separation (8 M HNO_3; 0,5 M HNO_3)

U-233 spike solution:

Concentration: ∿ 2 mg/ml
Isotopic ratios: U-235/U-233 = 0.00111
U-238/U-233 = 0.1352
Standard for calibration: NBS chemical standard 950a, 99.94 % pure, nat. uranium

Pu-242 spike solution:

Concentration: ∿ 0.5 mg/ml
Isotopic composition: Pu-238: 0.627 %, Pu-239: 0.200 %, Pu-240: 1.421 %, Pu-241: 0.483 %, Pu-242: 97.187 %, Pu-244: 0.082 %
Standard for calibration: NBS 949a

Laboratory code II:

Sample preparation:

Uranium: Addition of $KMnO_4$, TPAN-hexone extraction
Plutonium: Redox cycle: NH_2OH, HCl; $NaNO_2$: TTA-extraction

U-233 spike solution:

Concentration: 480.08 μg U-233/ml ± 0.437 (SD of mean)

Isotopic ratios: U-234/U-233 = 0.0001975
U-235/U-233 = 0.0003961
U-238/U-233 = 0.004989
Standard for calibration: NBS chemical standard 950a,
99.94 % pure, nat. uranium

Pu-242 spike solution:

Concentration: 8.565 µg Pu-242/ml ± 0.018 (SD of mean)
Isotopic ratio: Pu-239/Pu-242 = 0.000181
Standard for calibration: NBS metal standard 949; 99.94 % pure
Isotopic composition: Pu-239: 94.39 %, Pu-240: 5.293 %,
Pu-241: 0.300 %, Pu-242: 0.015 %

Laboratory code III:

Sample preparation:

a) About 0.25 g of the resin, suspended in 8 M HNO_3, are transferred to a glass column (⌀ 5 mm, height 10 cm) containing a little glass wool at the lower end, and washed with 1 ml of the acid.

b) The sample, dissolved in 8 M HNO_3 and containing about 0.1-1 µg Pu, is brought onto the resin and then washed with 6 ml 8 M HNO_3 according to the uranium content, and elution carried out using 3 ml 0.35 M HNO_3.

c) The plutonium concentration in the eluant is determined roughly by α-spectrometry and this solution is evaporated to dryness in a filtered air stream at 80-100°C. The residue is dissolved in 1 M HNO_3 to give a plutonium concentration of ca. 10 ng/µl.

d) An amount of solution containing 1-5 ng Pu is placed in the centre of a filament and mass spectra of the uranium and plutonium isotopes are recorded.

e) A calibrated mixture of the tracer isotopes U-233 and Pu-242 is added to another sample of the same weight as that used in (b) above. The amounts of uranium and plutonium in the tracer mixture must approximately correspond to those in the sample.

f) 0.3 ml 1 M NH_2OH; HCl is added to the mixture of sample and tracer, which is then heated to 50°C and allowed to cool for 5 minutes. 0-1 ml 1 M $NaNO_2$ are then added and, after evolution of the nitrous gases, the solution is stirred and warmed gently.

g) This solution is then treated as in b-d above.

U-233 spike solution:

Concentration: 6.4719 × 10^{17} atoms/g solution
Atomic ratios and standard for calibration not reported.

Pu-242 spike solution:

Concentration: 52.8698 × 10^{14} atoms/g solution
Standard for calibration: NBS metal standard 949b, purity 99.99 ± 0.08 % Pu-239.

Isotopic ratios: Pu-240/Pu-239:0.01973
Pu-241/Pu-239:0.000332
Pu-242/Pu-239:0.000

Laboratory code IV:

The uranium concentration was determined by X-ray fluorescence spectrometry. The plutonium concentration of these diluted samples was too low for analysis by this analytical technique.

Method: A weighed aliquot of the sample is mixed with a defined amount of thorium nitrate solution. In the solution the ratio of the intensities of the uranium and the thorium $L\alpha_1$-lines are compared.

Lit: P.A. Pella et.al., Anal. Chim. Acta 47, 431 (1969)

Laboratory code V:

Mass spectrometric isotope dilution technique was used. Details on sample preparation and spike solutions were not reported.

7.5.3 Reported Analytical Results

In Table 7.5-1, the reported concentration values for uranium and plutonium are compiled together with the dates of spiking and mass spectrometric measurement[1]. All determinations were made using isotopic dilution analysis with the exception of those for uranium given under laboratory code IV which were carried out by X-ray fluorescence spectrometry[2].

The values obtained by laboratory II were reported in mg/l solution. In order to make them comparable with the other data, they were converted to mg/g solution using the densities of 1.1707 g/ml (sample A) and 1.1706 g/ml (sample B) determined by this laboratory on September 8, 1970.

In principle, correction of the plutonium concentration values for the decay of the isotope Pu-241 would be necessary because of the different dates of analyses at the individual laboratories. However, being in the order of 0.1 % only, this correction was not applied in this test.

7.5.4 Evaluation and Discussion

7.5.4.1 Review of data

Comparison of the data obtained on the uranium as well as the plutonium concentration determinations (Table 7.5-1) shows in general no significant differences between the A and B samples. This is confirmed by statistical tests according to Appendix II,2 based on the results obtained per laboratory[3]. This means that from the data obtained in this experiment, no in-

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1) To facilitate further discussions, a running number was assigned to the analyses in column 3.

2) At the Ispra Meeting (Appendix I), only the results of three laboratories and the X-ray fluorescence determinations were available since laboratory V was hindered to perform the analysis before February 1971.

3) Only for the plutonium determinations of laboratory III a significant difference between the mean values of the analyses 3 and 4 on sample A and 5 and 6 on sample B is confirmed with a probability of error below 10 %. However, as discussed later, this difference is very probably caused by the different dates of spiking and analyses and not specific for the samples.

Table 7.5-1: Interlabtest V: Reported Concentration Determinations

Laboratory code	Sample description	Analysis identification number	Date of spiking	Uranium		Plutonium	
				Date of mass spectrometric analysis	Concentration [mg U/g sol.]	Date of mass spectrometric analysis	Concentration [µg Pu/g sol.]
1	2	3	4	5	6	7	8
I	A_1 1)	1	20.7.	25.8.	0.880	10.8.	2.82
	A_2 1)	2	20.7.	25.8.	0.916	10.8.	- 2)
	B	3	20.7.	26.8.	0.9136	11.8.	2.76
	B	4	20.7.	26.8.	0.8938	11.8.	2.63
II	A	1	13.4.	14.4.	0.8759 3)	15.4.	2.850 3)
	A	2	13.4.	24.4.	0.8724 3)	24.4.	2.886 3)
	B	3	13.4.	15.4.	0.8769 3)	15.4.	2.855 3)
	B	4	13.4.	24.4.	0.8721 3)	24.4.	2.856 3)
III	A	1	19.5.	13.6.	0.8947	13.6.	- 2)
	A	2	19.5.	13.6.	0.8903	13.6.	- 2)
	A	3	28.9.	1.10.	0.9165	1.10.	2.961
	A	4	28.9.	1.10.	0.9150	1.10.	2.928
	B	5	19.5.	13.6.	0.8981	13.6.	2.881
	B	6	19.5.	13.6.	0.8981	13.6.	2.889
IV 4)	A	1		27.7.	0.8940		
	A	2		27.7.	0.8992		
	A	3		27.7.	0.8972		
	A	4		27.7.	0.9026		
V	A	1	1.2. 71	10.2. 71	0.898	2.2. 71	2.899

Remark: All dates refer to 1970 if not otherwise stated.

1) The indices 1 and 2 indicate different bottles of the same sample solution.

2) Analysis rejected by the laboratory.

3) The original values were reported in mg/l solution. They were converted to mg/g solution using the densities of 1.1707 g/ml (sample A) and 1.1706 g/ml (sample B) determined by the laboratory on September 8, 1970.

4) Analysed by X-ray fluorescence spectrometry.

homogeneity of the tank solution or failures in the preparation of the composite samples were indicated (7.5.1.2) and that no distinction between the A- and B-samples is necessary for the further evaluation.

In Figure 7.5-1, for each laboratory the relative deviation of the mean value from the mean of these means is shown for the uranium as well as the plutonium concentration determinations. The indicated error bars correspond to the relative standard deviation of the mean values. In case of laboratory V, the dashed lines represent the relative standard deviation estimated by this laboratory as one single analysis only was performed.

The Pu/U ratios shown in Figure 7.5-1 were calculated for each laboratory from the means of the uranium and plutonium concentration values.

Concerning the plutonium concentration determinations the value obtained by laboratory I deviates significantly from the others. The laboratory reports that the difference of nearly 5 % obtained on the two measurements of sample B (Table 7.5-1, analyses 3 and 4) is clearly outside the reproducibility normally obtained. Therefore it is assumed that the material in this sample bottle was not homogeneous (solid, undissolved particles) or that there was at least partially polymerisation of plutonium causing incomplete homogenization with the plutonium of the spike solution and thereby unsatisfactory performance of the separation process on the ion exchange column. The analytical result obtained on sample A shows a distinctly higher value which is given in Figure 7.5-1 in brackets for comparison.

In connection with these indications for instability of the sample solution it is of interest to consider the measurements performed by laboratory III and the comments given by this laboratory. As it can be seen in Table 7.5-1, the values of analyses 3 and 4 are higher compared to the others for uranium as well as plutonium1). Since spiking of the samples for these analyses (3 and 4)

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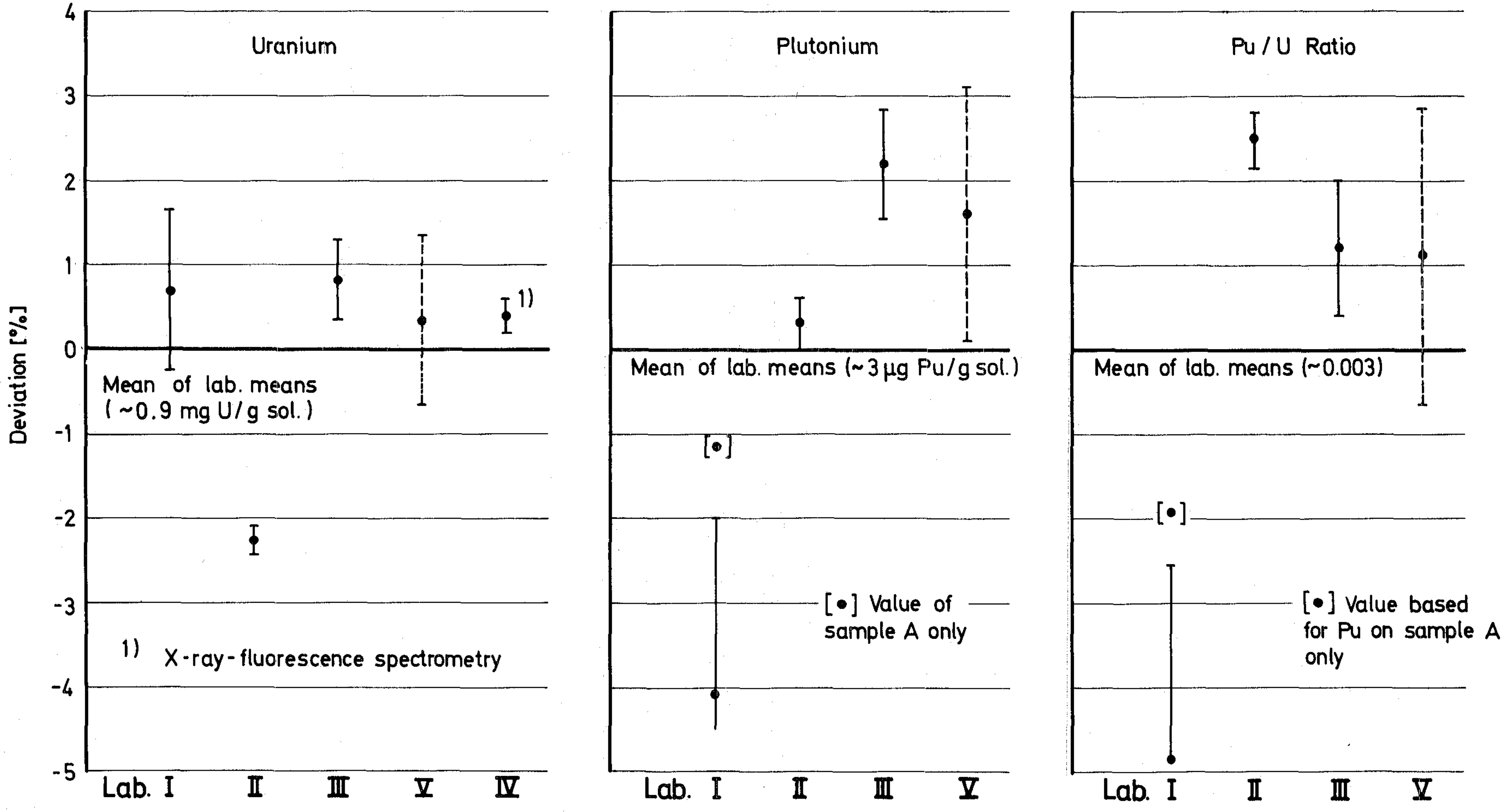
1)The significance of these differences is confirmed by a statistical test according to Appendix II,2 with a probability of error below 1 % and below 10 % for the uranium and plutonium values, respectively.



(Mean values per laboratory; error bars indicate ± 1σ range of these means)

Fig. 7.5-1 Interlabtest V: U-and Pu-Concentrations of Active Feed Solutions Determined by Isotopic Dilution Analyses was made more than four months later than for the others, the laboratory assumes that these differences are caused by evaporation during the storage time. This is confirmed by the fact, that the Pu/U ratios calculated from the analyses at the two different dates agree within 0.2 %. On the other hand, this constancy of the Pu/U ratio indicates that there was no change in the sample composition during more than four months due to effects specific for plutonium like polymerisation or plating out.

Unfortunately, the basis of experimental data seems to be too small to draw any further conclusions from these observations and the effects indicated by the measurements of laboratory I on the time dependence or on other parameters which may influence the stability of plutonium samples1).

Considering the concentration determinations of uranium (Figure 7.5-1), the low value obtained by laboratory II deviates significantly from the others. No clear indication for the reason could be found. As mentioned before, the values for this laboratory were calculated using density measurements performed about five months after analyses (7.5.3). However, the assumption of an increase of sample density caused by evaporation during storage time would explain this effect only partially as comparison of the Pu/U-ratio (Figure 7.5-1) with those obtained by the laboratories III and V shows2).

7.5.4.2 Estimation of error components

Because of the uncertainties in the causes for the different deviations observed (7.5.4.1) the choice of data on which error consideration should be based is not free of a certain arbitrariness. Besides this, the limited number of data available from this test leads necessarily to considerable different results of error calculations if any values are excluded. Therefore, as already mentioned in 7.5.1.1, the error estimations and considerations given in the following should be considered as preliminary information, but not as final statements on the capabilities of the isotopic dilution analysis of active feed solutions.

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1) In this connection reference is made to the development of special techniques for stable sample storage [7-9].

2) The results of laboratory I may be excluded from this consideration because of the reasons discussed before.

For the uranium as well as the plutonium determinations the estimates of the variances for the precision and the interlaboratory deviation were calculated (Appendix II,3)¹⁾.

Corresponding to the layout of the experiment, the precision (or reproducibility) describes the deviations obtained by repeated analyses of the same sample within one individual laboratory. It includes all randomly distributed errors of chemical sample preparation, spiking procedures and mass spectrometric measurements. To the interlaboratory deviation contribute e.g. differences of the sample material due to evaporation, wall effects and polymerisation (plutonium) in connection with the different dates of analysis, systematic error components of the chemical sample preparation procedures and calibration errors. According to the opinion of the analysts expressed at the Ispra Meeting (Appendix I), spike calibration errors are of minor importance.

In case of uranium, the analysis of variances was based on all results obtained by isotope dilution technique (laboratories I, II, III and V, Table 7.5-1).
For calculation of the relative standard deviation of the precision, the analyses 3 and 4 of laboratory III were considered separately in order to avoid contribution of the probable evaporation effect (7.5.4.1) to this error component.

Concerning the plutonium analyses, all measurements reported (Table 7.5-1) were used for the calculation of the interlaboratory deviation. For the calculation of the precision, however, the values obtained by laboratory I remained disregarded for the reasons discussed before (7.5.4.1) and the analyses 3 and 4 of laboratory III were treated in the same manner as in the case of uranium mentioned above.

In the following Table 7.5-2, the calculated relative standard deviations of error components are summarized. In addition, the total error for one single analysis calculated from these data is given (Appendix II,5).

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1) In this case, the index "j" refers to the laboratory, the index "ν" to the analysis identification number.

Table 7.5.2: Interlabtest V: Calculated RSD of Error Components

	Precision RSD [%]	Interlaboratory deviation RSD [%]	Total error of single analysis RSD [%]
Uranium:	1.1	1.4	1.7
Plutonium:	0.6	2.7	2.7

As already mentioned, there is a considerable uncertainty in these values due to the small number of data on which they are based. If e.g. the uranium measurements of laboratory II (Figure 7.5-1) are considered as outliers and excluded from the calculation, the interlaboratory deviation becomes insignificant.

At the Ispra Meeting (Appendix I), the analysts expressed the opinion that the relative standard deviation for the precision of the isotope dilution analyses is between 0.4 % and 0.7 % for routine measurements, being for plutonium probably somewhat higher than for uranium. The average value of 1.1 % obtained by analysis of variances for the precision of the uranium concentration determinations (Table 7.5-2) is outside of these limits. However, considering the precisions calculated for the individual laboratories separately, better agreement with those estimations is indicated. In the following Table 7.5-3, the precisions per laboratory calculated from the data of this test are summarized together with the values reported on the basis of long term experience.

Table 7.5-3: Interlabtest V: Calculated and Reported Long Term Precision of the Uranium Concentration Determinations per Laboratory

Laboratory code	Number of analyses on which calculations were based		Precision calculated from the data of this experiment RSD [%]		Reported long term precision RSD [%]	
	U	Pu	U	Pu	U	Pu
I	4	-[1)]	1.9	-[1)]	0.6	0.8
II	4	4	0.3	0.6	0.5	0.7
III	4	4	0.4	0.5	0.6	0.6
V	1	1	-	-	not reported	
IV[2)]	4	0	0.4	-	1.0	1.0[3)]

1)Not calculated, as values are not representative (7.5.4.1).
2)Determination by X-ray fluorescence spectrometry.
3)Based on long term experience with samples of higher Pu-concentrations than those used in this test.

7.5.5 Analytical Efforts

The laboratories were asked to report average values in manhours necessary for the isotopic dilution analysis of uranium and plutonium performed on one sample in duplicate. It was asked to subdivide the values according to

a) sample preparation
b) mass spectrometric measurement
c) α-spectrometric determination of Pu-238
d) spectra evaluation and calculations.

The reported data are compiled in the following Table 7.5.4:

Table 7.5.4: Interlabtest V: Analytical Efforts (Manhours) Reported by Each Laboratory.
(Values based on one analysis in duplicate for determination of U and Pu)

Laboratory code	Reported manhours for				
	sample preparation	mass spectrometric measurement	α-spectrometric measurement	evaluation	total analysis
I	4	10	1	4	19
II	6	8	1	10	25
III	2	8	2	5	17

Since these values are related to routine conditions of analysis, efforts for calibration of spike solutions etc. are not included.

7.6 Summary

The concentrations of uranium and plutonium in samples of product solutions were analysed by different wet-chemical methods and X-ray fluorescence spectrometry (Interlaboratory Tests I and II). The average values of the relative standard deviations calculated for the error components of these analyses and the possible sources for these errors are summarized in Table 7.6-1.

Table 7.6-1: Calculated RSD of Error Components for Concentration Determinations of Uranium and Plutonium in Product Samples.

Error component	Possible sources of errors	RSD of error component [%] U	Pu
Sampling error	Inhomogeneity of tank solution, dilution step after sampling (Pu).	not significant	not significant
Sample error	Sample preparation in laboratories, sample instability (Pu).	not significant	0.49
Interlaboratory deviation	Differences in standards used and corrections applied, random components.	0.20	0.25
Precision	Random components influencing the single measurement.	0.11*)	0.24*)

*)Calculation based on wet-chemical methods only.

According to these results the main error component found in the determination of uranium concentrations is due to deviations between the laboratories partially using different analytical methods. By contrast, for plutonium concentration determinations, the instability of the samples - probably caused by polymerisation and plating out - contributes most significantly to the total error of a single measurement. This contribution may include errors due to the impeded manipulations in glove boxes during sample preparation in the laboratories.

No significant inhomogeneity of the tank solutions was indicated. However, it should be noted that the samples for each test were taken from one single batch only.

The suitability of density determinations for checking the homogeneity was confirmed for uranium solutions provided the measurements are performed by the same laboratory.

Using the same product solution samples as for the concentration determinations by wet-chemical methods mentioned above, the errors involved in the isotopic ratio determinations of uranium and plutonium by thermionic mass spectrometry were investigated (Interlaboratory Tests III and IV). Three error components were distinguished: the scan error, describing the precision of the single isotopic ratio of one run, the run error, introduced by measurement on different filaments loaded with the same sample, and the interlaboratory deviation. Their relative standard deviations in dependence on the atomic ratio are shown in Figures 7.6-1 and 7.6-2 for the measurements on uranium and plutonium, respectively.

As appears from these figures, all of the three error components under consideration are of the same order of magnitude and increase markedly with decreasing isotopic ratio.

Compared to uranium measurements, a considerable number of outliers was observed in the isotopic determinations of plutonium leading easily to erroneous results which are difficult to detect if there are no comparison values of other laboratories available. In case of the isotope Pu-241 they are most probably due to the rapid ß-decay, although the americium formed was separated chemically prior to the meas-

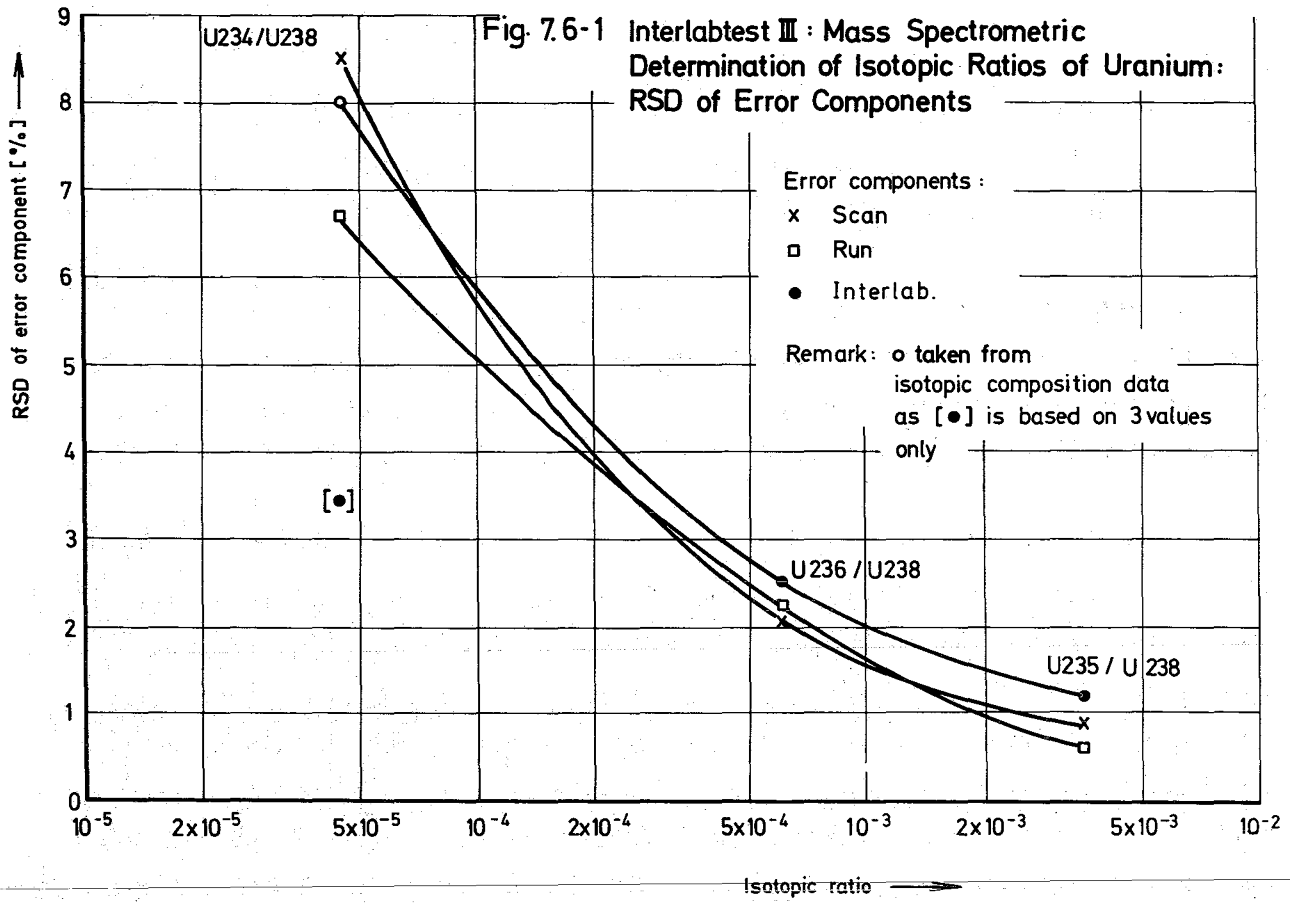

Fig. 7.6-1 Interlabtest III : Mass Spectrometric Determination of Isotopic Ratios of Uranium: RSD of Error Components

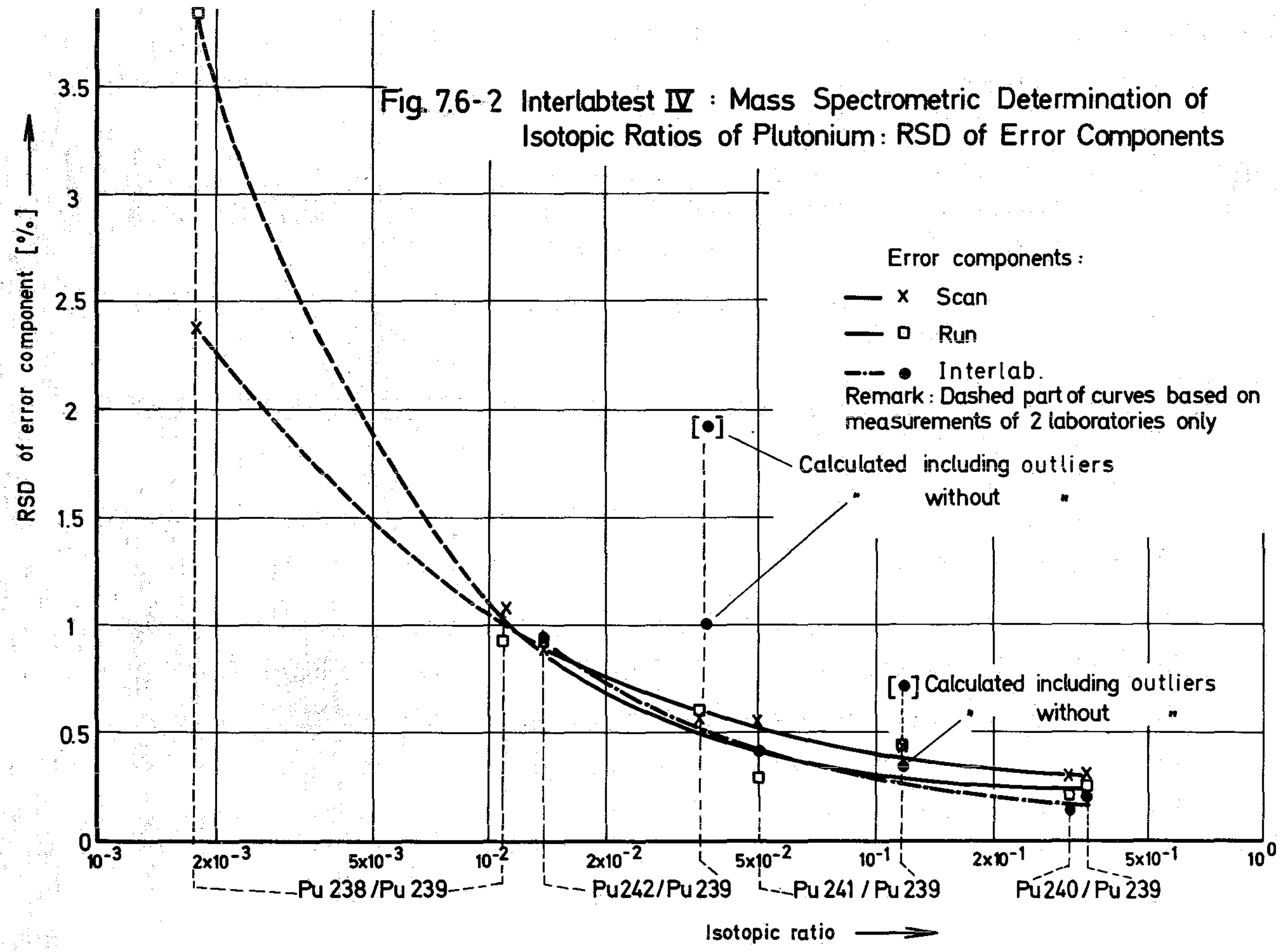

Fig. 7.6-2 Interlabtest IV : Mass Spectrometric Determination of Isotopic Ratios of Plutonium: RSD of Error Components

urements. The outliers found in the determinations of the isotope Pu-242 can be explained most likely by cross contamination and memory effects appearing in the mass spectrometer since this isotope in its highly enriched form is used also as a spike in isotope dilution analysis.

For the determination of the Pu-238 content (up to 0.7 % in this experiment), all laboratories preferred α-spectrometry. In average, a precision of about 1 % was obtained for the single activity ratio measurement which seems to be somewhat better than expected from long term experience.

For the concentration determinations of uranium and plutonium in active feed solutions by mass spectrometric isotope dilution analysis (Interlaboratory Test V), the evaluation could be based on a rather limited number of data only. The test was planned as a preliminary study on which further, more elaborated investigations could be based. Therefore, the results obtained (Table 7.6-2) should be considered as indicative and not as final statements on the capability of this analytical technique. This applies particularly to the value calculated for the precision of uranium determinations which is assumed to be between 0.4 % and 0.7 % according to general experience.

Table 7.6-2: Calculated RSD of Error Components for Concentration Determinations of Uranium and Plutonium in Active Feed Solutions by Mass Spectrometric Isotope Dilution Analysis.

	Precision RSD [%]	Interlaboratory deviation RSD [%]
Uranium	1.1	1.4
Plutonium	0.6	2.7

In respect to their application for safeguards purposes, information on the efforts of the different analytical procedures were demanded from the laboratories. As the laboratories accounted differently for some calibration procedures, dead time between analyses, maintenance of instruments etc., in some cases the reported data deviate considerably from each other. Therefore, no average values were calculated but the lowest and highest values reported are given in the following Table 7.6-3.

Table 7.6-3: Reported Efforts (Manhours) for the Analytical Procedures Investigated

Type of analyses	Manhours per analysis in duplicate	
	Uranium	Plutonium
Concentration determination of product samples by wet chemical methods	3.5 to 6 *)	2 to 20 *)
by X-ray fluorescence spectrometry	3 *)	2 *)
Isotopic composition determination of product samples by mass spectrometry	4 to 7	6 to 12.5
U- and Pu-concentration determination of active feed solution by mass spectrometric isotope dilution technique	17 to 25	

*) Data refer to one analysis in triplicate.

Acknowledgments

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Appendix I

Conclusions and Recommendations of the Analytical Working Group Meeting at Ispra

(October 6-8, 1970)

1. Session (Chairman: H. Frittum, IAEA)

Interlaboratory Test I: **"Concentration and Density Determination of Uranium Product Samples".**

For this particular batch additional circulation seems not to be necessary.

Precision seems to be dependent upon the method and the type of laboratory. The gravimetric method for pure materials seems to give the highest precision followed by oxidimetry and X-ray fluorescence with the lowest precision.

There is a need to discuss the question of effort and tamperproofness of samples.

The density can be used as an indicator of homogeneity. For pure products the differences of duplicate density determinations should not exceed 0.14 % (95 % conf. level).

The interlaboratory variance consisted of the following:

- Different standards used
- Errors in standardization
- Random components

The evaluation group asked for the reporting of rejected values and their rejection criterias in order to find the outlier criterias. Recommendations for further interlabtests are welcomed.

For the final evaluation the following subjects are recommended:

- Significance test on density measurements for the single laboratory
- Significance test on density measurements between laboratories
- Significance test on uranium concentration measurements for the single laboratory
- Significance test on uranium concentration measurements between laboratories
- Estimation of precision for the single laboratory
- Estimation of the total standard deviation

Recommendations

1. Investigate the problem of finding the best mean value, eventually in form of a weighed mean. The problem of standardization is here of great importance.
2. In future interlabtests NBS standard 950a may be used.
3. For comparison reasons standardization of electrical methods by chemical standards is necessary.
4. The amount of uranium for interlaboratory test samples should be not less than 2.5 g per sample.

2. Session (Chairman: A. von Baeckmann, GFK)

Interlaboratory Test II: "Concentration and Density Determination of Plutonium Product Samples".

1. Due to the different dilutions of samples A, B and C, it is suggested to evaluate the results separately.
2. Most of the laboratories prefer to use oxidimetric methods with slight modifications and different endpoint determinations.
3. The following is recommended for further interlaboratory tests:
    a) To distribute solutions of different concentrations
    b) To distribute standards and request the results obtained from these standards
    c) To request the use of different methods if possible (e.g. mass spectrometric isotope dilution, gravimetry, potential controlled coulometry etc.)
4. Errors and sources of errors.
    a) Instability of the samples.
    It was noted that better sample vials must be obtained (e.g. sealed silica ampoules or dried samples in aluminium capsules). The plutonium concentration in the samples should not exceed 10 mg/g solution and the acidity should not be lower than 3 M.
    b) Standard.
    It was noted that the NBS 949 standard requires a correction for the Pu-241 decay.

Because of the differences between the isotopic composition of the standards and the samples a correction factor must be applied. The laboratories are requested to report their corrections.

c) Glove box techniques.

d) Organic and inorganic impurities.
It is suggested that in further interlaboratory tests, impurity estimates are given by the shipper.

3. Session (Chairman: A.E. Cameron, O.R.N.L.)

Interlaboratory Test III: "Isotopic Analysis of Uranium Product Samples by Mass Spectrometry".

1. We think we must accept data as reported by individual laboratories and not attempt to apply further rejection criteria.
2. Contrary to other experience, (long time), the precision found for a single scan was worse than the precision found for single runs.
3. The group felt that the errors given as a function of the isotopic composition in Figure 4.1 [1] quite well represented long time laboratory experience for routine measurements.
4. It is recommended for further interlaboratory tests to use samples with higher ^{235}U content which would be more representative of spent power reactor fuels.
5. It was concluded that for this test it was better to do the statistical evaluation only for atomic ratios. For further interlaboratory tests it was recommended that peak heights be reported for individual isotopes and to base the common evaluation of atomic ratios or weight percentages on this primary information. There was no opinion expressed about the rejection of the total scan if one isotope signal was rejected.
6. All laboratories measure on the U^+ ion. No laboratory loads samples from higher than 1 N HNO_3 because of the danger of attack on the rhenium filaments. All laboratories reporting use rhenium filament material.
7. All laboratories use N.B.S. uranium standards for evaluation of instrumental errors.

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1) Please refer in this connection to Figure 7.3-4.

8. To avoid confusion in further studies, the mass discrimination factor and its application should be clearly specified.

4. Session (Chairman: H. Bokelund, EUROCHEMIC)

Interlaboratory Test IV: "Isotopic Analysis of Plutonium Product Samples by Mass Spectrometry and α-Spectrometry".

1. Atom ratios 241/239 should be related to a common date.
2. Suggested possiblility for small samples: Eliminate interferences from Am-241 by measuring oxide ions of plutonium; Am appears not to form oxide ions.
3. In some cases significant differences between mean values of laboratories seem to exist. Possible reasons are: 1) Cross contamination (especially with Pu-242 from spike usage). It is recommended to investigate this possibility in each laboratory. 2) The risk of interference from organic material contained in very small Pu-samples. 3) Pu-241 decay; it is suggested that samples are analyzed within a month after Am-separation.
4. In some cases the interlaboratory standard deviation was greater than expected from the former experience.
5. It is assumed that a mass spectrometer calibrated with uranium standards will also give correct results for plutonium.
6. One laboratory reported on the possibility of correcting the mass 238 for uranium-238 by adding U-235 as a reference. Another potential source of uranium interference is the ion source itself.
7. The question was raised at what Pu-238 abundance mass spectrometry becomes preferable to α-spectrometry. No recommendation was made.
8. The only evident reason for precise measurements of Pu-238 is to know the α-activity for calorimetry. For this purpose α-spectrometry seems to be favoured because of freedom from uranium interference.
9. The use of common half life values is recommended.
   The half lives to be used should be furnished by the organizer of future interlaboratory comparisons.

5. Session (Chairman: G.H. Debus, BCMN (EURATOM))

Interlaboratory Test V: "Determination of Uranium and Plutonium Concentrations in Active Feed Solutions by Mass Spectrometric Isotope Dilution Analysis".

1. It was a general opinion of the group that the relative standard deviation of concentration determinations of U and Pu are between 0.4 and 0.7 % within the laboratory for routine measurements. It seems that the error on Pu is somewhat higher than on U.

2. The interlab-variation observed in this limited test was obviously larger. It was believed that this could be attributed to

   i) Evaporation,
   ii) Wall effects and polymerisation,
   iii) Chemical treatment,
   iv) Difference in date of analysis.

   It is not believed that the interlaboratoriums differences are due to spike calibration errors ($1\sigma \simeq 0.3$ %).

3. The group expressed the opinion that for further experiments the sample distribution could be based on the following procedure:

   i) Sample solution added to the spike in the plant,
   ii) Distribution of a spiked standard solution,
   iii) The minimum quantity of sample material should be 50 µg of the heavy element to be analysed.

4. It was noticed that only 3 participants reported their results. To complete the information it is recommended:

   i) that the other laboratories report the results of isotope dilution and/or isotopic composition,

   ii) that all participating laboratories report their chemical procedures and send remarks on observed difficulties.

Appendix II

Analysis of Variances

by R. Avenhaus

II.1 The Linear Hypothesis

All types of measurements occuring in the interlabtests considered here can be written in the following form (see Fig. 7.AII-1)

$$y_{ij\nu} = \mu + a_i + b_{ij} + e_{ij\nu} \tag{II,1}$$

where

$$i = 1 \,\ldots\ldots\, r; \; j = 1 \,\ldots\ldots\, s_i; \; \nu = 1 \,\ldots\ldots\, n_{ij}$$

In the case of the concentration or density determinations $y_{ij\nu}$ is the result of the ν-th repeated measurement of the j-th laboratory at the i-th sample. μ is the true value of the concentration (density) in the tank, a_i is the inhomogeneity of the i-th sample, b_{ij} is the difference between the true concentration (density) of the i-th sample, $\mu_i = \mu + a_i$ are the expectation values of the measurements of the j-th laboratory at the i-th sample (i.e. the interlab error). $e_{ij\nu}$ is the reproducibility of the y-th measurement of the j-th laboratory at the i-th sample.

In the case of the isotopic ratio determinations $y_{ij\nu}$ is the result of the ν-th measurement (scan) of the j-th run of the i-th laboratory. μ is the interlab error of the i-th laboratory, b_{ij} is the run error of the j-th run of the laboratory and $e_{ij\nu}$ is the reproducibility (scan error).

The expectation values and variances of the random variables $e_{ij\nu}$, b_{ij} and a_i are assumed to be

$$E\,(e_{ij\nu}) = E\,(b_{ij}) = E\,(a_i) = 0 \tag{II,2}$$

$$\mathrm{var}(e_{ij\nu}) = \sigma_e^2,\ \mathrm{var}(b_{ij}) = \sigma_b^2,\ \mathrm{var}(a_i) = \sigma_a^2$$

Furthermore the random variables $e_{ij\nu}$, b_{ij} and a_i are assumed to be independent.

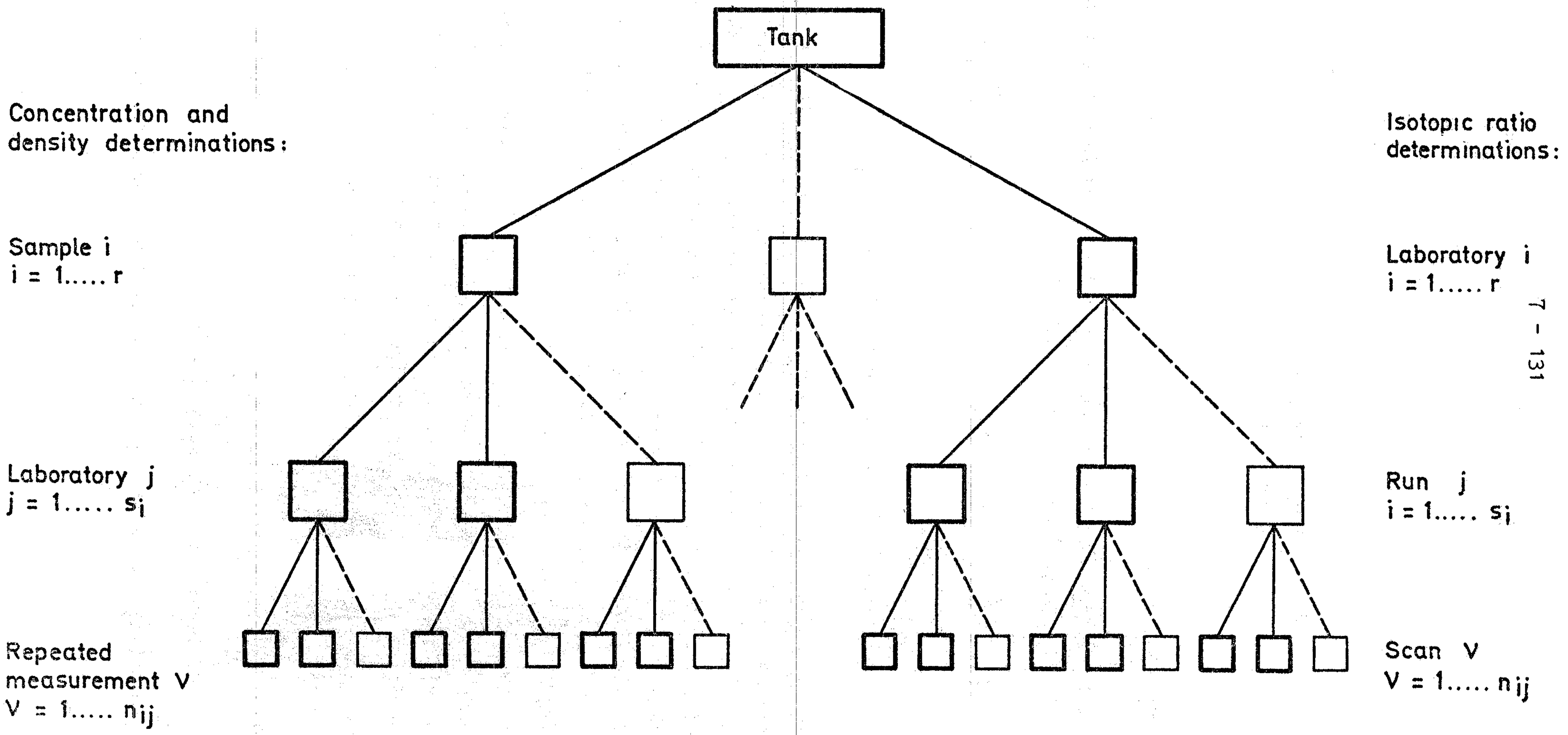

Fig. 7.AII -1 : Models for the Analyses of Variances

II.2 Significance Test

In this part the method is described to decide wether or not the mean value of different groups of measurements are significantly different. In other words, it is tested whether or not the error component b_{ij} is significantly different from zero.

In order to facilitate the representation, the following special application is considered: It shall be decided whether for a fixed sample i the mean values obtained by different laboratories j (e.g. on the concentration or density) are significantly different from zero, i.e. whether there is a significant interlaboratory deviation.1)

As the index i, describing the sample in the case considered here is fixed, the error component a_i can be ignored in this connection and the relation (II,1) is simplified to

$$y_{j\nu} = \mu + b_j + e_{j\nu} \qquad (II,3)$$

(The index i is omitted now). For the construction of the test the following two quantities are important:

$$SQ_A = \sum_{j=1}^{s} n_j (y_{j.} - y_{..})^2$$

$$SQ_R = \sum_{j=1}^{s} \sum_{\nu=1}^{n_j} (y_{j\nu} - y_{j.})^2 \qquad (II,4)$$

Here,

$$y_{j.} = \frac{1}{n_j} \sum_{\nu=1}^{n_j} y_{j\nu} \qquad (II,5)$$

is the average value of all the measurements of the j-th laboratory,

$$y_{..} = \frac{1}{N} \sum_{j=1}^{s} \sum_{\nu=1}^{n_j} y_{j\nu} \qquad (II,6)$$

is the average value of all the measurements of all laboratories,

---

1)For other applications, the formulas of this test remain unchanged, if the indices i, j and ν are correspondingly attributed to the quantities which are considered as fixed (i), whose mean values are to be compard (j) and which form the elements of these mean values (ν).

$$N = \sum_{j=1}^{s} n_j \qquad \text{(II,7)}$$

is the total number of measurements.

It is assumed that $y_{j\nu}$ is normal distributed. Then the test consists in comparing the expression

$$V_0 = \frac{N-s}{s-1} \times \frac{SQ_A}{SQ_R} \qquad \text{(II,8)}$$

with the quantity C; C is determined by the F-statistic with (s-1, N-s) degrees of freedom and depends on the error first kind α:

$$F_{s-1,N-s}\ (C) = 1-\alpha \qquad \text{(II,9)}$$

If V_0 is greater than C, then b_j is significantly different from zero for the sample considered in particular.

The test can be understood qualitatively in the following way: SQ_A describes the deviation of the total average value $y_{..}$ of all the measurements from the average value per laboratory $y_{j.}$, SQ_R describes the deviation of the individual measurements of each laboratory from the average value per laboratory $y_{j.}$. It is clear that the value of V_0 must be large if b_j differs significantly from zero. In the case s = 2 and $n_j = n$ the condition for the test is given by

$$\frac{y_{1.}-y_{2.}}{\sqrt{S_1^2 + S_2^2}} \gtrless \frac{C}{n}^{\frac{1}{2}}$$

where

$$S_\kappa^2 = \sum_{\nu=1}^{n} \frac{(y_{\kappa\nu}-y_\kappa)^2}{n-1}\,, \qquad \kappa = 1,2$$

In the case n = 10 and α = 0.05 this becomes

$$\frac{y_{1.}-y_{2.}}{\sqrt{S_1^2+S_2^2}} \gtrless 0.7$$

II.3 Estimation of σ_b^2 and σ_e^2; Confidence Limits in the Orthogonal Case

If only two error components are considered, the unbiased estimates of the variances can be calculated according to the formulas given in the following Table 7.AII-1.

Table 7.AII-1: Analysis of Variances in the Not Orthogonal Case for Two Types of Errors.

SQ	DG	MQ	E(MQ)
$SQ_A = \sum_{j=1}^{s} n_j \, (y_{j.} - y_{..})^2$	$f_A = s-1$	$MQ_A = \frac{SQ_A}{f_A}$	$\sigma_e^2 + k\sigma_b^2$
$SQ_R = \sum_{j=1}^{s} \sum_{\nu=1}^{n_j} (y_{j\nu} - y_{j.})^2$	$f_R = \sum_{j=1}^{s} n_j - s$	$MQ_R = \frac{SQ_R}{f_R}$	σ_e^2

Here,

$$y_{j.} = \frac{1}{n_j} \sum_{\nu=1}^{n_j} y_{j\nu} \qquad y_{..} = \frac{1}{N} \sum_{j=1}^{s} \sum_{\nu=1}^{n_j} y_{j\nu} \tag{II,10}$$

$$N = \sum_{j=1}^{s} n_j \qquad k = \frac{1}{s-1} \left(N - \frac{1}{N} \sum_{j=1}^{s} n_j^2\right)$$

From the last column of Table 7.AII-1 one obtains

$$E(MQ_R) = \sigma_e^2; \quad E(MQ_A) = \sigma_e^2 + k \cdot \sigma_b^2 \tag{II,11}$$

Therefore, the unbiased estimates $\hat{\sigma}_e^2$ and $\hat{\sigma}_b^2$ of σ_e^2 and σ_b^2 are given by

$$\hat{\sigma}_e^2 = MQ_R \tag{II,12}$$

$$\hat{\sigma}_b^2 = \frac{1}{k} (MQ_A - MQ_R)$$

where MQ_A and MQ_R are functions of experimental data according to Table 7.AII-1.

In order to be able to estimate the validity of the approximations, one wants to have confidence limits for $\tilde{\mu}$, σ_b^2 and σ_e^2. This, however, is only possible in the orthogonal case: $n_j = n$.

In the following, it is assumed that b_j and $e_{j\nu}$ are normal distributed.

Confidence limits for $\tilde{\mu}$ in the orthogonal case

The parameter $\tilde{\mu}$ is estimated by y.., its variance is given by

$$\text{var}(y..) = \frac{1}{ns} (\sigma_e^2 + n\sigma_b^2) \tag{II,13}$$

In consequence, if one replaces σ_e^2 and σ_b^2 by its unbiased estimates according to (II,12), the confidence limits for $\tilde{\mu}$ are given by

$$(y.. - C\sqrt{\frac{MQ_A}{ns}} \leq \tilde{\mu} < y.. + C\sqrt{\frac{MQ_A}{ns}}) \tag{II,14}$$

Here, C is determined by the t-statistic with s-1 degrees of freedom and depends on the error first kind α:

$$F_t(C) = 1 - \frac{\alpha}{2} \tag{II,15}$$

Confidence limits for σ_e^2 in the orthogonal case

The confidence limits for σ_e^2 are given by

$$(\frac{SQ_R}{C_2} \leq \sigma_e^2 < \frac{SQ_R}{C_1}) \tag{II,16}$$

Here, C_1 and C_2 are determined by the χ^2-statistics with N-s degrees of freedom:

$$F_{\chi 2}(C_1) = \frac{\alpha}{2} ; \quad F_{\chi 2}(C_2) = 1 - \frac{\alpha}{2}$$

Confidence limits for σ_b^2/σ_e^2 in the orthogonal case

It is not possible to obtain confidence limits for σ_b^2 alone; the confidence limits for σ_b^2/σ_e^2 are given by

$$\left(\frac{1}{n}\left(C_1 \cdot \frac{MQ_A}{MQ_R} - 1\right) \leq \frac{\sigma_b^2}{\sigma_e^2} < \frac{1}{n}\left(C_2 \cdot \frac{MQ_A}{MQ_R} - 1\right)\right) \qquad (II,17)$$

where C_1 and C_2 are determined by the F-statistics with $(s-1,N-s)$ and $(N-s,s-1)$ degrees of freedom:

$$F_{(s-1,N-s)}\left(\frac{1}{C_1}\right) = 1-\frac{\alpha}{2}\,;\quad F_{(N-s,s-1)}(C_2) = 1-\frac{\alpha}{2} \qquad (II,18)$$

II.4 The General Case: Estimation of σ_a^2, σ_b^2 and σ_e^2

In the case of three error components i.e. in the case that b_{ij} is not equal zero and that the numbers s_i and n_{ij} in (II,1) explicitly depend on i and j, it is not possible to construct confidence intervals; one only can give unbiased estimates for the quantities in question. In order to obtain these estimates the following Table is to be considered:

Table 7.AII-2: Analysis of Variances in the Not Orthogonal Case for Three Types of Errors.

SQ	DG	MQ	E(MQ)
$SQ_A = \sum_{i=1}^{r} \frac{Y_{i..}^2}{n_{i.}} - \frac{Y_{...}^2}{N}$	$f_A = r-1$	$MQ_A = \frac{SQ_A}{f_A}$	$k_{11}\sigma_a^2 + k_{12}\sigma_b^2 + \sigma_e^2$
$SQ_B = \sum_{i=1}^{r} \sum_{j=1}^{s_i} \frac{Y_{ij.}^2}{n_{ij}} - \sum_{i=1}^{r} \frac{Y_{i..}^2}{n_{i.}}$	$f_B = \sum_{i=1}^{r} s_i - r$	$MQ_B = \frac{SQ_B}{f_B}$	$k_{22}\sigma_b^2 + \sigma_e^2$
$SQ_R = \sum_{i=1}^{r} \sum_{j=1}^{s_i} \sum_{\nu=1}^{n_{ij}} y_{ij\nu}^2 - \sum_{i=1}^{r} \sum_{j=1}^{s_i} \frac{Y_{ij.}^2}{n_{ij.}}$	$f_R = N - \sum_{i=1}^{r} s_i$	$MQ_R = \frac{SQ_R}{f_R}$	σ_e^2

Here,

$$Y_{ij.} = \sum_{\nu=1}^{n_{ij}} y_{ij\nu} \qquad Y_{i..} = \sum_{j=1}^{s_i} Y_{ij.} = \sum_{j=1}^{s_i} \sum_{\nu=1}^{n_{ij}} y_{ij\nu}$$

$$Y_{...} = \sum_{i=1}^{r} \sum_{j=1}^{s_i} \sum_{\nu=1}^{n_{ij}} y_{ij\nu} \qquad \text{(II,19)}$$

$$n_{i.} = \sum_{j=1}^{s_i} n_{ij} \qquad N = \sum_{i=1}^{r} \sum_{j=1}^{s_i} n_{ij}$$

<u>Note:</u>

Contrary to the expressions (II,5) and(II,6), the expressions (II,19) are only sums, not mean values. In order to stress this point, capital letters are used here.

The coefficients k_{11}, k_{12}, k_{22} occuring in Table 7.AII-2 are given by

$$k_{11} = \frac{1}{r-1} \left(N - \frac{1}{N} \sum_{i=1}^{r} n_i^2\right)$$

$$k_{12} = \frac{1}{r-1} \left[\sum_{i=1}^{r} \left(\sum_{j=1}^{s_i} \frac{n_{ij}^2}{n_i} \right) - \frac{1}{N} \sum_{i=1}^{r} \sum_{j=1}^{s_i} n_{ij}^2 \right] \qquad \text{(II,20)}$$

$$k_{22} = \frac{1}{\sum_{i=1}^{r} s_i - r} \left[N - \sum_{i=1}^{r} \left(\sum_{j=1}^{s_i} \frac{n_{ij}^2}{n_{i.}} \right) \right]$$

From the last column of Table 7.AII-2 one obtaines for the quantities σ_e^2, σ_b^2 and σ_a^2 the following unbiased estimates $\hat{\sigma}_e^2$, $\hat{\sigma}_b^2$ and $\hat{\sigma}_a^2$:

$$\hat{\sigma}_e^2 = MQ_R$$

$$\hat{\sigma}_b^2 = \frac{1}{k_{22}} \left[MQ_B - MQ_R \right]$$

$$\hat{\sigma}_a^2 = \frac{1}{k_{11}} \left[MQ_A - \frac{k_{12}}{k_{22}} MQ_B - \left(1 - \frac{k_{12}}{k_{22}}\right) MQ_R \right] \qquad \text{(II,21)}$$

II.5 "Best" Estimate of the True Value; Variance of this "Best" Estimate

It is assumed again that there exist

$$N = \sum_{i=1}^{r} \sum_{j=1}^{s} n_{ij} \qquad \text{(II,22)}$$

measurement results. Then the question arises how to form with the help of these N values a "best" estimate for the true, unknown value μ.[1]

It can be shown that the "best" estimate $\hat{\mu}$ in the sense of an unbiased estimate with minium variance is given by the mean of the N measurement results.

$$\hat{\mu} = \frac{1}{N} \sum_{i=1}^{r} \sum_{j=1}^{s_i} \sum_{\nu=1}^{n_{ij}} Y_{ij\nu} \qquad \text{(II,23)}$$

The variance of this mean value is given by

$$\text{var } \hat{\mu} = \frac{1}{N^2} \text{ var } \sum_{i=1}^{r} \sum_{j=1}^{s_i} \sum_{\nu=1}^{n_{ij}} (\mu + a_i + b_{ij} + e_{ij\nu})$$

or

$$\text{var } \hat{\mu} = \frac{1}{N^2} \quad \sum_{i=1}^{r} (\sum_{j=1}^{s_i} n_{ij})^2 \, \sigma_a^2 + \sum_{i=1}^{r} \sum_{j=1}^{s_i} n_{ij}^2 \, \sigma_b^2 + N \, \sigma_e^2 \qquad \text{(II,24)}$$

In the orthogonal case, that is in the case

$$s_i = s \qquad n_{ij} = n \qquad \text{(II,25)}$$

one obtaines with

$$N = \sum_{i=1}^{r} \sum_{j=1}^{s} n = rsn \qquad \text{(II,26)}$$

for the variance of $\hat{\mu}$

$$\text{var } \hat{\mu} = \frac{1}{(rsn)^2} \quad \sum_{i=1}^{r} (sn)^2 \cdot \sigma_a^2 + \sum_{i=1}^{r} sn^2 \cdot \sigma_b^2 + rsn \cdot \sigma_e^2$$

or

$$\text{var } \hat{\mu} = \frac{\sigma_a^2}{r} + \frac{\sigma_b^2}{rs} + \frac{\sigma_e^2}{rsn} \qquad \text{(II,27)}$$

---

[1] As mentioned in the introduction of this Chapter it was not the aim of these interlaboratory tests to find the best estimates of the true values. However, if one wants to calculate the variance of the total resulting error of a set of N measurement results, one first has to give a prescription how to form a mean value.

Appendix III

Description of Mass Spectrometer and Measurement Technique Applied by ORNL

by A.E. Cameron

OAK RIDGE NATIONAL LABORATORY
November 1970

The measurements of isotopic composition of uranium and plutonium for this exercise were made on one of our tandem magnetic instruments with pulse counting for ion detection. The radius of the ion path in each magnetic stage is 12 inches (30 cm). The instruments are assembled in the "C" configuration and the ion optical geometry is symmetrical. The pumping is with a "dry" system, using sputter pumps (VacIon).

The filament arrangement is a "V" rhenium filament and the system of handling several of these at once has been described[1]. Because of the ion counting feature of the instruments, it is possible to use very small samples - 10 ng to 0.01 ng, depending upon the chemical purity and form of the sample. Also, the very clean spectrum at high mass permits measurements of adjacent masses without "toe correction". This also permits more precise measurements to be made on the minor isotopes. A sensitivity of circa 1 ppm for the minor isotopes is attainable, although not always on the instrument used for the measurements reported. That particular instrument is used for isotopic composition measurements on the transuranium elements and the multiplier background gradually increases because of deposition of intensely radioactive materials on and around the first dynode.

Because of the difficulty of scanning the magnetic fields in perfect synchronism, we adopted the practice of scanning by sweeping the accelerating voltage. Since we record data in 200 or 400 channels of memory in a multichannel analyzer, the sweep which we use is that of the horizontal sweep of the analyzer oscilloscope. This is a stair-step function which is amplified and applied in series with the regular accelerating voltage, usually 8 kv. A number of mass units are swept and this is adjustable by means of the "sweep amplifier". The spectrum is displayed and counts are stored in appro-

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1) W.H. Christie and A.E. Cameron, Rev. Sci. Instrum 37, 336 (1966).

priate channels of the memory. This "linear sweep" wastes time in sweeping the valleys. Accordingly, we normally take data in what we call a "sub-group" mode. In this arrangement the individual peaks are swept only over the flat top. It is possible to set the number of times a peak is swept to improve statistics.

The analyzer memory is broken into subgroups of 50 channels, and the peak usually occupies 45-48 of them. The sweeping sequence used in these measurements is to sweep 233, 234, 235, 236, 237, 238 and 239 each once. The 233 position is always monitored as is the 239. Mass 237 is used for background correction in most cases. This sequence is repeated 200 times with each channel gated open for 1.25 millisecond. The stair-step function which is being amplified is also the voltage which gates the channels, so that synchronism is maintained between channel and accelerating voltage.

At the end of 200 sweeps, the memory channels are dumped onto a magnetic tape, and the sweep is begun again. The dumping takes only two or three seconds so that data taking is almost continuous. The counting rate on the major isotope is held at about 2×10^5 sec^{-1} to minimize the "count loss" correction. The overall dead time of the system is measured at about 0.08 μsec.

It is, of course, necessary to calibrate the system. For this we use the NBS 500 standard. The ratio of 235/238 in this standard is 0.997 and the 234/235 is 0.01043. The 235/238 observed ratio is used to establish a "voltage" correction, since the counting rate on the two peaks is essentially identical. The count loss correction for the overall system is established from the 234/235 ratio. The computer program is fed the estimated "tau" (count loss) and the measured counts on the three peaks. By an iterative process the computer arrives at a voltage correction per mass unit and the count loss correction. The "tau" is observed to hold very constant, but the voltage correction cannot be so well established or maintained. A typical calibration would be a "tau" of 0.085 microseconds, and calculated voltage correction of .0040/mass.

The usual isotopic composition measurement which we made on uranium and plutonium will consist of ten (10) measurements, each of 200 scans. The magnetic tape on which the dump from the analyzer memory is stored is fed to our IBM 1130 computer, together with the voltage correction and the dead time correction. Since we usually use the "sub-group" mode, the computer seeks the center of the flat-top peak, and then establishes how many channels are to be summed in the peak. Any channels which are bad, e.g., dropped, noise spikes, etc., are corrected to the average of the channels in the flat top, usually about 48. The computer prints out the details of channels which were corrected, identifying the channels and detailing the correction.

The "raw" counts for each isotope for each determination are printed out. The final sheet, a copy of which for uranium is attached, (Fig. 7.AIII-1) gives the corrected counts per isotope and the calculated ratios. The calculation is initially in atom ratio or in atom percent, which is our usual manner of reporting, and is converted to weight percent for this particular exercise.

The things which cause the operator to reject data are typically a run which shows drifting ratios, which has a high background - indicating a dirty sample - and which is usually indicated by the counts observed in the 237 position, or sometimes one which shows the presence of ^{233}U when this should not be present in the sample. This tends to indicate that some cross-contamination has occurred in sample preparation or mounting. A marked change in the temperature of the filament during the run would mean that sufficient sample had not been loaded and there might be the possibility of uranium from the filament material being observed. We chemically clean and then bake out all the filaments in vacuum for circa 30 minutes at a temperature of 2200 °C observed on an optical pyrometer. This temperature and the temperature quoted for sample running are <u>not</u> corrected for emissivity.

The temperatures are coded on the printout for start and finish. For example, 7271 under the heading TEMP means a starting temperature of 1720 and an ending temperature of 1710. For plutonium runs it might typically be 5253, which is 1520 to start and 1530 to end.

Starred (*) entries in the printout are not used in the calculation of the average for that isotope. The computer program has rejected these as being outside the preset limits. This will generally have negligible effect upon the results. It will not affect the other ratios, but may have a slight effect in that the sum of the isotopes may not be exactly 100 %. The operator generally makes a final correction to the large isotope to insure exact addition.

Note:

Long-term experience on uranium measurements with a two-stage instrument on the U010 standard (1% 235) are:

1σ = 1% on 234/235
1σ = 0.8 % on 236/235
1σ = 0.8 % on 235/238

OAK RIDGE NATIONAL LABORATORY
November 1970

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SAMPLE NO. NBS 010        SAMPLE NAME                  DATE  6 21 71    MACH/CART/SEQ 1151    OPERATOR EM    TAU=0.099

INDEX NO.     1            2            3            4            5            6            7            8            9            10
MASS NUM.    238          235          234          236          237            0            0            0            0            0
VOLT COR.    1.0000       0.9820       0.9760       0.9880       1.0000       0.0000       0.0000       0.0000       0.0000       0.0000
SWEEP FA.     1.           2.          16.          16.            4.           1.           1.           1.           1.           1.

COR.CNTS. 11673258.    237106.      10269.       13207.          19.           0.           0.           0.           0.           0.

                                                 11= 236-237

                                                 12= 234-237

                                                 13= 238+235+234+ 11

RATIO    12/13    3/13     2/13     4/13    11/13     1/13     2/ 3     1/ 3     2/11     1/11     3/ 2    11/ 2     2/ 1     0/ 0
EXP.      E -5     E -5     F -2     E -5     E -5     E -1     E  2     E  4     E  2     E  4     E -3     E -3     E -2     E  0


RUN 1    5.1725   5.2383   1.0044   6.9348   6.8689   9.8983   1.9174   1.8895   1.4622   1.4410   5.2153   6.8388   1.0147   0.0000
T=6867   0.1718   0.1675   0.0066   0.1940   0.1977   0.0131   0.0625   0.0604   0.0431   0.0414   0.1702   0.2017   0.0067   0.0000

RUN 2    5.0470   5.1101   0.9966   6.9648   6.9017   9.8991   1.9503   1.9371   1.4440   1.4342   5.1272   6.9248   1.0068   0.0000
T=6867   0.1660   0.1619   0.0064   0.1903   0.1937   0.0128   0.0630   0.0614   0.0415   0.0402   0.1657   0.1993   0.0065   0.0000

RUN 3    5.4804   5.5416   1.0066   6.7135*  6.6523*  9.8981   1.8164   1.7861   1.5131   1.4879*  5.5052   6.6086   1.0169   0.0000
T=6867   0.1698   0.1661   0.0064   0.1840   0.1874   0.0126   0.0556   0.0535   0.0436   0.0419   0.1686   0.1907   0.0064   0.0000

RUN 4    5.5482   5.5482   1.0062   7.0857   7.0857   9.8981   1.8137   1.7840   1.4201   1.3969   5.5135   7.0414   1.0166   0.0000
T=6867   0.1658   0.1658   0.0063   0.1886   0.1886   0.0126   0.0553   0.0533   0.0388   0.0371   0.1683   0.1924   0.0064   0.0000

RUN 5    5.5411   5.5411   1.0146   6.9490   6.9490   9.8972   1.8311   1.7861   1.4601   1.4242   5.4610   6.8486   1.0251   0.0000
T=6867   0.1607   0.1607   0.0062   0.1811   0.1811   0.0122   0.0542   0.0518   0.0390   0.0371   0.1618   0.1832   0.0062   0.0000

RUN 6    5.3938   5.5287   1.0182   7.1846   7.0497   9.8969   1.8418   1.7900   1.4444   1.4038   5.4294   6.9232   1.0288   0.0000
T=6867   0.1827   0.1742   0.0067   0.1998   0.2072   0.0132   0.0592   0.0564   0.0435   0.0412   0.1747   0.2085   0.0068   0.0000

RUN 7    5.4115   5.4115   0.9892   7.1985   7.1985   9.8998   1.8280   1.8293   1.3742   1.3752   5.4701   7.2765*  0.9992   0.0000
T=6867   0.1709   0.1709   0.0066   0.1983   0.1983   0.0131   0.0589   0.0577   0.0389   0.0379   0.1764   0.2061   0.0066   0.0000

RUN 8    5.6775   5.6994   1.0068   6.9926   6.9707   9.8980   1.7666   1.7366   1.4444   1.4199   5.6605   6.9232   1.0172   0.0000
T=6867   0.1760   0.1746   0.0066   0.1946   0.1958   0.0131   0.0553   0.0532   0.0416   0.0399   0.1772   0.1996   0.0067   0.0000

RUN 9    5.1334   5.1766   1.0048   6.9248   6.8816   9.8983   1.9411   1.9121   1.4602   1.4383   5.1515   6.8483   1.0151   0.0000
T=6867   0.1679   0.1651   0.0065   0.1922   0.1946   0.0130   0.0631   0.0610   0.0423   0.0406   0.1676   0.1986   0.0066   0.0000

RUN10    5.5938   5.6153   1.0036   7.0762   7.0546   9.8983   1.7873   1.7627   1.4227   1.4031   5.5947   7.0286   1.0140   0.0000
T=6867   0.1734   0.1720   0.0065   0.1943   0.1955   0.0130   0.0559   0.0540   0.0404   0.0388   0.1751   0.2000   0.0066   0.0000


AVG.     5.3989   5.4384   1.0051   7.0329   6.9949   9.8982   1.8463   1.8178   1.4435   1.4147   5.4104   6.8859   1.0155   0.0000
S.D.     0.0679   0.0634   0.0025   0.0348   0.0362   0.0002   0.0196   0.0207   0.0113   0.0073   0.0585   0.0434   0.0026   0.0000
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Fig. 7 AIII - 1 : Computer Printout of Mass Spectrometric Measurement at ORNL
(NBS - Standard U 010)

JEX - 70

Chapter 8

Stable Samples of Dissolver Solutions for Input Analysis

by

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Abstract

To avoid the problems introduced by the storage instability of dissolver solutions, a new sampling technique was used. Known portions of diluted dissolver solutions were dried in Aluminium-Capsules. For the analysis the capsule together with the evaporated sample inside was dissolved. Comparisons between preliminary analysis of the conventional and new technique are given in Tab.1.

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8.1. Objectives

The storage-stability of samples from dissolved irradiated fuels is influenced by radiolysis which may lead in the first place to a loss of solvent and a change of concentration in the sample, in the second place a plating of Plutonium at the walls of the container may occur because of a depletion of acid. To avoid these problems we tried in the frame of the Mol-III experiment to use a new sample conditioning technique. An aliquot of the input solutions is weighed in a Al-capsule. The solution is carefully dried, precaution was taken that no spattering during evaporation had occured. Than the Al-capsule is closed. Later for the analysis the container together with the evaporated sample was dissolved. This brings the advantage that all material of the sample was made available for the analysis. Storage of the sample over a long period is possible.

8.2. Sample preparation

Unfortunately we had to use the diluted solutions of the dissolved fuel material because of limitations in transportation. Aliquots from a diluted composite sample E-I, which consisted of material from the VAK-reaktor, were taken. Besides this we prepared three other samples from the originaly concentrated dissolver solution, but due to transportation problems these samples are still in Mol and will not be considered here. The technique of sample preparation is rather simple. In the preweighed Al-capsule about one ml of dissolver solution is pipetted and the weight exactly determined. This was done for both, the diluted and the undiluted dissolver solution. The filled Al-capsules are inserted after weighing into an Al-block heated up to 80°C. To speed up the evaporation a stream of filtered air is passed over the surface of the solution, care is taken, that no material during the evaporation gets lost. About four hours is needed to dry one sample. Fig. 8-1 shows schemetically the evaporation apparatus.

8.3. Analysis

The capsules are dissolved in a preweighed flask of about 500 ml with 10 ml HNO_3 (10n). A few drops of Hg $(NO_3)_2$ were added. This addition has to be done very carefully because the reaction starts very suddenly. When the reaction leveled off, 50 ml of nitric acid was added until the capsule and the sample were completely dissolved. This dissolution took about 5h. Then the sample was diluted with additional 10 ml of water to avoid a cristallisation of the Aluminiumnitrate during the cooling of the solution. The solution was weighed and an aliquot was taken for analysis. To this aliquot the corresponding amounts of U- and Pu-spikes were added. The analysis follows our normal procedure (1). However because of the high viscosity of the Al-nitrate solution we used a batch technique for the extraction step : the resin was added into the solution. Later the resin was transfered into a ion exchange-column which was treated according our usual chemical separation procedure.

8.4. Results and discussion

The results from four capsules are listed in the Table 8-1. The first column gives the number of the capsule, the second column the date of analysis, the following two columns the concentration of Uranium and Plutonium in μg/g dissolver solution and the last column the U/Pu ratio. For the first capsule the analysis was incomplete. We got only one result for Uranium. The average is given for all values with 1 σ deviation. We also received a diluted liquid sample of this solution like all other Mol III-samples. Unfortunately the analysis was performed rather late in october '70. The results are also given in the table. The agreement between these results and those of the capsules for the U/Pu ratio and for the Pu-concentration is good but one has to consider the error on the Pu value, of about 2 %. The agreement for the Uranium values is within the error limits. The results are not satisfactory, because the obtained precision for the analysis of the three capsules is too low, especialy for Pu, but this may be explained : as mentioned in the beginning we had to use the diluted solution. Furthermore our capsules were thickwalled. This gave a ratio of Al-atoms to Pu-atoms of about 4.10^7 that means for 4.10^7 Al-atoms only 1 Pu-atom is present in the solution.

Especially the oxidation and reduction of Pu seems to be incomplete. This step is essential to ensure that the Pu of the sample and the spike will have the same chemical behavior. For the Uranium the ratio of Al/U is $2x10^5$ but as one can see from the results the precision was acceptable. Therefore we expect that the technique will bring better results for undiluted samples. This will be shown with the analysis of the three remaining capsules in Mol for which the Al/Pu ratio is $1,6 \times 10^5$ and the Al/U ratio $1,3 \times 10^3$ and with the analysis of twenty samples from a dissolved BWR fuel encapsuled in a new and lighter Al-can.

8.5. References

(1) L.Koch. Radiochimica Acta 12 160-162 (1969)

Comp. Sample E-I	Date of analysis	Concentration (µg/g sol.)		U/Pu ratio
		U	Pu	
Dry capsule 1	3.11.1971	728.0	-	
" 2	2.02.1971	725.8	3.854	188.3
		729.1	3.795	192.1
" 3	2.02.1971	727.0	3.730	194.9
		729.7	3.717	196.3
" 4	3.12.1970	735.0	3.844	191.2
		735.4	3.935	186.9
mean value		730.0 ± 0.52%	3.813 ± 2.16%	191.5
analysis of liquid sample	13.10.1970	724.4	3.791	191.2
		724.9	3.818	189.7
mean value		724.7 ± 0.04%	3.805 ± 0.36%	190.3
analysis of operator		714.1	3.72	191.8

Table 1 : Comparisons between U- and Pu-concentrations of the dried samples and liquid samples

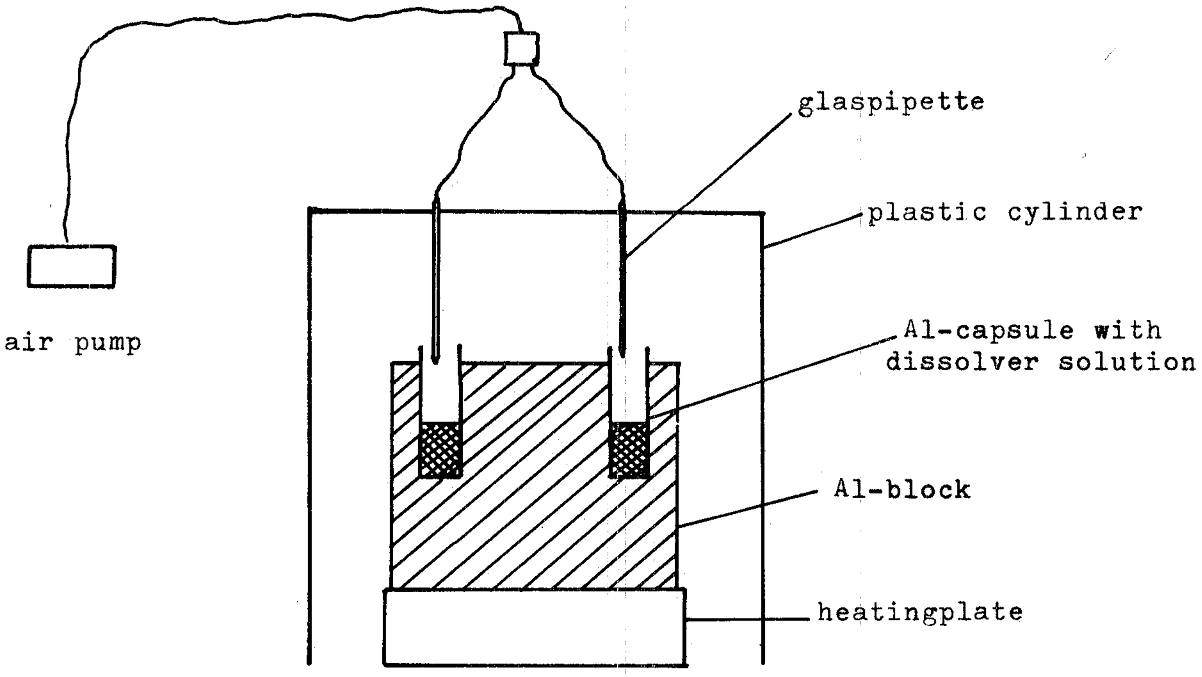

Fig 8.1. Evaporation apparatus

9. CONCLUSIONS

The JEX-70 experiment provided a wealth of information and results, the interpretation and use of which will surely extend over some time to come. However, conclusions relevant to each specific area of activities have been presented at the end of each chapter dealing with these activities. It appears also worthwhile to draw some conclusions of a general nature which might be of some use in carrying out experiments of a similar nature.

The overall success of such an experiment depends to a large extent on the clarity with which the objectives are defined and the extent to which such objectives can be realized in an industrially operating facility. All the plant data relevant for the planning and execution of the experiment should be available to the group responsible for the execution of such experiments. It goes without saying that a close cooperation has to exist between the facility management and the operators on the one hand and the organizing group on the other hand. Since most of the objectives of an integral experiment involve the whole of the facility and since the operating events in a facility relevant to such experiments seldom occur in a predictable manner, a certain flexibility in the capability of the organizing group is essential to ensure smooth execution of such experiments.

Gamma-spectrometry measurements in connection with the identification of irradiated fuel elements have supplied a large volume of additional information. It appears possible that this information can be utilized for other safeguards measures also, for example, for validation of the operator's data, for an independent estimation of the fuel element burnup and for isotope correlation techniques. Further experimental determinations are however, required before the actual importance of such applications can be assessed in a realistic manner. The measurement operations and the determination procedures are fairly simple so that no elaborate arrangements are required for the planning and execution of such experiments.

Simulation of process flows has turned out to be an important tool particularly during the planning stage of integral experiments. The method turned out to be very useful to estimate the influence of different process parameters on the physical inventory determination technique with the help of isotopic analyses. For example it could be shown that the most important parameter which influences the accuracy of this method was the ratio of the batch-to-batch variations of the concentrations of the used isotope inside a superbatch to the isotopic step itself. It could also be shown that within the investigated range of concentrations, the accuracy with which a physical inventory can be determined with the help of this method is proportional to this ratio. Another important recommendation which can be made on the basis of the simulation results is that the individual batches inside a single superbatch should be arranged in such a way that no trend in the sequence of concentrations of the relevant isotope occurs.

The actual results and experience obtained from this method in the course of the JEX-70 experiment have established the fact, that such a method would have a great potential as a supplementary safeguards tool for closing the material balance more frequently than is envisaged for normal operation, without in any way hampering the plant operations. The advantage of this method lies in the possibility of a timely detection of fissile material in case of a diversion. The amount of fissile material which is required in a superbatch to use this method successfully, should be approximately three times the amount which can be stored in the largest process tank in the facility. Clearly, such a method is applicable only in a reprocessing plant. However, the ease with which such a method can be applied, may be improved considerably if the arrangements and the sequence of fuel elements required for generating the isotopic step function can be carried out at the reactor from which these fuel elements are transported. In that case no additional effort would be required at the reprocessing plant.

The MIST techniques could be extended successfully to the natural uranium heavy water type fuel elements on the basis of experimental data obtained during the JEX-70 experiment. It appears however, very desirable to broaden the spectrum of data for a successful application of MIST techniques. A collection and extension of data on this technique should therefore be carried out on a worldwise basis. It is interesting to note at this point that an international group consisting mostly of the participants of the JEX-70 experiment has been established particularly for this purpose. Similarly, another group to obtain data on MUF which is the most important safeguards indicator, has also been established. All the participants of the JEX-70 experiment are members of this group.

The interlaboratorium tests on different analytical measurement methods have also supplied a very large volume of information and amount of data. They permit a number of fairly important general conclusions to be drawn.

a) It is desirable to simplify the transport regulations for small samples containing active materials. The present regulations are rather stringent and quite often cause difficulties and delays particularly when samples have to be transported on an international level.

b) The major part of the error in the case of methods for estimation of plutonium concentration, appears to be caused by aging of the samples. Further investigations are essential to determine whether this is the case and on the possibilities of eliminating such errors. In this connection the whole problem of sampling procedures, sample storage and transport for plutonium samples needs to be considered. Another point of interest in connection with plutonium analysis is that quite often outliers of plutonium analyses data were obtained in the case of those laboratories which carry out plutonium analyses on a routine basis. Such outliers may be caused by cross contaminations. However, such outliers cannot normally be identified by the same laboratory unless an interlaboratory test has been carried out.

c) Sufficient amount of data on isotopic dilution methods could not be obtained during the JEX-70 experiment. It is very desirable that an analysis of different components of error be made particularly for this method since at present, this is the only method used extensively for the estimation of plutonium concentrations in the dissolver solution. For this purpose similar interlaboratorium tests need to be conducted.

d) The results of the error propagation indicate that the random component of all the measurement methods investigated may be considered to be quite reasonable and need not be improved further for safeguards purposes. The major component which contributes to all the measuring methods appears to be the interlaboratory deviations and has to be considered as a systematic error. It is desirable to investigate the causes for this type of error and if possible, eliminate such causes. For this purpose also, interlaboratorium tests under well defined conditions for the respective methods have to be carried out in the future.

e) A significant improvement in the accuracy of the measurement methods investigated can be obtained if uniform standards can be used for calibration of the methods. Also use of the same values of different constants as well as units will also improve the quality of the methods. An international body consisting of the interested laboratories could investigate this problem.