ESARDA
EUROPEAN SAFEGUARDS RESEARCH AND DEVELOPMENT ASSOCIATION

**Esarda Working Group on Isotopic Correlations and Reprocessing Input Analysis**

# The Isotope Correlation Experiment

ICE

## FINAL REPORT

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ESARDA 2/81

EUROPEAN SAFEGUARDS RESEARCH AND DEVELOPMENT ASSOCIATION

# Esarda Working Group on Isotopic Correlations and Reprocessing Input Analysis

# The Isotope Correlation Experiment

Edited by

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## ESARDA

ESARDA is an association of European organizations formed to advance and harmonize research and development for safeguards. It also provides a forum for the exchange of information and ideas between nuclear facility operators and safeguarding authorities.

Its partners as of 1st June 1982 were:

- The European Atomic Energy Community
- The Kernforschungszentrum Karlsruhe (KfK) - Fed. Rep. of Germany
- The Centre d'Etude de l'Energie Nucléaire - Studiecentrum voor Kernenergie (CEN/SCK) - Belgium
- The Comitato Nazionale per la Ricerca e per lo Sviluppo dell'Energia Nucleare e delle Energie Alternative (ENEA) - Italy
- The Stichting Energie Onderzoek Centrum Nederland (ECN) - Netherlands
- The United Kingdom Atomic Energy Authority (UKAEA) - Great Britain
- The Energistyrelsen - Denmark
- The Commissariat à l'Energie Atomique (CEA) - France

## Working Group on Isotopic Correlations and Reprocessing Input Analysis

One of the themes of collaboration among ESARDA partners has long been the "isotopic correlations" and the "reprocessing plant input analysis". A working group was therefore set up, with a view to promoting and coordinating research work, exchanging information and providing reciprocal assistance in these fields.

The working group is composed of representatives of the various member-organizations of ESARDA and some nuclear industries of the relevant countries. In 1977 the ESARDA Steering Committee decided to accept observers to the working group from the IAEA (Vienna) and BNWL (Richland, U.S.A.).

A number of activities has been carried out by the group, including theoretical analysis of relations between isotope abundances in irradiated fuels, generation and collection of experimental isotopic data, statistical correlation of these data and, most importantly, exercises of application of ICT and other evaluation techniques to the data collected at the reprocessing input. This report contains the results of the last exercise, ICE.

The group has recently been renamed "Working Group for Reprocessing Input Verification".

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## Abstract

The ESARDA working group on Isotopic Correlation Techniques, ICT and Reprocessing Input Analysis performed an Isotope Correlation Experiment, ICE with the aim to check the feasibility of the new technique. Ten input batches of the reprocessing of the KWO fuel at the WAK plant were analysed by 4 laboratories. All information to compare ICT with the gravimetric and volumetric methods was available. ICT combined with simplified reactor physics calculation was included.

The main objectives of the statistical data evaluation were detection of outliers, the estimation of random errors and of systematic errors of the measurements performed by the 4 laboratories. Different methods for outlier detection, analysis of variances, Grubbs' analysis for the constant-bias model and Jaech's non-constant-bias model were applied. Some of the results of the statistical analysis may seem inconsistent which is due to the following reasons. For the statistical evaluations isotope abundance data (weight percent) as well as nuclear concentration data (atoms/initial metal atoms) were subjected to different outlier criteria before being used for further statistical evaluations. None of the four data evaluation groups performed a complete statistical data analysis which would render possible a comparison of the different methods applied since no commonly agreed statistical evaluation procedure existed.

The results prove that ICT is as accurate as conventional techniques which have to rely on costly mass spectrometric isotope dilution analysis. The potential of outlier detection by ICT on the basis of the results from a single laboratory is as good as outlier detection by costly interlaboratory comparison.

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

# 1. Introduction

The ESARDA working group on Isotopic Correlation Techniques and Reprocessing Input Analysis decided at its meeting, on September 1st, 1977 at Karlsruhe to perform an Isotope Correlation Experiment - ICE.

This report summarizes the experimental activities, the subsequent evaluations and conclusions in order to optimize a follow-up experiment.

## 1.1 Scope of the experiment

In the past the Isotope Correlation Technique had been developed to a state where its feasibility could be only proved by a field test. The aims of such an undertaking were defined as:

- the determination of the accuracy of ICT (and other related techniques) under normal operating conditions of the reprocessing plant and routine safeguards inspection.
- the evaluation of the additional effort for safeguards inspection and analysis.
- the proving of its benefits for safeguards and other fuel management purposes.
- the identification of additional information required in applying this technique.
- the checking of the applicability of proposed ICT procedures (e.g. databanks).

The present safeguards practice, which includes the possibility of analysing the reprocessing input solution by three independent laboratories (plant operator, IAEA safeguards analytical laboratory, EURATOM-European Commission safeguards analytical laboratory) opens the possibility for statistical evaluations. Therefore, the technique of interlaboratory comparison became a more important part of the experiment than had been anticipated at the beginning. This led to a considerable change of the original scope of the experiment. Agreeing on adequate statistical methods and setting up appropriate techniques took most of the time required for evaluating the experiment and are responsible for the delay in the final report.

## 1.2 Participants of ICE

The participants in the Isotope Correlation Experiment belonged to the ESARDA working group on Isotope Correlation and Reprocessing Input Analysis (table 1.1). The task performed by each participant are listed and can be grouped into:

- description of fuel history (fabrication and irradiation) by KWU and KWO,
- reprocessing input data (fuel identification, dissolver volume, density, dilution, and sampling) by WAK, IAEA, and EURATOM-inspection,
- analysis of reprocessing input samples by IRCH-KfK (referee laboratory), WAK, IAEA-SAL, EURATOM-ECSAM (TUI),
- evaluation by BNWL, Hanford, CEA, Cadarache, CEN, Mol, ECN, Petten, IAEA, Vienna, JRC, Karlsruhe, KfK, Karlsruhe.

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

Table 1.1: Participants of Isotope Correlation Experiment

## 2. Experimental

The experiment was conducted under the normal working conditions of the reprocessing plant WAK at Karlsruhe subjected to routine safeguards procedures. The samples comprised ten consecutive dissolution batches each making up exactly one half of the fuel assembly. The fuel was chosen randomly because the assemblies preselected originally for the ICE could not be dissolved in sequence due to their position in the storage pool. For an input analysis the present safeguards procedure involves the sampling of the accountability tank and the subsequent dilution of the sample at the reprocessing plant. Aliquots of this dilution were analysed by the plant and the two safeguards laboratories. Analyses routinely made include the concentration of uranium isotopes (masses 235, 236, 238) and plutonium (masses 238 - 242). In addition, fission products (Xe, Kr longlived γ-emitters), transplutonides (Am, Cm) and the burn-up by Nd-148 were determined at the European Institute for Transuranium Elements. Volumes, densities and dilution factors of the samples were observed at the plant. There were no measurements of head-end losses (shearing, residues on hulls and on filters). The uranium weight of the fuel assembly at the time of fabrication was supplied by KWU/KWO together with its irradiation history (table 2.1).

### 2.1 Fuel history

The fuel derived from the Kernkraftwerk Obrigheim, KWO, and consisted of enriched $UO_2$ clad in circaloy 4. Information - as required for ORIGEN calculations - concerning U-235 initial enrichment, burn-up achieved, number of irradiation cycles, power factors, etc. are summarized (tables 2.1 and 2.2).

| IRRADIATION TIME (d) | POWER (%) | POWER IN MW/t FOR ASSEMBLY NR: | | | | |
|---|---|---|---|---|---|---|
| | | 168 | 170 | 171 | 172 | 176 |
| 5.8 | 100 | 28.4 | 19.0 | 25.6 | 31.8 | 27.5 |
| 1 | 0 | | | | | |
| 79.6 | 100 | 28.4 | 19.0 | 25.6 | 31.8 | 27.5 |
| 2 | 0 | | | | | |
| 33.5 | 100 | 28.4 | 19.0 | 25.6 | 31.8 | 27.5 |
| 41.5 | 0 | | | | | |
| 131.5 | 100 | 28.4 | 19.0 | 25.6 | 31.8 | 27.5 |
| 5.8 | 0 | | | | | |
| 36.9 | 100 | 28.4 | 19.0 | 25.6 | 31.8 | 27.5 |
| 28 | 0 | | | | | |
| 126.9 | 100 | 37.7 | 38.4 | 38.4 | 28.3 | 38.1 |
| 9.2 | 0 | | | | | |
| 84.7 | 100 | 37.7 | 38.4 | 38.4 | 28.3 | 38.1 |
| 3.5 | 0 | | | | | |
| 23 | 100 | 37.7 | 38.4 | 38.4 | 28.3 | 38.1 |
| 3 | 0 | | | | | |
| 60 | 100 | 37.7 | 38.4 | 38.4 | 28.3 | 38.1 |
| 13.8 | 87.0 | 32.8 | 33.4 | 33.4 | 26.5 | 33.1 |
| 380 | 0 | | | | | |
| 246.7 | 100 | 31.4 | 32.1 | 31.4 | 31.1 | 31.1 |

Table 2.1: Irradiation history of KWO fuel assemblies

### 2.2 Head-end process at WAK during ICE and sampling procedure.

For a dissolution a fuel assembly was transferred into the mechanical treatment cell, where it was dismantled and 90 of the 180 fuel pins belonging to a geometrical half of the fuel were taken out. The pins were chopped directly into the dissolver vessel. The dissolution took place over a period of 5 to 6 hours. Recycled acids containing only traces of U and Pu were utilized. After dissolution the solution was transferred into an intermediate vessel (s. fig. 2.1) and a second dissolution took place over approximately 3 to 4 hours. The solution again was transferred to the intermediate vessel. The content of the intermediate vessel was then passed through a filter into the input accountability tank. The dissolver was rinsed twice and the rinse solution transferred via the intermediate vessel into the input accountability tank. Now the hulls were removed from the dissolver vessel. Nuclear material remaining on the hull was estimated on previous dissolution to be 0.1 %. The transferred solution in the accountability tank was mixed by air sparging. During this step the input accountability tank was sampled (s. below). After sampling the volume and density were measured.

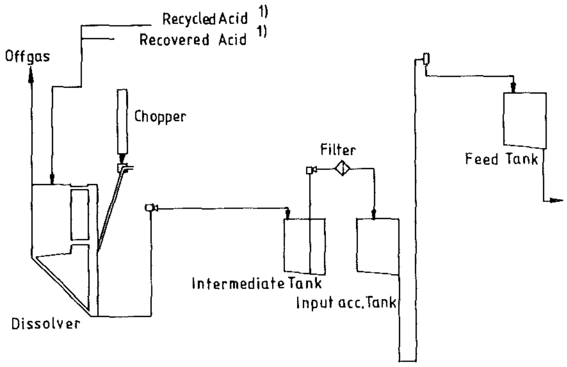

Figure 2.1: Tank scheme at head-end process

[1] Recycled acid is the purified nitric acid containing only traces of Pu and U. Recovered acid originates from the concentration of process streams containing recoverable amounts of Pu and U. It is used to adjust the acidity of the feed stream.

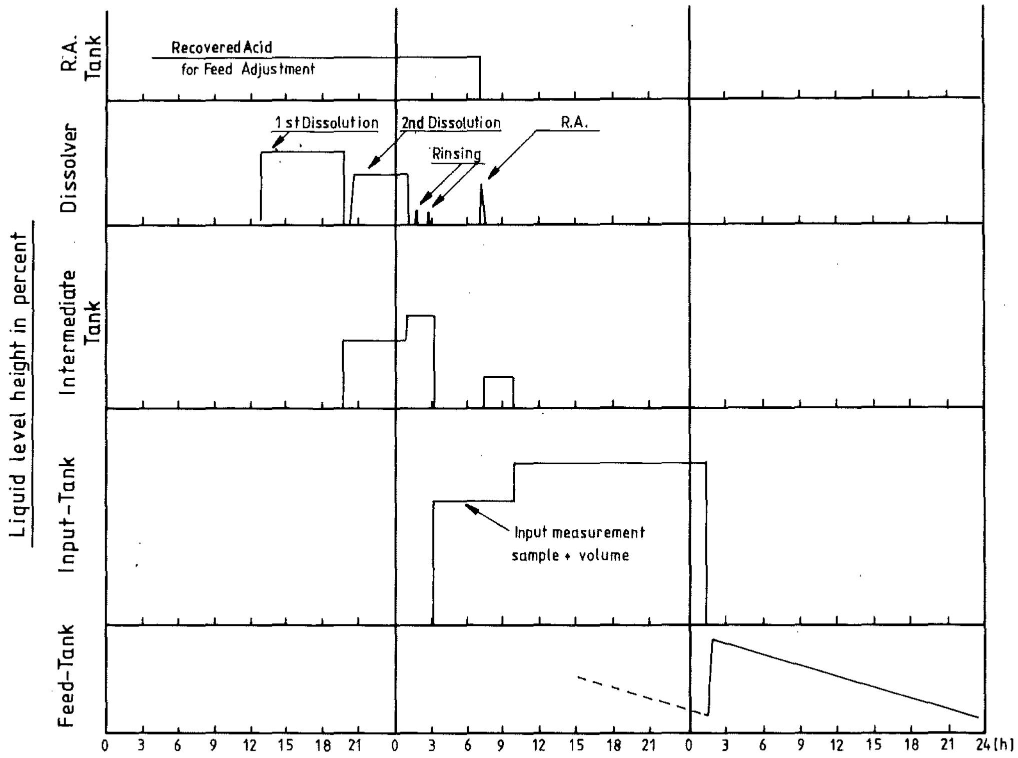

Figure 2.2: Transfer of solutions

The sequence of operation is summarized (fig. 2.2):

1. A fuel assembly is transferred into the mechanical treatment cell.
2. The KWO fuel assembly is dismantled and 90 of the 180 fuel pins are taken for the dissolver charge.
3. The 90 fuel pins are chopped directly into the dissolver.
4. Dissolution takes place over a time period of 5 to 6 hours. Recycled acid, containing traces of U and Pu is utilized for dissolution.
5. Dissolver solution is transferred into an intermediate vessel, and the 2nd dissolution takes place over 3 to 4 hours.This solution is again transferred into the intermediate vessel (fig. 2.1).
6. The content of the intermediate vessel is transferred via a filter into the input accountability tank.
7. The dissolver is rinsed twice. The rinse solutions are transferred via the intermediate vessel into the input accountability tank.
8. The hulls are removed from the dissolver.
9. The solution in the input accountability tank is mixed by air-sparging.
10. Sampling of the input accountability vessel takes place during air-sparging.
11. Volume measurement is performed after sampling.
12. After sampling and volume measurement the input solution is adjusted with recycled acid.

Sampling was performed after steps 1 to 9 have been completed.

The sampling device consisted mainly of a vacuum assisted airlift. The sample solution was circulated through the sample bottle which was held on a needle block. All steps involved in sampling were done automatically.

The sampling procedure provided for taking of 10 samples:

- 1st sample was taken after 15 min flushing of the sample solution circuit, this sample was disposed off.
- all following samples were taken after 5 min flushing.
- 2nd, 3rd, 4th were taken for homogeneity test by density measurements. The solution was considered to be homogeneous, when the density measurements did not differ by more than 0.0008 g/ml. If not, sampling was recommenced.
- 7th sample was taken for input analysis by isotope dilution mass-spectrometry (IDMS).

From the 7th sample bottle two weight aliquots (A,B) are diluted with 1.5M $HNO_3$. The dilution factor is ca. 1:200. Samples for external analysis (IRCH, TUI, IAEA) were taken from dilution A. The operator carried out measurements on both dilutions (A+B).

## 2.3 Analytical Procedures

### 2.3.1 Euratom Safeguards Laboratory, European Institute for Transuranium Elements, Karlsruhe (TUI)

MASS SPECTROMETRY

Equipment

A fully automatic mass spectrometer (CH5) with a high vacuum lock controlled by a Varian 620 I computer is in use for routine measurements. The computer controls all mass spectrometer operations without human aid(1).

Preparations of Filaments

Pre-heated Re filaments are welded onto throw-away beads. The two-filament method is used.

Heating

In the heating programme a preheating step is built in for both filaments to achieve a degassing of the ionisation filament and a penetration of the sample into the sample filament. The heating speed is controlled by the vacuum pressure of the total ionisation current. The ionisation filament is heated up to a prefixed ion current for the Re isotope 187 of about $10^{-13}$ A.

Concentration

The samples were conditioned to the following approximate concentrations:

U 100 ng/µl, Pu 10 ng/µl.

An amount of 2 µl for U and 10 µl for Pu was plated on the sample filament.

Scanning

The scanning of the isotopes was done by a peak-jumping system from the lowest up to the highest isotope. The number of scans was 3 x 10 scans. Between the 3 runs the machine was refocussed.
The sequence of the peak-jumping was a → b ..... a → b.

Detection

The detection system is normally either a Faraday cage or a multiplier system. In this particular case the multiplier system was used.

Computing

The results of the automatic mass-spectrometer were shown on a recorder and simultaneously printed on a teletype. The atom ratios with their corresponding standard deviations were fed into the main computer and corrected for mass discrimination, contamination by naturally occuring elements (in the case of Nd) etc.

CHEMICAL CONDITIONING

Sample dispensing and spiking

An amount of sample containing about 2 µg Pu was weighed into a test-tube. Corresponding amounts of U-233 and Pu-242 spikes were added by weight, the acidity adjusted until 8M in $HNO_3$ and vigorous mixing carried out.

Redox Procedure

About 500 µl of a 2M $NH_2OH_2Cl$ solution were added and the mixture mixed vigorously until a reaction occured. The solution was heated for an hour at 80°C and then evaporated to dryness overnight. The residue was taken up in 500 µl 8M $HNO_3$.

Separation Procedure

The solution was put on an anion exchange column, 0.6 g Dowex 1x8, 200 - 400 mesh. The column was washed with 8M $HNO_3$ and the Pu eluted with 0.35M $HNO_3$. The eluate was evaporated to dryness and taken up in 100 µl 1M $HNO_3$. About 5 µl of this were evaporated on a V2A planchet for α counting. The concentration of Pu was then estimated from these counts.

A suitable quantity of the rest of the solution was used for the mass spectrometry. The complete procedure was carried out at the same time on an unspiked solution.

ALPHA SPECTROMETRY

An automatic sample changer connected to a methane flow and a semiconductor counter were used for the α-spectrometric analyses. The total α counts were measured for each sample using the gas flow counter and the α spectrum was determined using the semiconductor detector combined with a 400 channel analyser.

Data from these measurements were transmitted to a PDP-11 computer and the reduced results then transferred to an IBM 370 computer for subsequent evaluation(2).

### 2.3.2 IAEA Safeguards Analytical Laboratory (SAL)

The procedure outlined in figure 2.3 is based on the use of dried mixed U-233/Pu-242 spikes and a chemical treatment recommended by Los Alamos(3).

The following is a summarized description of the analytical procedure used in SAL.

Scope of application

Isotopic and isotopic dilution analysis of diluted solutions of spent fuel containing 2 - 20 µg/ml of plutonium, 0.5 to 2 mg/ml of uranium, and up to 10 mCi/ml of fission products.

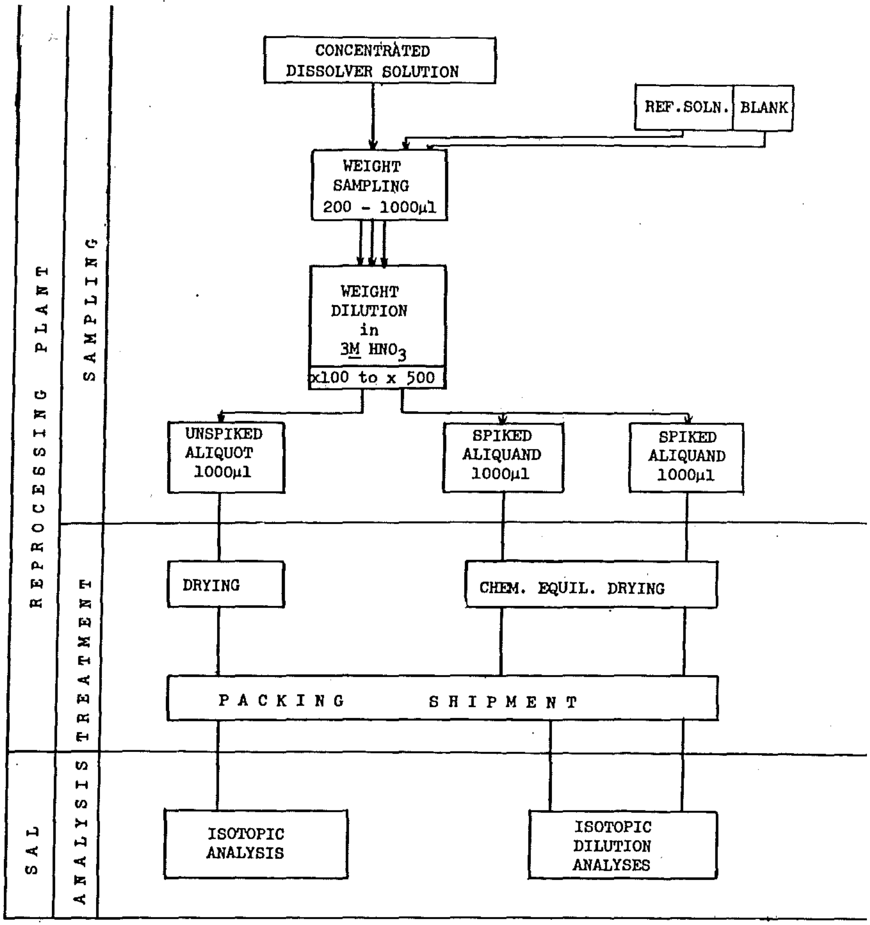

Figure 2.3: Scheme for the sampling and analysis of spent fuel solution following the "Dry Spike Technique".

Equipment

5 ml penicillin vials (Pyrex).

5 ml penicillin vials containing certified amounts of dried mixed U-233/Pu-242 spikes.

For the ICE experiment the spikes used contained about 9 µg of Pu-242 and 0.8 mg of U-233 in nitrate form.

Fuming enclosure (figure 2.4).

Ion exchange disposable chromatographic columns Kontes.

Procedure

Add about 1 ml of diluted solution of spent fuel to a tared penicillin vial containing a certified spike, stopper the vial immediately.

Measure the gross weight of the vial and calculate the net weight of the sample to the nearest 0.1 mg.

Add 1 ml of a mixture of 8<u>M</u> $HNO_3$, 1<u>M</u> $HClO_4$, 0.01<u>M</u> HF.

Evaporate to 0.1 ml and fume at 180°C overnight in the enclosure (figure 2.4).

Redissolve in 12<u>M</u> HCl.

Adsorb U and Pu on anion exchange resin Bio Rad 1x2, 200-400 Mesh ($\phi$ 8 mm x H 30 mm), and wash free from Am and most fission products with 8 ml 12<u>M</u> HCl.

Elute Pu with 8 ml 12<u>M</u> HCl - 0.1<u>M</u> HI.

Elute U with 8 ml 0.1<u>M</u> HCl.

Evaporate the collected U and Pu fractions to dryness and fume twice with 1 ml of 8<u>M</u> $HNO_3$.

Redissolve in 1<u>M</u> $HNO_3$ to obtain solutions containing 50 µg/ml of U or Pu.

Measure the isotopic composition on the 2-stage ORNL mass spectrometer(4)

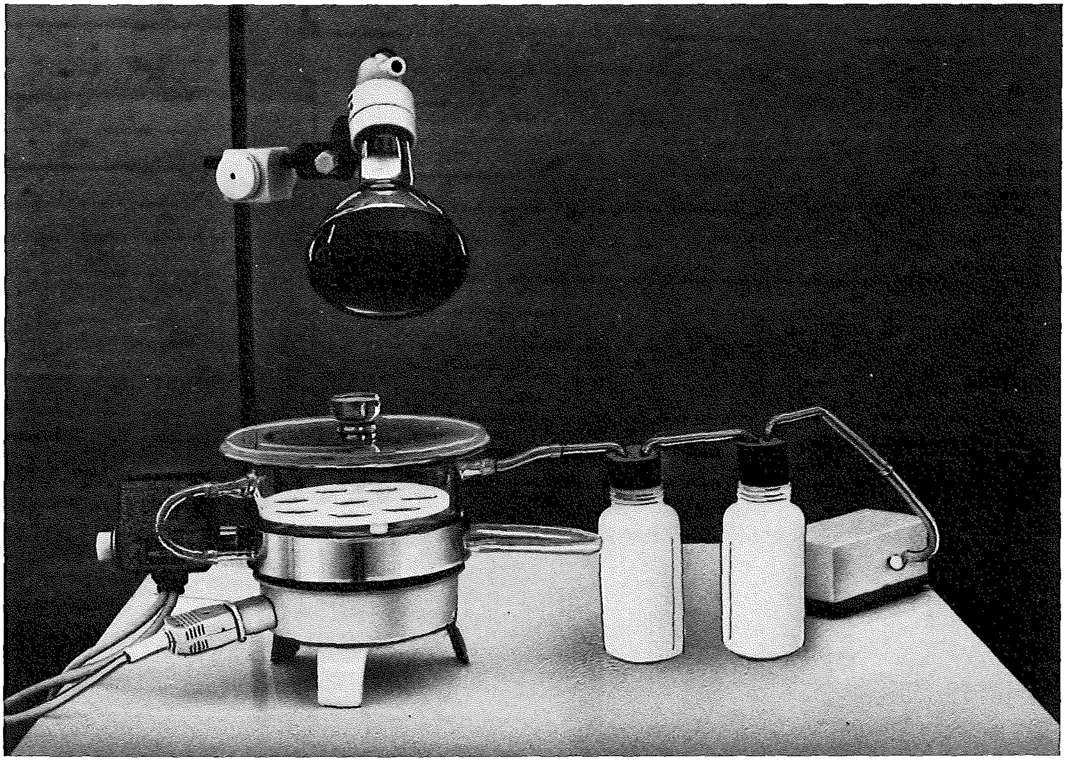

Figure 2.4: Enclosure for the fuming and drying of spent fuels samples

Loading 50 ng U or Pu
single filament source
filament temperature 1750 °C for U
1500 °C for Pu
isotopic abundance sensitivity 2 ppm
calibration with respect to NBS.500
precision of isotope ratio measurements

$\frac{233}{238}$, $\frac{235}{238}$, $\frac{242}{239}$ v = 0.5%

$\frac{240}{239}$ v = 0.2%

$\frac{241}{239}$ v = 1%

$\frac{234}{238}$, $\frac{236}{238}$, $\frac{238}{239}$ v = 2%

### 2.3.3 Referee Laboratory, Institut für Radiochemie, KfK (IRCH)

Procedure: Isotopic Dilution Technique

To the weighed aliquotes of the diluted sample and of the spike solution 0.5 ml $HNO_3$ (8M) is added. The mixture is evaporated nearly to dryness. Addition of 0.5 ml $HNO_3$ (8M) and the evaporation step is repeated (2x). This evaporation step is done to dissociate polymeric species of Pu.

Take up with 0.5 ml $HNO_3$ (4M) 0.1 ml Fe(II)$SO_4$-solution. Mix well and heat to ∿ 70°C for 5 min.

Add 50 µl of $NaNO_2$ (2.5M) to oxidize Pu to Pu(IV) state and evaporate the mixture to near dryness to reduce volume.

Dissolve with $HNO_3$ to make solution 8M.

Transfer to anion exchange column for separation of U and Pu.

Carefully wash the wall of the column with 500 µl $HNO_3$ (8M), to ensure that all of the sample is absorbed on the column.

Complete the elution of unabsorbed fission products with 5 ml $HNO_3$ (8M).

Elute the main U content with 3 ml $HNO_3$ (8M) with 500 µl portions. Evaporate these 3 ml nearly to dryness for mass spectrometry analysis.

Wash the column with 50 ml $HNO_3$ (8M).

Elute Pu with 30 ml (0.5M) $HNO_3$; evaporate nearly to dryness for Pu-mass-analysis.

### 2.4 Reported data

The following comprises the results from the fabrication of the fuel assemblies and those obtained from the analyses of the dissolver solution sample.

The weight of each quarter of a fuel element has been calculated to check its symmetry (table 2.2). This was done in order to see whether the halving of the element in one of the two possible ways would produce significant differences in the input batches. It turned out that the weight of each quarter of the fuel element was only different by 0.4 % and could not explain the differences in the amount of fuel observed in the input analyses. The specifications for the Pu/$UO_2$ stoichiometrie was 2.00 ± 0.01 %.

The WAK operator data are summarized in table 2.4. The corresponding input batch numbers with their exposure as calculated by the shipper, volume, density and dilution of dissolver solution are indicated. Please note that the concentration of uranium and plutonium as given by WAK refer to the undiluted dissolver solution.

The analyses data of the referee laboratory (IRCH) are given in table 2.5. For part of the input batches the analyses are incomplete due to a lack of sufficient material.

The analyses of the IAEA-inspection have been collected in table 2.6.

The results of the European Institute for Transuranium Elements are given in table 2.7. The errors reported refer to duplicate measurements. Activity ratios of selected fission products are given in table 2.8.

For comparison purposes the results of the different laboratories were transformed in the following way: The Pu-241 concentration was corrected for decay to the date of reactor shut down (half live 14.6y). Also for the results of the Transuranium Institute, the Pu-238 has been corrected for build-up by Cm-242 decay. The same was done for the reported fission product data. In-pile decay corrections, however, have been not applied.

For comparison and handling, the analytical data of the 4 laboratories have been transformed into the notation used at the European Institute for Transuranium Elements i.e. atoms per initial metal atoms, IMA(5), cleaned from outliers by use of Grubbs' criterion at α = 0.01 (see chapters 3.1 and 4.2) and averaged (table 2.9). This table shows for each input batch the burn-up, Ft (total fission/IMA) and the Cm-244 content as obtained by the European Institute for Transuranium Elements. The variation coefficients of the averaged data were calculated by use of eq. (3-13) and are given in table 2.10.

| | | | | | |
|---|---|---|---|---|---|
| 1. Fuel assembly number: | 168 | 170 | 171 | 172 | 176 |
| 2. U-235 enrichment (w/o): | 3.10 | 3.10 | 3.10 | 3.10 | 3.10 |
| 3. Total uraniumoxide (g): | 311 196.5 | 311 042.5 | 311 595.0 | 310 683.5 | 311 785.5 |
| 4. Uraniumoxide I quarter of fuel element: | 77 762.0 | 77 791.5 | 77 873.0 | 77 679.5 | 77 898.5 |
| 5. Uraniumoxide II quarter of fuel element: | 77 814.0 | 77 749.5 | 77 864.0 | 77 691.0 | 77 972.5 |
| 6. Uraniumoxide III quarter of fuel element: | 77 803.5 | 77 736.0 | 77 960.5 | 77 613.0 | 77 910.5 |
| 7. Uraniumoxide IV quarter of fuel element: | 77 817.0 | 77 765.5 | 77 897.5 | 77 700.0 | 78 004.0 |

Table 2.2: Fabricator data (KWU) of fresh fuel assemblies

| | | | | | |
|---|---|---|---|---|---|
| 1. Fuel assembly number: | 168 | 170 | 171 | 172 | 176 |
| 2. Input batch number: | 86+87 | 94+95 | 88+89 | 92+93 | 90+91 |

Table 2.3: Corresponding numbers of assemblies and batches

| 1. Input batch number: | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2. Date of analysis: | 30.1.78 | 31.1.78 | 1.2.78 | 2.2.78 | 6.2.78 | 13.2.78 | 27.2.78 | 10.2.78 | 7.2.78 | 8.2.78 |
| 3. Fuel exposure (shipper data MWd/t): | 30018 | 30018 | 30052 | 30052 | 29647 | 29647 | 26976 | 26979 | 27764 | 27764 |
| 4. Volume of dissolver solution (l): | 581.224 | 542.128 | 531.977 | 543.729 | 465.251 | 471.038 | 480.636 | 522.210 | 494.539 | 569.835 |
| 5. Density of dissolver solution (kg/l) 20°C: | 1.4267 | 1.4632 | 1.4792 | 1.4706 | 1.5012 | 1.4985 | 1.4895 | 1.4632 | 1.4776 | 1.4385 |
| 6. Dilution factor: | 303.14 | 284.12 | 301.25 | 308.99 | 332.03 | 303.21 | 304.03 | 310.66 | 327.57 | 337.35 |
| 7. Total uranium concentration (g/kg): | 160.31 | 165.6 | 168.0 | 168.0 | 191.5 | 187.0 | 191.3 | 176.0 | 187.5 | 165.2 |
| 8. Total plutonium concentration (g/kg): | 1.391 | 1.460 | 1.416 | 1.437 | 1.663 | 1.576 | 1.494 | 1.466 | 1.461 | 1.354 |
| 9. Isotopic composition of U-234 (w/o): | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 |
| 10. Isotopic composition of U-235 (w/o): | 1.01 | 0.94 | 1.02 | 0.99 | 0.95 | 1.03 | 1.09 | 0.99 | 1.13 | 1.04 |
| 11. Isotopic composition of U-236 (w/o): | 0.39 | 0.40 | 0.39 | 0.39 | 0.39 | 0.38 | 0.37 | 0.38 | 0.37 | 0.39 |
| 12. Isotopic composition of U-238 (w/o): | 98.50 | 98.65 | 98.57 | 98.59 | 98.64 | 98.57 | 98.52 | 98.61 | 98.47 | 98.55 |
| 13. Isotopic composition of Pu-238 (w/o): | 1.24 | 2.14 | 1.20 | 1.24 | 1.27 | 1.19 | 2.09 | 1.43 | 1.05 | 1.28 |
| 14. Isotopic composition of Pu-239 (w/o): | 58.71 | 57.34 | 59.43 | 58.73 | 57.56 | 59.54 | 59.66 | 58.43 | 61.00 | 59.04 |
| 15. Isotopic composition of Pu-240 (w/o): | 23.54 | 23.68 | 23.40 | 23.73 | 23.96 | 23.38 | 23.03 | 23.84 | 22.89 | 23.56 |
| 16. Isotopic composition of Pu-241 (w/o): | 11.29 | 11.48 | 11.30 | 11.51 | 11.63 | 11.37 | 10.98 | 11.46 | 11.05 | 11.43 |
| 17. Isotopic composition of Pu-242 (w/o): | 5.22 | 5.36 | 4.67 | 4.78 | 5.57 | 4.52 | 4.25 | 4.84 | 4.02 | 4.69 |

Table 2.4: Results of input analyses by the WAK operator

| 1. Input batch number: | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2. Date of analysis: | - | 31.1.78 | 2.2.78 | 22.2.78 | 23.2.78 | 29.3.78 | 31.3.78 | 6.4.78 | 11.5.78 | 14.7.78 |
| 3. Total uranium concentration (g/kg): | 164.00 | 164.93 | 170.36 | 164.10 | 187.43 | 186.41 | 184.27 | 173.63 | 179.70 | 159.84 |
| 4. Total plutonium concentration (g/kg): | - | - | 1.433 | - | 1.688 | 1.637 | 1.525 | 1.533 | 1.491 | 1.471 |
| 5. Isotopic composition of U-234 (w/o): | - | 0.019 | 0.020 | 0.020 | 0.020 | 0.020 | 0.021 | 0.020 | 0.020 | 0.020 |
| 6. Isotopic composition of U-235 (w/o): | - | 0.968 | 1.020 | 0.993 | 0.953 | 1.026 | 1.093 | 0.998 | 1.120 | 1.031 |
| 7. Isotopic composition of U-236 (w/o): | - | 0.402 | 0.388 | 0.394 | 0.402 | 0.389 | 0.377 | 0.393 | 0.374 | 0.390 |
| 8. Isotopic composition of U-238 (w/o): | - | 98.611 | 98.570 | 98.593 | 98.626 | 98.566 | 98.509 | 98.589 | 98.486 | 98.560 |
| 9. Isotopic composition of Pu-238 (w/o): | - | 1.51 | 1.42 | 1.44 | 1.47 | 1.41 | 1.35 | 1.46 | 1.33 | 1.42 |
| 10. Isotopic composition of Pu-239 (w/o): | - | 57.49 | 59.26 | 58.76 | 58.08 | 59.59 | 60.37 | 58.66 | 61.20 | 59.37 |
| 11. Isotopic composition of Pu-240 (w/o): | - | 24.16 | 23.48 | 23.59 | 23.91 | 23.32 | 23.14 | 23.81 | 22.83 | 23.55 |
| 12. Isotopic composition of Pu-241 (w/o): | - | 11.64 | 11.27 | 11.44 | 11.57 | 11.22 | 10.94 | 11.33 | 10.74 | 11.16 |
| 13. Isotopic composition of Pu-242 (w/o): | - | 5.20 | 4.57 | 4.77 | 4.97 | 4.45 | 4.20 | 4.75 | 3.90 | 4.49 |

Table 2.5: Results of remeasurements of input analyses by the referee laboratory, IRCH, KfK

| 1. Input batch number: | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2. Date of analysis: | 6.9.78 | 7.9.78 | 7.9.78 | 7.9.78 | 4.6.78 | 4.6.78 | 5.6.78 | 8.6.78 | 10.6.78 | 11.8.78 |
| 3. Total uranium concentration (g/kg): | 159.88 | 162.74 | 168.10 | 162.75 | 189.03 | 186.90 | 184.27 | 173.35 | 180.92 | 159.84 |
| 4. Total plutonium concentration (g/kg): | 1.386 | 1.467 | 1.438 | 1.448 | 1.664 | 1.58245 | 1.51559 | 1.5241 | 1.478 | 1.471 |
| 5. Isotopic composition of U-234 (w/o): | 0.020 | 0.019 | 0.020 | 0.019 | 0.021 | 0.022 | 0.023 | 0.019 | 0.020 | 0.020 |
| 6. Isotopic composition of U-235 (w/o): | 1.014 | 0.943 | 1.023 | 0.986 | 0.950 | 1.022 | 1.104 | 1.002 | 1.117 | 1.027 |
| 7. Isotopic composition of U-236 (w/o): | 0.388 | 0.403 | 0.385 | 0.391 | 0.394 | 0.383 | 0.373 | 0.390 | 0.370 | 0.383 |
| 8. Isotopic composition of U-238 (w/o): | 98.579 | 98.634 | 98.571 | 98.604 | 98.635 | 98.571 | 98.500 | 98.588 | 98.492 | 98.570 |
| 9. Isotopic composition of Pu-238 (w/o): | 1.49 | 1.65 | 1.47 | 1.54 | 1.63 | 1.48 | 1.38 | 1.55 | 1.27 | 1.48 |
| 10. Isotopic composition of Pu-239 (w/o): | 59.25 | 57.56 | 59.31 | 58.86 | 58.04 | 59.73 | 60.33 | 58.12 | 61.30 | 59.40 |
| 11. Isotopic composition of Pu-240 (w/o): | 23.66 | 24.25 | 23.55 | 23.68 | 23.95 | 23.29 | 23.20 | 23.52 | 22.84 | 23.56 |
| 12. Isotopic composition of Pu-241 (w/o): | 11.03 | 11.39 | 11.11 | 11.17 | 11.42 | 11.08 | 10.89 | 11.20 | 10.71 | 11.08 |
| 13. Isotopic composition of Pu-242 (w/o): | 4.57 | 5.15 | 4.56 | 4.74 | 4.96 | 4.43 | 4.24 | 5.54 | 3.88 | 4.48 |

Table 2.6: Results of remeasurements of input analyses by the IAEA

| 1. Input batch number: | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2. Date of analysis: | 15.2.78 | 28.1.78 | 6.3.78 | 12.4.78 | 21.4.78 | 11.4.78 | 28.3.78 | 27.4.78 | 25.4.78 | 21.4.78 |
| 3. Total uranium concentration (g/kg): | 157.03<br>± 0.31 | 162.51<br>± 0.07 | 167.04<br>± 0.26 | 163.43<br>± 0.36 | 186.64<br>± 0.04 | 185.30<br>± 0.21 | 185.94<br>± 0.04 | 172.03<br>± 0.08 | 180.88<br>± 0.23 | 160.69<br>± 0.03 |
| 4. Total plutonium concentration (g/kg)*: | 1.447<br>± 0.27 | 1.479<br>± 0.10 | 1.466<br>± 0.42 | 1.462<br>± 0.28 | 1.683<br>± 0.03 | 1.609<br>± 0.32 | 1.535<br>± 0.44 | 1.509<br>± 0.02 | 1.511<br>± 0.94 | 1.386<br>± 0.28 |
| 5. Isotopic composition of U-234 (w/o): | 0.019±5.26 | 0.019±4.76 | 0.020±2.72 | 0.018±0.19 | 0.020±0.04 | 0.021±0.65 | 0.019±1.57 | 0.021±2.51 | 0.018±23.05 | 0.017±14.75 |
| 6. Isotopic composition of U-235 (w/o): | 0.995±0.24 | 0.924±0.01 | 1.013±0.30 | 0.983±0.11 | 0.950±0.20 | 1.025±0.48 | 1.095±0.10 | 1.003±0.46 | 1.169±3.04 | 1.024±0.77 |
| 7. Isotopic composition of U-236 (w/o): | 0.384±0.25 | 0.397±0.12 | 0.384±0.08 | 0.390±0.43 | 0.401±0.49 | 0.385±0.20 | 0.379±0.17 | 0.393±0.55 | 0.375±4.05 | 0.381±0.41 |
| 8. Isotopic composition of U-238 (w/o): | 98.602 | 98.661 | 98.583 | 98.609 | 98.629 | 98.569 | 98.509 | 98.582 | 98.438 | 98.578 |
| 9. Isotopic composition of Pu-238 (w/o)*: | 1.59±0.92 | 1.65±0.81 | 1.174±0.38 | 1.50±0.34 | 1.61±0.58 | 1.42±0.26 | 1.049±0.27 | 1.53±0.16 | 1.25±0.14 | 1.40±0.45 |
| 10. Isotopic composition of Pu-239 (w/o): | 58.96 | 57.28 | 58.485 | 58.78 | 57.93 | 59.60 | 59.57 | 58.54 | 61.11 | 59.38 |
| 11. Isotopic composition of Pu-240 (w/o): | 23.49<br>± 0.24 | 24.11<br>± 0.19 | 23.15<br>± 0.15 | 23.55<br>±0.005 | 23.86<br>± 0.12 | 23.26±0.05 | 22.81±0.12 | 23.73±0.16 | 22.80±0.30 | 23.51±0.10 |
| 12. Isotopic composition of Pu-241 (w/o): | 11.35<br>± 0.16 | 11.79<br>± 0.99 | 12.67<br>± 0.34 | 11.40<br>± 0.27 | 11.58<br>± 0.62 | 11.21±0.13 | 12.40 ±0.09 | 11.37±0.26 | 10.87±0.43 | 11.19±0.47 |
| 13. Isotopic composition of Pu-242 (w/o): | 4.61±0.18 | 5.17±0.16 | 4.51 ±0.22 | 4.77±0.21 | 5.03±0.36 | 4.50±0.15 | 4.17 ±0.21 | 4.83±0.10 | 3.97±0.06 | 4.52±0.90 |

* corrected for decay of Cm-242

Table 2.7: Results of remeasurements of input analyses by TU

Variation coefficients are given in per cent.

| Input batch number | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| Kr-84/83 | - | 2.780 | 2.698 | 2.657 | 2.751 | 2.751 | 2.637 | 2.707 | 2.551 | 2.648 |
| Kr-83/86 | - | 2.412 | 2.428 | 2.392 | 2.411 | 2.306 | 2.449 | 2.430 | 2.520 | 2.414 |
| Kr-84/86 | - | 0.6706 | 0.6551 | 0.6356 | 0.6632 | 0.6343 | 0.6459 | 0.6579 | 0.6428 | 0.6391 |
| Xe-132/131 | 2.282 | 2.579 | 2.473 | 2.457 | 2.463 | 2.402 | 2.336 | 2.479 | 2.288 | 2.373 |
| Xe-131/134 | 0.3077 | 0.2810 | 0.3016 | 0.2865 | 0.2924 | 0.2972 | 0.3040 | 0.2973 | 0.3085 | 0.3015 |
| Xe-132/134 | 0.7021 | 0.7247 | 0.7458 | 0.7042 | 0.7203 | 0.7139 | 0.7102 | 0.7372 | 0.7059 | 0.7153 |
| Xe-136/134 | 1.468 | 1.525 | 1.537 | 1.534 | 1.521 | 1.506 | 1.484 | 1.541 | 1.482 | 1.498 |
| Cs-134/137* | - | 1.245 | 1.111 | 1.773 | 1.159 | 1.146 | 1.067 | 1.127 | 1.086 | 1.119 |
| Nd-146/145 | 0.9699 | 0.9779 | 0.9661 | 0.9722 | 0.9780 | 0.9660 | 0.9549 | 0.9733 | 0.9475 | 0.9656 |
| Nd-143/148 | 2.329 | 2.342 | 2.362 | 2.354 | 2.338 | 2.357 | 2.439 | 2.305 | 2.455 | 2.368 |
| Nd-144/148 | 3.548 | 3.613 | 3.590 | 3.632 | 3.662 | 3.572 | 3.623 | 3.567 | 3.566 | 3.549 |
| Nd-145/148 | 1.908 | 1.898 | 1.926 | 1.926 | 1.920 | 1.917 | 1.953 | 1.888 | 1.959 | 1.926 |
| Nd-146/148 | 1.851 | 1.856 | 1.860 | 1.873 | 1.878 | 1.852 | 1.865 | 1.837 | 1.856 | 1.860 |

Table 2.8: Atom and (*) activity ratios of selected fission products determined by TU

| Input batch number | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ft* | 2.953 | 3.151 | 2.945 | 3.024 | 3.076 | 2.909 | 2.758 | 3.043 | 2.696 | 2.920 |
| U-235 | 9.832 E-3 | 9.094 E-3 | 9.954 E-3 | 9.601 E-3 | 9.249 E-3 | 9.998 E-3 | 1.073 E-2 | 9.718 E-3 | 1.108 E-2 | 1.004 E-2 |
| U-236 | 3.764 E-3 | 3.868 E-3 | 3.760 E-3 | 3.777 E-3 | 3.838 E-3 | 3.725 E-3 | 3.653 E-3 | 3.768 E-3 | 3.620 E-3 | 3.743 E-3 |
| U-238 | 9.474 E-1 | 9.467 E-1 | 9.484 E-1 | 9.477 E-1 | 9.474 E-1 | 9.486 E-1 | 9.499 E-1 | 9.475 E-1 | 9.502 E-1 | 9.484 E-1 |
| Pu-238 | 1.186 E-4 | 1.499 E-4 | 1.102 E-4 | 1.151 E-4 | 1.236 E-4 | 1.105 E-4 | 1.168 E-4 | 1.202 E-4 | 9.354 E-5 | 1.132 E-4 |
| Pu-239 | 5.056 E-3 | 4.915 E-3 | 4.844 E-3 | 4.943 E-3 | 4.911 E-3 | 4.902 E-3 | 4.695 E-3 | 4.848 E-3 | 4.787 E-3 | 4.922 E-3 |
| Pu-240 | 2.009 E-3 | 2.048 E-3 | 1.907 E-3 | 1.980 E-3 | 2.021 E-3 | 1.909 E-3 | 1.795 E-3 | 1.962 E-3 | 1.780 E-3 | 1.946 E-3 |
| Pu-241 | 1.089 E-3 | 1.127 E-3 | 1.037 E-3 | 1.088 E-3 | 1.110 E-3 | 1.047 E-3 | 9.666 E-4 | 1.068 E-3 | 9.650 E-4 | 1.061 E-3 |
| Pu-242 | 4.022 E-4 | 4.417 E-4 | 3.681 E-4 | 3.952 E-4 | 4.297 E-4 | 3.634 E-4 | 3.229 E-4 | 4.089 E-4 | 3.047 E-4 | 3.724 E-4 |
| Cm-244* | 1.507 E-5 | 1.848 E-5 | 1.428 E-5 | 1.625 E-5 | 1.841 E-5 | 1.364 E-5 | 1.107 E-5 | 1.615 E-5 | 9.826 E-6 | 1.387 E-5 |
| U-235/U-238 | 1.038 E-2 | 9.606 E-3 | 1.050 E-2 | 1.013 E-2 | 9.763 E-3 | 1.054 E-2 | 1.129 E-2 | 1.026 E-2 | 1.166 E-2 | 1.059 E-2 |
| Pu-240/Pu-239 | 3.974 E-1 | 4.167 E-1 | 3.937 E-1 | 4.007 E-1 | 4.115 E-1 | 3.895 E-1 | 3.823 E-1 | 4.046 E-1 | 3.72 E-1 | 3.954 E-1 |
| Pu-241/Pu-240 | 5.420 E-1 | 5.503 E-1 | 5.436 E-1 | 5.493 E-1 | 5.493 E-1 | 5.484 E-1 | 5.386 E-1 | 5.446 E-1 | 5.421 E-1 | 5.451 E-1 |
| Pu-242/Pu-240 | 2.005 E-1 | 2.158 E-1 | 1.930 E-1 | 1.996 E-1 | 2.127 E-1 | 1.903 E-1 | 1.80 E-1 | 2.084 E-1 | 1.712 E-1 | 1.914 E-1 |
| Pu-242/Pu-241 | 3.699 E-1 | 3.922 E-1 | 3.551 E-1 | 3.633 E-1 | 3.873 E-1 | 3.471 E-1 | 3.341 E-1 | 3.826 E-1 | 3.157 E-1 | 3.512 E-1 |
| Pu/U | 9.026 E-3 | 9.0476 E-3 | 8.592 E-3 | 8.867 E-3 | 8.949 E-3 | 8.658 E-3 | 8.188 E-3 | 8.749 E-3 | 8.219 E-3 | 8.745 E-3 |

(*determined by TU only)

Table 2.9: Averaged analytical results in units of atoms/IMA. Outliers excluded according to Grubbs' criterion, $\alpha = 0.01$. Outliers are batch 90 (RCH) of U-235 and U-235/U-238, and batch 93 (SAL) of Pu-242/241.

| Input batch number | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| U-235 | 0.43 | 1.09 | 0.16 | 0.38 | 0.01 | 0.32 | 0.72 | 0.57 | 2.11 | 0.69 |
| U-236 | 0.38 | 0.88 | 0.54 | 0.39 | 1.33 | 0.85 | 1.42 | 1.51 | 0.60 | 1.30 |
| U-238 | 0.09 | 0.02 | 0.01 | 0.02 | 0.02 | 0.02 | 0.003 | 0.003 | 0.04 | 0.04 |
| Pu-238 | 10.74 | 22.26 | 11.39 | 15.08 | 11.97 | 12.80 | 27.45 | 11.29 | 15.44 | 15.13 |
| Pu-239 | 3.45 | 1.45 | 1.49 | 2.33 | 2.03 | 1.89 | 3.15 | 2.67 | 3.10 | 4.94 |
| Pu-240 | 2.93 | 2.55 | 1.48 | 1.98 | 1.55 | 1.84 | 2.84 | 2.40 | 2.83 | 4.74 |
| Pu-241 | 2.76 | 2.88 | 1.26 | 2.02 | 1.53 | 1.77 | 2.69 | 2.38 | 2.30 | 4.81 |
| Pu-242 | 5.65 | 0.87 | 1.01 | 2.01 | 4.46 | 1.95 | 2.23 | 8.54 | 2.36 | 3.34 |
| U-235/U-238 | 0.43 | 1.10 | 0.18 | 0.37 | 0.005 | 0.32 | 0.74 | 0.60 | 2.14 | 0.69 |
| Pu-240/Pu-239 | 0.53 | 1.11 | 0.41 | 0.46 | 0.52 | 0.33 | 0.51 | 0.31 | 0.31 | 0.35 |
| Pu-241/Pu-240 | 0.25 | 0.74 | 0.84 | 0.04 | 0.18 | 0.35 | 0.65 | 0.28 | 0.62 | 0.80 |
| Pu-242/Pu-240 | 8.40 | 3.41 | 1.93 | 0.59 | 5.61 | 0.91 | 1.30 | 7.87 | 1.61 | 2.18 |
| Pu-242/Pu-241 | 8.29 | 3.66 | 1.47 | 0.58 | 5.52 | 0.82 | 0.73 | 0.95 | 1.11 | 1.78 |
| Pu/U | 2.83 | 1.41 | 1.32 | 2.30 | 1.64 | 1.88 | 2.61 | 2.68 | 2.96 | 4.90 |

Table 2.10: Variation coefficients, V(%), of averaged data compiled in table 2.9

# 3. Data evaluation

The following chapter will be divided into three parts. The first one deals with a short description of the purely statistical methods used for data evaluation. Section 3.2 summarizes briefly two rather physically oriented techniques of data treatment, headed by the title "isotope correlation technique". (A more extensive description of all the methods may be found in appendices A, B, and C.) Finally, the third part is devoted to some examples of the results obtained by the application of the methods described in the previous sections.

## 3.1 Statistical methods

The main objectives of the statistical data evaluation are:

1) Detection but not interpretation of suspicious data, called outliers for simplification.
2) Estimation of random error variances (or imprecisions) and of systematic errors (biases) of the measurements performed by different laboratories on the same sample material.

The statistical methods dealt with are those of

1) outlier detection using the criteria of Dixon and Grubbs (chapter 3.1.1),
2) the analysis of variances (ANOVA) (chapters 3.1.2 and A.1),
3) Grubbs' analysis for the constant-bias model including the method of paired comparisons (chapters 3.1.3 and A.2),
4) Jaech's non-constant-bias model (chapters 3.1.4 and A.3), and
5) the isotope correlation technique embracing theoretical calculations (chapter 3.2.1 and appendix C) and regression analysis (chapters 3.2.2 and A.4).

### 3.1.1 Detection of outliers

Various criteria for detecting outliers had been used during the course of data evaluation of ICE, the most utilised being those of Dixon(1) and of Grubbs(2). An interesting approach for detecting outliers using Student's t-distribution is given in appendix B.

With the Dixon test the value $x_n$ of ordered data $x_1 < x_2 <\ldots x_{n-1} < x_n$ is tested for being an outlier by calculating the ratio of the ranges $(x_n - x_{n-k})/(x_n - x_i)$ and comparing these ratios with critical values of a given significance level $\alpha$ and the appropriate sample size. One disadvantage of the method may be that it does not specify error values relative to all data $x_1, \ldots x_n$ but refers only to some values $x_i$, $x_{n-k}$, where $i$ and $k$ are selected in advance. Frequently, one choses $i = k = 1$.

For the Grubbs criterion the ratios $(x_i - \hat{x})/s$, $i=1$ or $n$ are tested against distribution values for a given sample size or degree of freedom and a specified level of significance, where $\hat{x}$ signifies the predicted or the mean value of the $x_i$. The estimate of the standard deviation (s) of the population of data $x_i$ is obtained from all data including eventual outliers. The distribution derived by Grubbs takes into account the possible falsification of s. The Grubbs criterion can also deal with two outliers simultaneously.

Except for very obvious outliers each of the criteria selected different outlying measurements (see 3.3.1). Therefore, it was felt necessary to agree on one criterion which was used in the final evaluation of the experiment: that of Grubbs(2) for one and for two simultaneous outliers at the 1% significance level was chosen (see chapter 4).

Isotope correlations were used to identify outlying individual measurements as well as unusual batches. It was proposed that Grubbs' criterion should be applied in a similar way on an ad hoc basis, relating the maximum residual to the square root of the residual mean square of the estimated regression line $Y = b_o + b_1 \cdot X$. Since in this case an outlier may be due to either variable X or Y or both, different isotope correlations including either X or Y are needed for proper identification.

### 3.1.2 Analysis of variances

The two-way analysis of variances (ANOVA) for the fixed effects model with one measurement per batch and per laboratory (unreplicated analyses) and without interaction had been proposed for the data evaluation of ICE-1, although the mixed model seems to be more appropriate. (The mixed model means the influence of one factor (laboratory) was the fixed effect, the influence of the other factor (batches) being random.) The model used here can be described as

$$y_{ij} = \mu + b_i + a_j + e_{ij} \qquad (3\text{-}1)$$

$i = 1, \ldots, n$ denoting batches

$j = 1, \ldots, m$ denoting laboratories (or measurement methods)

$y_{ij}$ = value of sample or batch $i$ as measured by laboratory $j$

$\mu$ = overall mean

$\mu + b_i$ = "true" value of batch $i$

$a_j$ = bias of laboratory $j$

$e_{ij}$ = random error associated with $y_{ij}$

The analysis of variances then consists of splitting the variances of the $y_{ij}$, $i=1,\ldots n$, $j=1,\ldots m$ into the variances

1) due to laboratory influence,
2) due to batch variation, and
3) due to the random error of measurements.

Estimates of the main quantities of model (3-1), i.e. of $\hat{a}_j$, $\hat{b}_i$, $s_e^2$ and $\hat{\mu}$ (the latter being of no interest for the experiment) were derived by the method of least squares (see appendix A).

The following conditions were assumed for the derivation:

1) $\sum_{j=1}^{m} a_j = 0$, i.e. the mean bias equals zero (3-2)

2) $\sum_{i=1}^{n} b_i = 0$, (3-3)

3) $e_{ij}$ are independent and normally distributed with zero means and equal variances $\sigma_e^2$, i.e. $N(0,\sigma_e^2)$, $s_e^2$ being the estimate of $\sigma_e^2$.

An interesting approach which permits the estimation of the variances of measurement errors ($s_{e_j}^2$) for each laboratory separately instead of the pooled estimate ($s_e^2$), may be found in appendix B.

Several hypotheses should be tested:

1. Hypothesis $H_a$: all $a_j = 0$

i.e. no significant laboratory biases exist. If the F-test shows that significant biases exist than one can investigate bias contrasts with Student's t-test for means (see eq. (A-28)).

2. Hypothesis $H_b$:

$$\text{all } b_i = 0 \text{ or } \sigma_b^2 = \frac{1}{n-1} \sum_{i=1}^{n} b_i^2 = 0,$$

which means that differences in batch value are statistically insignificant. The hypothesis is tested with the F-test statistics. If, for a certain isotope concentration or isotope ratio hypothesis $H_b$ has to be accepted then it is useless to use these quantities for any isotope correlation.

### 3.1.3 Grubbs' constant-bias model

Grubbs' constant-bias (CB) model[(3,4)] may be applied when the bias between measured and true values of a batch is independent of the batch magnitude. It may be written as follows:

$$y_{ij} = x_i + a_j + e_{ij} \qquad (3\text{-}4)$$

$i = 1,\ldots,n$ denoting batches
$j = 1,\ldots,m$ denoting laboratories
$y_{ij}$ = value of batch $i$ as measured by laboratory $j$
$x_i$ = "true" value of batch $i$
$a_j$ = bias of laboratory $j$
$e_{ij}$ = random error associated with $y_{ij}$

The CB model corresponds to the analysis of variances approach (section 3.1.2) if one takes

$$x_i = \mu + b_i - \bar{a} \qquad (3\text{-}5)$$

$$\text{where } \bar{a} = \frac{1}{m} \sum_{j=1}^{m} a_j,$$

which according to equation (3-2) equals zero in the ANOVA approach but not necessarily so for Grubbs' CB model. For the CB model the following assumptions are made:

1) the $e_{ij}$ are independent and normally distributed with zero means and variances $\sigma_{e_j}^2$, i.e. $N(0,\sigma_{e_j}^2)$,

2) the $x_i$ and $e_{ij}$ are independent of each other.

Under these conditions estimates of biases $(\hat{a}_j)$, batch or process variances $(s_x^2)$, and and random error variances $(s_{e_j}^2)$, and the variances of those estimates are calculated. Details are given in appendix A.

When applying Grubbs' CB model it happens rather often that negative variances $(s_{e_j}^2)$ are calculated. This may be due to violation either of assumption (1), i.e. independency of the random errors $e_{ij}$ or of assumption (2), i.e. the random errors depend on batch magnitude $x_i$. In both cases the CB model is not suitable and the non-constant-bias model (see Section 3.1.4) should be tried.

Another reason for finding negative estimates of variances $s_{e_j}^2$ may be that large discrepancies between the $s_{e_j}^2$, $j = 1,\dots,m$ exist. When treating the data of at least $m = 4$ laboratories it was recommended that Grubbs' analysis should be repeated excluding in turn one of the laboratories, thus getting up to $m + 1$ estimates of variances. The analysis yielding negative variances should be omitted. Variance estimates with smallest variation (i.e. highest precision) should then be chosen. However, it should be noted that increasing the number of laboratories increases the precision of the estimated variances under certain conditions which for $m = 4$ reads

$$s_{e_4}^2 < 3 \cdot s_e^2 \qquad (3\text{-}6)$$

where $s_e^2 = \min (s_{e_1}^2, s_{e_2}^2, s_{e_3}^2)$.

An example is given in appendix B.

When solving the CB model by matrix calculus negative variances $(s_{e_j}^2)$ may be avoided by placing the additional constraints

$$s_{e_j}^2 > 0 \qquad j=1,\dots,m ,$$

which may be done by use of Harwell Subroutine MA20B/BD.

The estimation of biases $a_j$, $j=1,\dots,m$ is possible only if constraints are made on the parameters. This means that there is no way to estimate the absolute or true bias. In the ANOVA approach the constraint was made that the average bias obtained by summation over biases of all laboratories equals zero, (see eq. (3-2)).

For the Grubbs method one often selects the bias of one laboratory to be equal to zero and calculates the other biases relative to this laboratory.

As with the analysis of variances several hypotheses may be tested with Grubbs' analysis:

1. Hypothesis $H_a$: $a_j = a_k$,

   i.e. there is no significant bias between laboratory $j$ and laboratory $k$, tested with Student's t-test for means of differences. This results in a stronger test than when testing biases with the ANOVA approach.

2. Hypotheses about the random error variances $(s_{e_j}^2)$

   which can be tested with Jaech's Lambdatest(5,6):

   hypothesis $H_o$: all $s_{e_j}^2$ are equal,

   hypothesis $H_1$: all but one $s_{e_j}^2$ are equal.

   If hypothesis $H_o$ or $H_1$ is true, equal variances may be pooled and compared with the variance $s_e^2$ obtained by ANOVA.
   However, Jaech states: "... the test could be used with reasonable assurance of its validity for sample sizes of 15 and greater. ... For sample sizes smaller than 10, the test should be applied with discretion."(5)

### 3.1.4 Non-constant-bias model

The mathematical model for the situation when biases among laboratories are not constant but depend linearly on batch magnitude has been developed by Jaech(7,8) for $m > 2$ laboratories.

The non-constant-bias (NCB) model is written as

$$y_{ij} = c_j x_i + a_j + e_{ij} \qquad (3\text{-}7)$$

where the parameters are defined as in the Grubbs CB model, i.e.

$i = 1,\dots,n$ denoting batches
$j = 1,\dots,m$ denoting laboratories
$y_{ij}$ = value of batch $i$ as measured by lab. $j$

$x_i$ = "true" value of batch $i$
$e_{ij}$ = random error associated with the measured value $y_{ij}$
$c_j, a_j$ = parameters describing the bias of lab. $j$ in the following way:

| | | |
|---|---|---|
| $a_j = 0$ | and $c_j = 1$ | no bias of lab. $j$ |
| $a_j \neq 0$ | and $c_j = 1$ | constant bias |
| $c_j \neq 1$ | bias depends linearily on batch magnitude $x$ | |

The NCB model corresponds to a special case of the two-way analysis of variances with interaction.

As with the Grubbs CB model absolute biases cannot be estimated since constraints on $a_j$ and $c_j$ have to be made. Jaech$^{(7)}$ uses the side conditions

$$a_k = 0 \quad \text{and} \quad c_k = 1 \qquad (3\text{-}8)$$

i.e. he arbitrarily fixes the bias of the measurement of laboratory $k$ equal to zero, to which the biases of the other laboratories are then related.

Estimates of biases $(a_j, c_j)$, of individual random error variances $(s^2_{e_j})$, of batch values $(x_i)$ and of the variance (or precision) of those parameters can be derived. For further details see appendix A.

Procedures for testing the hypotheses

1. that all random error variances $(s^2_{e_j})$ are equal, and

2. that there exist biases $c_j \neq 1$ are given in ref. (7).

Both hypotheses are tested by Chi-square tests but will not be summarized in appendix A because these tests were not used in the data evaluation of ICE-1.

Similarily to the Grubbs CB model one may obtain up to m + 1 estimates for each $s^2_{e_j}$ by by excluding either none or in turn one of the laboratories from the analysis. The estimate with the smallest variance $(\mathrm{var}(s^2_{e_j}))$ could then be chosen provided all variances of the same analysis are greater than zero. However, it should be noted that the tests described in reference (7) refer only to parameter values coming from the same combination of laboratories.

As stated in appendix B, the use of the non-constant-bias model instead of the Grubbs constant-bias model and a transformation of data strongly reduces the number of negative estimates of random error variances. Thus, the NCB model should first be applied in order to check for significant biases $c_j \neq 1$ .

### 3.2 Isotope correlation technique

The main aims of the isotope correlation technique (ICT) are

1) consistency check within a group of measured data (mass-spectrometric data and mass-spectrometric isotope-dilution data),

2) consistency check with "historical" data of irradiated nuclear fuel, and

3) the evaluation of the mass balances of Pu and U.

ICT is based on the fact that among certain isotope abundances or nuclide contents, isotope abundance ratios, Pu/U ratio or burn-up of spent fuel, relationships exist which can be described by a polynomial function

$$Y = \sum_{i=o}^{k} b_i \cdot X^i \qquad (3\text{-}9)$$

where $X$ and $Y$ stand for quantities such as nuclide content, isotope abundance and/or isotope abundance ratios. The simplest case would be that of a linear relationship between $X$ and $Y$ which corresponds to $k = 1$ in equation (3-9), i.e.

$$Y = b_o + b_1 \cdot X \qquad (3\text{-}10)$$

In some cases more complicated relationships might be treated by equation (3-10) after appropriate data transformation, or by exponential functions.

For ICE-1, two different approaches have been used for determining the correlations.

#### 3.2.1 Theoretical calculations

With this method$^{(9)}$, described in more detail in appendix C, concentrations of nuclides (of uranium, of plutonium, and of cesium, as well as of Nd-148) were calculated as functions of burn-up starting with reactor data such as type of reactor and fuel, fuel composition and enrichment and taking into account the reactor power history.

Based on these functions, the ratios of Pu/U concentrations were calculated from measured isotope abundance ratios. An intercept $b_o = 0$ was assumed in all cases. The regression coefficients $b_1$ of these relationships were expressed as 3rd order polynomials $C_o + C_1 \cdot Ft + C_2 \cdot Ft^2 + C_3 \cdot Ft^3$, Ft being burn-up and where the coefficients $C_i$ depend on initial enrichment. Since $b_1$ depends on burn-up, the overall relation is not linear anymore but corresponds to a 3rd order polynomial (eq. (3-9)).

These calculations have been limited to a small number of correlations known to be the less sensitive to the approximations of the coefficient calculations.

Finally the input masses of uranium and plutonium were calculated by the gravimetric method (see chapter 4). It has been shown that this technique gives results as precise as analytical measurements.

### 3.2.2 Regression analysis

Regression analysis is the well known statistical method developed for fitting measured values $(x_i, y_i)$, which exhibit random errors, to a specified function, i.e. to equation (3-9) or (3-10). The parameters of those functions and their variances are determined by the least squares method which consists of minimizing the sum of squares (SS) of weighted residuals $(res_i)$ about the regression line:

$$SS = \sum_{i=1}^{n} w_i \cdot res_i^2 \qquad (3\text{-}11)$$

where

$res_i$ = difference between measured point $(x_i, y_i)$ and its value calculated according to the assumed function,

$w_i$ = statistical weight of the measured point, (for non-weighted measurements, $w_i = 1$).

$n$ = number of points $(x_i, y_i)$

For a linear regression function the correlation coefficient (R), confidence regions of the estimated regression line, and prediction intervals for a future observation may be estimated in addition to parameters of the regression function.

Procedures exist for testing the significance of the correlation coefficient, i.e. of $R \neq 0$, of the slope $b_1 \neq 0$, of the rest variance, and of the goodness of fit of the measured values to the estimated straight line when individual errors of each measured point are available.

When either variable X or Y is free of error these evaluations can be found in relevant statistical textbooks.

When one has to deal with errors in both directions several approaches exist for the definition and the determination of the minimum sum of squares (eq. (3-11)) and for the estimation of all possible parameters of the regression function. Details and references can be found in appendix A.

Table 3.1 lists the variables of a number of linear functions used in data evaluation of ICE-1 most of them having been recommended by Napier and Timmerman(10). For an illustration the numerical data of some of the correlations are presented in table 3.11.

Table 3.1: Variables of linear functions used in data evaluation of ICE-1

1. Pu/U ratio correlations

| | | |
|---|---|---|
| Pu/U | versus | Ft |
| Pu/U | " | U-236 (w/o) |
| Pu/U | " | D-U-235 (w/o) |
| Pu/U | " | Pu-240 (w/o) |
| Pu/U | " | Pu-241 (w/o) |
| Pu/U | " | Pu-242 (w/o) |
| Pu/U | " | (100 - Pu-239 (w/o)) |
| Pu/U | " | $(\text{Pu-242} \cdot \text{Pu-239})/(\text{Pu-240})^2$ |
| Pu/U | " | Cs-134/137 |

2. Burn up correlations

| | | |
|---|---|---|
| D-U-235 | versus | Ft |
| U-236 | " | Ft |
| Pu-239 IMA | " | Ft |
| Pu-240 IMA | " | Ft |
| Pu-241 IMA | " | Ft |
| Pu-242 IMA | " | Ft |
| Pu-242/Pu-240 | " | Ft |
| Pu/U | " | Ft |

$\text{D-U-235} = (\text{U-235}^o - \text{U-235})/\text{U-235}^o$

3. Isotope abundance functions

| | | |
|---|---|---|
| U-235 | versus | U-236 |
| U-235 | " | $(\text{Pu-239})^2$ |
| U-235 | " | Pu-240/Pu-239 |
| Pu-239 | " | Pu-241/Pu-240 |
| Pu-240 | " | $\text{Pu-239} \cdot (100 - \text{Pu-239})$ |
| Pu-240 | " | $(\text{Pu-239} \cdot \text{Pu-240})^2$ |
| Pu-241 | " | Pu-239 |
| Pu-241 | " | Pu-242/Pu-241 |
| Pu-242 | " | Pu-242/Pu-240 |
| $\text{Pu-239} \cdot \text{Pu-240}$ | " | $\text{U-235} \cdot \text{Pu-241}$ |
| $\text{Pu-240} \cdot \text{Pu-241}$ | " | $\text{U-235} \cdot \text{Pu-242}$ |
| $\frac{(\text{Pu-239})^2 \cdot (100 - \text{Pu-239})}{(\text{U-235})^2}$ | " | (100 - Pu-239) |

Table 3.1 continued

4. Correlations between nuclide concentrations and different isotope ratios

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| U-235 | versus | Pu-242/240 | or | D-U-235 | or | Cm-244 IMA | or | Xe-132/131 | or | Cs-134/137 |
| U-236 | " | Pu-242/240 | or | D-U-235 | or | Cm-244 IMA | or | Xe-132/131 | or | Cs-134/137 |
| U-238 | " | Pu-242/240 | or | D-U-235 | or | Cm-244 IMA | or | Xe-132/131 | or | Cs-134/137 |
| Pu-239 | " | Pu-242/240 | or | D-U-235 | or | Cm-244 IMA | or | Xe-132/131 | or | Cs-134/137 |
| Pu-240 | " | Pu-242/240 | or | D-U-235 | or | Cm-244 IMA | or | Xe-132/131 | or | Cs-134/137 |
| Pu-241 | " | Pu-242/240 | or | D-U-235 | or | Cm-244 IMA | or | Xe-132/131 | or | Cs-134/137 |
| Pu-242 | " | Pu-242/240 | or | D-U-235 | or | Cm-244 IMA | or | Xe-132/131 | or | Cs-134/137 |

5. Correlations between isotope ratios

| | | |
|---|---|---|
| U-235/U-238 | versus | U-236/U-238 |
| Pu-241/Pu-239 | " | Pu-240/Pu-239 |
| Pu-240/Pu-239 | " | U-235/U-238 |
| Pu-241/Pu-240 | " | Pu-240/Pu-239 |
| Pu-242/Pu-241 | " | Pu-240/Pu-239 |
| Pu-242/Pu-240 | " | Pu-240/Pu-239 |
| Pu-242/Pu-240 | " | Pu-242/Pu-241 |

## 3.3 Results of the statistical evaluation

The results presented in this section will have an illustrative nature to show how the different statistical methods have been used, it is not intended to present a complete statistical analysis of the data. The reason for this is that each of the participating data evaluation groups used different data sets but no group performed a complete statistical analysis which would render possible a comparison of the statistical methods described in section 3.1. The different data sets stem from the use of isotope abundance data (w/o) and of nuclide concentration data (atoms/IMA). Both data sets were subjected to Pu-241 decay corrections using different values of its half-live and analysed for outliers applying different outlier criteria.

### 3.3.1 Detection of outliers

Screening for outliers has been performed for both isotope abundance and nuclide concentration data. The results are compiled in tables 3.2 and 3.3. It may be worthwhile to point out that the different Pu-241 decay corrections mentioned above do not influence the outcome of the outlier analysis as long as all data of the same data set had been corrected the same way.

The Dixon criterion(1) was applied to the original data $y_{ij}$, $j=1,..m$ of batch $i$ (for definitions see chapter A.1) and to standardized data $y'_{ij}$, $i=1,...n$ of lab $j$, the standardization being

$$y'_{ij} = (y_{ij} - y_{i.})/s_{y_i} \qquad (3\text{-}12)$$

where

$$s^2_{y_i} = \frac{1}{m-1}\sum_{j=1}^{m}(y_{ij} - y_{i.})^2 \qquad (3\text{-}13)$$

is the variance of batch $i$ values when measured by $m$ laboratories.

The Grubbs criterion(2) was used for the original data $y_{ij}$, $j=1,...m$ and for multiple paired comparisons, i.e. it was applied to $i=1,..n$ differences of measurements ($v_{ijk}$) of lab $j$ and lab $k$ (see eq. (A-22)). In the latter case an outlier was attributed to lab $j$ when it was found in all possible paired comparisons involving lab $j$. To detect outliers using multiple paired comparisons the 2-$\sigma$-limits of the normal distribution had also been used.

With isotope correlations, datapoints were labeled outliers when they either lay outside the ± $2 \cdot s_{y.x}$-band (eq. (A-51)) of the regression-line or outside the 95% confidence limits of the regression for a single observation using the Student-t distribution. An outlier found with an isotope regression $Y = b_o + b_1 \cdot X$ was attributed to the variable $Y$ when it was also detected with isotope correlations involving $Y$ but other variables $X$.

Tables 3.2 and 3.3 reveal that each of the statistical methods and outlier criteria selects different data as outliers. Nevertheless, two main results can be stated. First, strong outliers such as SAL 93 of Pu-242, SAL 93 and WAK 90 of Pu-242/240 and Pu-242/241, or WAK 94 and WAK 95 of U-234 are found by most of the criteria and methods. Secondly, the results of the outlier detection by the isotope correlation technique, i.e. linear regression, compare well with those of the other methods. However, it should be kept in mind that in addition to detection of outliers due to measurement errors, outlying batches due to physical reasons are identified with ICT but

Table 3.2: Outliers detected by different statistical evaluation methods and outlier criteria. Nuclides refer to isotope abundance (w/o). Different α values originate from different statistical evaluations.

| quantity | Dixon criterion on standardized data[1] | paired comparison[2] | linear regression[3] |
|---|---|---|---|
| | α = 0.01 | normal distribution | α = 0.045 (± 2σ) |
| U-234 | | WAK 94+95 | |
| U-235 | | RCH 87, TU 94 | TU 94, WAK 93 |
| U-236 | | WAK 93 | WAK 95 |
| U-238 | RCH 87+94, SAL 94, TU 94 | TU 94 | |
| Pu-238 | | WAK 92 | |
| Pu-239 | WAK 88 | RCH 87 | RCH 87, SAL 93, WAK 87+92 |
| Pu-240 | | | WAK 87+92 |
| Pu-241 | RCH 87+94, TU 86;<br>RCH 88, SAL 88, TU 88,<br>WAK 88 | RCH 87+95, WAK 87+91+95 | RCH 87, TU 94, WAK 87 |
| Pu-242 | SAL 93 | SAL 93, WAK 90 | SAL 93, WAK 86+87+90 |
| U-235/U-238 | | - | - |
| Pu-241/Pu-239 | WAK 87; RCH 88, SAL 88,<br>TU 88, WAK 88 | - | - |
| Pu-242/Pu-239 | WAK 93 | - | - |
| U total | | RCH 86 | |
| Pu total | - [4] | RCH 95 | |
| Pu/U | - | | RCH 95, TU 86, WAK 92+93+94+95 |

[1] $y'_{ij} = (y_{ij} - y_{i.})/s_{y_i}$ (see eq. (3-12))

[2] multiple application to differences of measurements as defined in eq. (A-22)

[3] linear regression based on data of SAL

[4] -no evaluation performed

Table 3.3: Outliers detected by different statistical evaluation methods and outlier criteria. Nuclides refer to nuclide concentration (atoms/IMA).

| quantity | Dixon criterion on original data | original data | paired comparison[1] | linear regression[2] |
|---|---|---|---|---|
| | α = 0.05 | Grubbs criterion | α = 0.05 | Student - t α = 0.05 |
| U-234 | WAK 87+94+95 | WAK 94 | TU 93, WAK 94+95 | SAL 92, TU 95, WAK 94+95 |
| U-235 | RCH 90 | RCH 90 | TU 94 | |
| U-236 | WAK 93 | WAK 93 | | |
| U-238 | SAL 87, WAK 86+93 | SAL 87, WAK 92+93 | | WAK 86 |
| Pu-238 | SAL 89 | | SAL 94, WAK 92 | WAK 92 |
| Pu-239 | WAK 87+89+92+93 | WAK 87+89+92 | | |
| Pu-240 | WAK 87 | WAK 87 | | |
| Pu-241 | WAK 92 | WAK 93 | | |
| Pu-242 | RCH 95, WAK 92 | RCH 95 | SAL 93 | SAL 93, WAK 90 |
| U-235/U-238 | RCH 90 | RCH 90 | TU 94 | TU 94 |
| Pu-240/Pu-239 | WAK 87090+94 | WAK 87+90+94 | WAK 88 | |
| Pu-241/Pu-239 | WAK 94 | | | |
| Pu-242/Pu-240 | SAL 93, WAK 88+90 | SAL 93, WAK 90+95 | SAL 93, WAK 90 | SAL 93, WAK 86+90 |
| Pu-242/Pu-241 | SAL 93, WAK 86+90 | SAL 93, WAK 86+90 | SAL 93, WAK 90 | SAL 93, WAK 86+90 |
| U total | WAK 94+95 | - [3] | - | - |
| Pu total | | - | - | - |
| Pu/U | TU 86, WAK 92+93 | - | - | - |

---

[1] multiple application to differences of measurements as defined in eq. (A-22)

[2] linear regression based on data of RCH + SAL + TU + WAK

[3] -no evaluation performed

not with the other statistical methods, except for the Dixon criterion applied to standardized data.

The latter method may select a complete batch as an outlier instead of a single measurement as can be seen in table 3.2, column 1, where batch 88 of Pu-241 and of Pu-241/Pu-239 are labeled as outliers. Furthermore, table 3.3 shows that the Dixon criterion at the significance level $\alpha = 0.05$ seems to point out too many data as outliers.

Finally, it should be noted that the initial search for outliers of Pu-isotopes should be done on isotope abundance data and only subsequently on nuclide concentration data. The influence of data transformation from isotope abundance to nuclide concentration is shown for U-235 and Pu-239 in figures 3.1 and 3.2. The graphs show clearly that in contrast to the U-235 data the spread of the Pu-239 data as indicated by the standard deviations of the batches is much larger for nuclide concentration data than for those of isotope abundances. This is due to the imprecisions of the plutonium content measurements. Thus, the increased standard deviation reduces the selectivity of the outlier detection. As an example take batch 95 of the Pu-239 isotope abundance measurement. The Grubbs criterion applied to the original data of 4 laboratories labels WAK 95 as an outlier with significance level $\alpha = 0.01$ whereas in the Pu-239 nuclide concentration determination no outlier can be detected any more because the variation coefficient of batch 95 is raised from 0.29 % for the Pu-239 isotope abundance to 4.94 % for the Pu-239 nuclide concentration.

As a summary of this chapter the following can be stated:

1. Screening for outliers in Pu-isotope determinations should be done on isotope abundance data and only subsequently on nuclide concentration data.

2. Strong outliers are found with all outlier criteria and statistical methods applied.

All results presented in chapters 3.3.2 and 3.3.3 are based on data from which outliers had been removed exept for a few statistical analyses which had been performed on the total data.

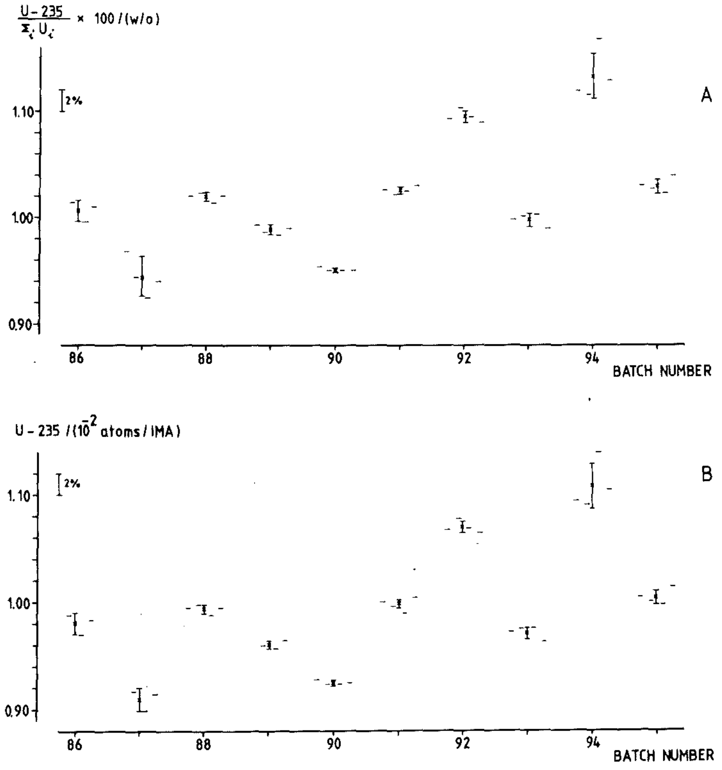

Figure 3.1: Isotope abundance (A) and nuclide concentration (B) of U-235.
Order of laboratories: RCH - SAL - TU - WAK

batch mean ± 1s

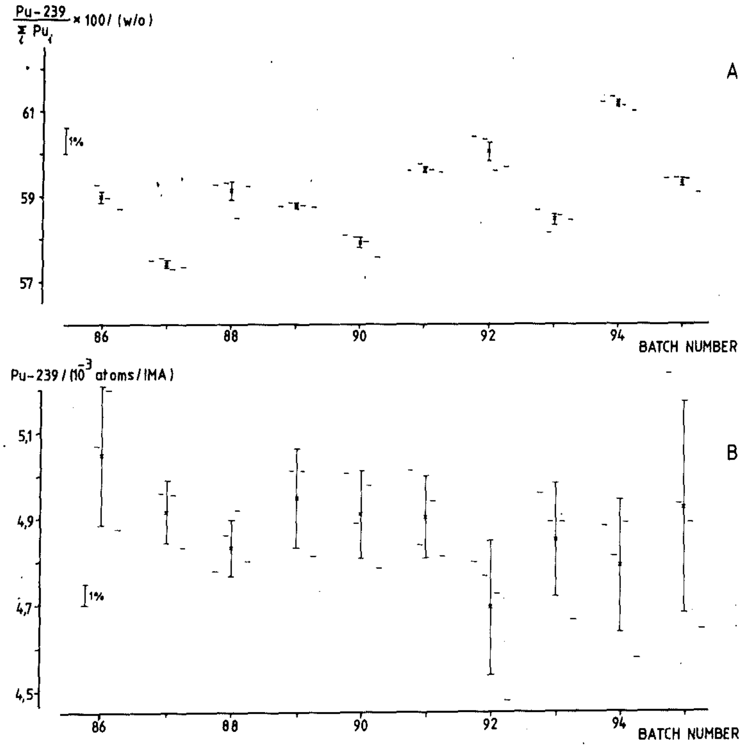

Figure 3.2: Isotope abundance (A) and nuclide concentration (B) of Pu-239.
Order of laboratories: RCH - SAL - TU - WAK

I batch mean ± 1s

### 3.3.2 Estimation of random errors

1. Grubbs' constant-bias model (CBM) and ICT

The random error variances $(s^2_{e_j})$ and the inherent variances $(\mathrm{var}(s^2_{e_j}))$ were calculated according to equations (A-25) and (A-26) respectively. The variation coefficients $(V_j)$ are given in table 3.4 for the isotope abundance data and in table 3.5 for the nuclide concentration data.

Those variation coefficients

$$V_j = s_{e_j} / y_{.j} \cdot 100\ (\%)\ , \qquad j=1,\ldots 4 \qquad (3\text{-}14)$$

are chosen which have the smallest variance $\mathrm{var}(s^2_{e_j})$, i.e. highest precision out of those values estimated by applying Grubbs' analysis to all of the four data sets and then to all combinations of three data sets excluding in turn one data set from the analysis as described in section 3.1.3. Dashes indicate that there are no estimates available from calculations which yield positive variances for each of the laboratories. In addition, table 3.5 contains variation coefficients (V(IC)) obtained by use of eq. (A-52) for different isotope regressions $Y = b_o + b_1 \cdot X$ , where the independent variable X was presumed to be free of error.

The increased measurement imprecision of nuclide concentrations in comparison to isotope abundances as shown in tables 3.4 and 3.5 was already stated in section 3.3.1.

The results obtained for variation coefficients (V) by the Grubbs constant-bias model and by the isotope correlation technique as shown in table 3.5 for nuclide concentration data show acceptable agreement for Pu-isotopes and for U-238, thus showing that ICT may replace additional measurements needed for the evaluation of measurement imprecision. In most cases V(IC), calculated by ICT, exceeds V(GR), calculated by Grubbs' method, since minor systematic errors which increase the estimated value of V(IC) cannot be excluded (for details see section A.4.3). It should also be noted that because of the small sample number $(n \leq 7)$ the imprecisions $(\mathrm{var}(s^2_{e_j}))$ of the estimated variances $(s^2_{e_j})$ are of the same order as the variances themselves. An attempt to reduce those imprecisions may be found in appendix B; the results of an application to isotope abundance data are presented in table B.2. Large scatter between V(GR) and V(IC) is found for U-235 measurements of all laboratories. This is

Table 3.4: Variation coefficient[1] (V) as estimated according to Grubbs' constant-bias model (CBM) (eq. (A-25)) and to the non-constant-bias model (NCBM) (eq. (A-40)). Outliers excluded using the Dixon criterion(1) on standardized data at $\alpha = 0.01$. Nuclides refer to isotope abundance (w/o).

| quantity | Model | RCH | | SAL | | TU | | WAK | |
|---|---|---|---|---|---|---|---|---|---|
| | | n[2] | V | n | V | n | V | n | V |
| U-234 | CBM | 9 | 2.90 | 9 | 4.10 | 9 | 8.09 | | -[3] |
| | NCBM | 9 | 3.03 | 9 | 3.89 | 9 | 8.01 | | - |
| U-235 | CBM | 9 | 0.79 | 9 | 0.56 | 9 | - | 9 | 0.79 |
| | NCBM | 9 | 0.79 | 9 | 0.56 | 10 | 1.25 | 9 | 0.78 |
| U-236 | CBM | 9 | 0.22 | 9 | 0.67 | 9 | 0.88 | 9 | 1.24 |
| | NCBM | 9 | 0.21 | 9 | 0.68 | 9 | 0.87 | 9 | 1.23 |
| U-238 | CBM | 7 | 0.007 | 7 | 0.004 | 7 | 0.006 | | - |
| | NCBM | 7 | 0.007 | 7 | 0.004 | 7 | 0.006 | | - |
| Pu-238 | CBM | 9 | 6.12 | 9 | 3.37 | 9 | 3.95 | 10 | 25.6 |
| | NCBM | 9 | 5.82 | 9 | 3.34 | 9 | 4.08 | 10 | 25.7 |
| Pu-239 | CBM | 8 | 0.14 | 8 | 0.29 | 8 | 0.14 | 8 | 0.39 |
| | NCBM | 8 | 0.14 | 8 | 0.30 | 8 | 0.13 | 8 | 0.38 |
| Pu-240 | CBM | 9 | 0.22 | 10 | 0.51 | 9 | 0.38 | 9 | 0.77 |
| | NCBM | 9 | 0.24 | 10 | 0.56 | 9 | 0.37 | 9 | 0.77 |
| Pu-241 | CBM | | - | | - | | - | | - |
| | NCBM | | - | | - | | - | | - |
| Pu-242 | CBM | 8 | 0.41 | 8 | 0.48 | 8 | 0.83 | | - |
| | NCBM | 8 | 0.47 | 8 | 0.39 | 8 | 0.88 | 8 | 3.79 |
| U total | CBM | | - | | - | | - | | - |
| | NCBM | | - | | - | | - | | - |
| Pu total | CBM | 7 | 0.29 | 7 | 1.29 | 10 | 0.89 | 10 | 0.35 |
| | NCBM | | - | 7 | 1.31 | 10 | 1.04 | | - |

[1] variation coefficients ($V_j = s_{e_j}/y_{.j} \cdot 100(\%)$) with smallest variance ($var(s_{e_j}^2)$) are chosen as described in section 3.1.3

[2] n = number of samples

[3] - no estimate available from calculation yielding positive variances for each of the laboratories.

probably due to crosscontamination which increases the scatter of the data points around the regression line.

Furthermore, V(IC) values for an isotope Y based on the measurement of one laboratory estimated by different isotope correlations show only slight scatter. Outlying values suggest that the assumptions made, i.e. X free of error and linear model, are not fulfilled.

The statistical significance of the differences among the imprecisions ($s_{e_j}^2$) of the nuclide concentration data was evaluated by use of Jaech's $\lambda$-test(5,6), the results of which are presented in table 3.6. It should be remarked, that the data sets of tables 3.5 and 3.6, although both apply to nuclide concentrations, differ slightly because of the different outlier criteria used. Table 3.6 shows that the measurement performances of the laboratories involved in this experiment were in many cases statistically not different, significant differences were found for U-234, U-235, Pu-238, Pu-241 as well as for Pu-241/ Pu-239 determinations. No such tests were performed on isotope abundance data.

## 2. Non-constant-bias model

The results of the statistical analysis using the non-constant-bias model (NCBM) applied to isotope abundances may be found in table 3.4 within the lines labeled NCBM. Variation coefficients ($V_j$) entered in the table

Table 3.5: Comparison of variation coefficients (V(%)) obtained by Grubbs' constant-bias model (eq. (A-25)), and by isotope correlations (eq. (A-52)). Isotope correlations $Y = b_o + b_1 \cdot X$, where X is presumed to be free of error. Outliers excluded according to the Grubbs criterion(2) at $\alpha = 0.05$, samples 88 and 90 to 95 for nuclide concentration data (atoms/IMA).

| quantity | Method<br>GR=Grubbs analysis<br>IC=Isotope Correlation | RCH | SAL | TU | WAK |
|---|---|---|---|---|---|
| U-235 | V (GR) | 0.36 | 0.46 | 0.32 | 1.04 |
| | V (IC) for | | | | |
| Y = U-235 | X = Pu-240/239 | 1.41 | 2.17 | 1.63 | 1.86 |
| | Pu-242/240 | 0.94 | 1.91 | 1.25 | 1.57 |
| | Pu-242/241 | 1.48 | 2.17 | 1.52 | 1.67 |
| | Nd-146/145 | | | 1.44 | |
| U-238 | V (GR) | 0.02 | 0.02 | 0.03 | 0.02 |
| | V (IC) for | | | | |
| Y = U-238 | X = Pu-240/239 | 0.03 | 0.03 | 0.04 | 0.05 |
| | Pu-242/240 | 0.04 | 0.02 | 0.04 | 0.03 |
| | Pu-242/241 | 0.04 | 0.03 | 0.04 | 0.04 |
| | Nd-146/145 | | | 0.04 | |
| Pu-239[1] | V (GR) | | 1.15 | 0.46 | 1.50 |
| | V (IC) for | | | | |
| Y = Pu-239 | X = U-235/238 | | 1.69 | 0.83 | 2.13 |
| | Pu-240/239 | | 1.76 | 0.92 | 2.51 |
| | Pu-242/240 | | 1.90 | 0.84 | 2.20 |
| | Pu-242/241 | | 1.99 | 0.88 | 2.25 |
| Pu-240 | V (GR) | 2.80 | 0.71 | 0.59 | 1.78 |
| | V (IC) for | | | | |
| Y = Pu-240 | X = U-235/238 | 1.99 | 1.52 | 0.86 | 1.43 |
| | Pu-240/239 | 2.23 | 0.96 | 0.77 | 2.69 |
| | Pu-242/240 | 2.35 | 1.59 | 0.54 | 2.19 |
| | Pu-242/241 | 2.65 | 1.46 | 0.70 | 2.60 |
| | Nd-146/145 | | | 0.86 | |
| Pu-241 | V (GR) | 3.02 | 0.99 | 1.01 | 0.69 |
| | V (IC) for | | | | |
| Y = Pu-241 | X = U-235/238 | 2.20 | 1.29 | 2.23 | 2.05 |
| | Pu-240/239 | 2.73 | 1.02 | 1.34 | 3.19 |
| | Pu-242/240 | 2.79 | 1.41 | 0.83 | 2.74 |
| | Pu-242/241 | 3.09 | 1.40 | 1.16 | 3.16 |
| | Nd-146/145 | | | 1.27 | |
| Pu-242 | V (GR) | 2.77 | 0.72 | 1.87 | 5.40 |
| | V (IC) for | | | | |
| Y = Pu-242 | X = U-235/238 | 2.23 | 2.96 | 2.09 | 2.27 |
| | Pu-240/239 | 2.48 | 1.22 | 1.99 | 4.75 |
| | Pu-242/240 | 2.52 | 1.64 | 1.48 | 2.19 |
| | Pu-242/241 | 3.21 | 1.48 | 1.93 | 2.82 |
| | Nd-146/145 | | | 2.00 | |

[1] Calculations based on 10 samples (88 to 95) available only for SAL, TU, and for WAK

correspond to random error variances $(s^2_{e_j})$ which have the minimum $\mathrm{var}(s^2_{e_j})$ values from the CB model since the parameter $\mathrm{var}(s^2_{e_j})$ was not estimated in the NCB model.

For Pu-241 and U-total no data set combination resulted in positive values for the random error variances for either of the laboratories. The total number of calculated negative variances is almost equal for both the CB and the NCB model. For the NCB model this number can be reduced considerably after an appropriate data transformation as described in appendix B. The results of the NCB model applied to standardized data may be found in table B.2.

Table 3.6: Laboratory random error variances $(s^2_{e_j})$ tested for significant differences with the $\lambda$-test proposed by Jaech(5). Variances estimated by Grubbs' constant-bias model (eq. (A-25)). Nuclide concentration data are in units of atoms/IMA. Outliers were excluded according to the Dixon criterion(1) at $\alpha = 0.05$. Samples 88 and 90 to 95.

| quantity | significant difference |
|---|---|
| U-234 | yes |
| U-235 | yes |
| U-236 | no |
| U-238 | -1) |
| Pu-238 | yes |
| Pu-239 | - |
| Pu-240 | no |
| Pu-241 | yes |
| Pu-242 | - |
| U-235/U-238 | no |
| Pu-240/Pu-239 | no |
| Pu-241/Pu-239 | yes |
| Pu-241/Pu-240 | no |
| Pu-242/Pu-240 | - |
| Pu-242/Pu-241 | - |
| U total | no |
| Pu total | no |
| Pu/U | no |

1)

- no test performed since the Grubbs analysis yielded in this case a negative estimate of variances

3. Analysis of variances (ANOVA)

The work done within the frame of ANOVA consists mainly of two tests based on the F-distribution.

a) The mean of the random error variances $(s^2_{e_j})$, i.e.

$$\frac{1}{m} \sum_{j=1}^{m} s^2_{e_j} \; , \qquad (3\text{-}15)$$

estimated by the Grubbs CB model was compared to the random error variance $(s^2_e)$ estimated by ANOVA via eq. (A-7) for isotope abundance data, i.e. the term

$$\mathrm{ERROR} = \frac{1}{m} \sum_{j=1}^{m} s^2_{e_j} \, / \, s^2_e \qquad (3\text{-}16)$$

was tested versus $F(\alpha; \nu_{CBM}, \nu_{ANOVA})$ with $\alpha = 0.05$, although it was not previously tested if pooling of the $s^2_{e_j}$ was possible. The degree of freedom

$$\nu_{CBM} \sim (n-1) \frac{\left(\sum_{j=1}^{m} s^2_{e_j}\right)^2}{\sum_{j=1}^{m} s^4_{e_j}} \qquad (3\text{-}17)$$

was derived from Satterthwaite's formula, whereas $\nu_{ANOVA} = \nu_r$ according to table A.1. In no case was the ERROR-term significant, which means the pooled estimate obtained by the CB model and $s^2_e$ obtained by ANOVA should both be valid estimates of the precision.

b) Nuclide concentration data were tested for their applicability to isotope correlations by testing the hypothesis $H_b$ of the analysis of variances, i.e. by checking the test parameter

$$F_b = \frac{m(n-1)}{n} \cdot \frac{V^2_{IB}}{V^2_{IL}} \qquad (3\text{-}18)$$

against the value $F(\alpha; n-1, (m-1)\cdot(n-1))$ of the F-distribution at significance levels $\alpha = 0.01$ and 0.05. For further details see section A.1, eq. (A-17).

In table 3.7 the interlaboratory coefficients of variation $(V_{IL})$, the interbatch coefficients of variation $(V_{IB})$ and the correspondent $F_b$-values are given. Those of U-234, Pu-238 and Pu-239 marked with an asterisk are smaller than $F(0.05; 6, 18) = 2.66$. This means that the batch variation is not significantly different from the random error variance, thus labeling these isotopes as inadequate for isotope correlations.

Table 3.7: Interlaboratory coefficient of variation ($V_{IL}$ (%)) and interbatch coefficient of variation ($V_{IB}$ (%)) as calculated by the analysis of variances (eq. (A-12) and (A-13)). Outliers were excluded according to the Dixon criterion$^{(1)}$ at $\alpha = 0.05$. Single nuclides refer to nuclide concentration (atoms/IMA). Samples 88 and 90 to 95.

| quantity | $V_{IL}$ | $V_{IB}$ | $F_b^{1)} = \frac{V_{IB}^2}{V_{IL}^2} \cdot \frac{m(n-1)}{n}$ |
|---|---|---|---|
| U-234 | 5.03 | 3.52 | 1.8* |
| U-235 | 0.95 | 6.09 | 147.9 |
| U-236 | 0.96 | 2.03 | 16.1 |
| U-238 | 0.036 | 0.119 | 39.3 |
| Pu-238 | 16.3 | 12.6 | 2.15* |
| Pu-239 | 2.34 | 1.84 | 2.23* |
| Pu-240 | 2.52 | 4.90 | 13.6 |
| Pu-241 | 2.61 | 4.93 | 12.8 |
| Pu-242 | 2.79 | 11.3 | 59.1 |
| U-235/U-238 | 0.97 | 5.97 | 136.4 |
| Pu-240/Pu-239 | 0.30 | 3.44 | 473.0 |
| Pu-241/Pu-239 | 0.75 | 3.88 | 96.3 |
| Pu-241/Pu-240 | 0.48 | 0.59 | 5.5 |
| Pu-242/Pu-240 | 2.98 | 6.55 | 17.4 |
| Pu-242/Pu-241 | 1.59 | 6.01 | 51.4 |
| U total | 1.05 | 6.69 | 146.1 |
| Pu total | 1.89 | 5.60 | 31.6 |
| Pu/U | 2.47 | 3.10 | 5.7 |

F - statistic : F (0.01; 6, 18) = 4.01
F (0.05; 6, 18) = 2.66

* $F_b$ < F (0.05; 6, 18)

1) $F_b$ : test parameter as defined in eq. (3-18, (A-17) and (A-20)

The underlying assumption of no significant laboratory biases was not fulfilled for some items of table 3.7 as follows partly from table 3.10 of section 3.3.3. In such a case $V_{IL}^2$ underestimates the random error variance ($s_e^2$) (see eq. (A-15)) and therefore, according to eq. (3-18), some items of table 3.7 should also have been marked with an asterisk.

### 3.3.3 Estimation of biases

The estimation of biases, i.e. of systematic errors by use of ICT is possible only if reliable "historical" data of the same reactor type, the same fuel type and composition and of the same burn-up range exist as is the case for the Obrigheim reactor. Only one isotope correlation (Pu-239/Pu-241 versus Pu-240/Pu-242) including present and historical data has been examined and this showed a discrepancy in decay time corrections.

1. Non-constant-bias model

The parameters $c_j$ expressing the dependency of biases on batch magnitude as described by the NCB model (eq. (3-7)), were determined for isotope abundances. The $c_j$ were calculated relative to WAK measurements, i.e. $c_{WAK} = 1.0$ was presumed. The results may be found in table 3.8 for the analysis of 4 laboratories (WAK; RCH, SAL, TU) and of 3 laboratories (WAK; SAL, TU). No tests concerning the statistical significance of the $c_j$ deviating from 1.0 have been undertaken. Nevertheless, some features can be pointed out.

The comparison of the results of the 4-lab analysis with the 3-lab analysis shows that for the first one the deviations of the $c_j$ from 1.0 are in most cases much smaller indicating a precision increase although the number of samples used in the analysis was usually higher in the 3-lab case.

For the 4-laboratory analysis deviations of the $c_j$ from 1.0 of about -4% and more for all laboratories are found for U-234 and Pu-242, suggesting that the assumption of $c_{WAK} = 1.0$ for WAK could be wrong.

Furthermore, $c_{RCH}$ of Pu-238 and of U-total as well as $c_{TU}$ of Pu-241 show larger deviations from 1.0 than the $c_j$ of the other two remaining laboratories, indicating a non-constant bias of the RCH and TU measurements. In all other cases the constant-bias model seems to be acceptable, since the $c_j$ do not differ too much from 1.0.

No attempt has been made to determine the constant portion ($a_j$) of the bias defined by the non-constant-bias model.

Table 3.8: Estimation of biases $c_j$ (eq. (A-37)) of the non-constant-bias model based on $c_{WAK} = 1.000$, outliers excluded according to the Dixon criterion$^{(1)}$ on standardized data at $\alpha = 0.01$. Nuclides refer to isotope abundance (w/o).

| quantity | number of labs$^{1)}$ | $n^{2)}$ | RCH | SAL | TU |
|---|---|---|---|---|---|
| U-234 | 4 | 9 | 0.933 | 0.962 | 0.871 |
| U-235 | 4 | 9 | 0.999 | 0.998 | 1.005 |
| | 3 | 10 | - | 0.960 | 1.183 |
| U-236 | 4 | 9 | 1.014 | 1.004 | 1.007 |
| | 3 | 10 | - | 1.259 | 0.866 |
| U-238 | 4 | 7 | 1.000 | 1.000 | 1.000 |
| | 3 | 9 | - | 1.000 | 1.000 |
| Pu-238 | 4 | 9 | 0.956 | 1.032 | 1.002 |
| | 3 | 10 | - | 0.813 | 1.023 |
| Pu-239 | 4 | 8 | 1.004 | 1.002 | 1.020 |
| | 3 | 9 | - | 1.003 | 1.020 |
| Pu-240 | 4 | 9 | 1.001 | 1.000 | 1.015 |
| | 3 | 10 | - | 1.192 | 1.348 |
| Pu-241 | 4 | 6 | 0.996 | 0.994 | 0.884 |
| | 3 | 8 | - | 0.996 | 0.888 |
| Pu-242 | 4 | 8 | 0.961 | 0.955 | 0.980 |
| | 3 | 9 | - | 0.940 | 0.964 |
| U total | 4 | 9 | 1.083 | 0.983 | 0.980 |
| | 3 | 10 | - | 0.960 | 0.965 |
| Pu total | 4 | 7 | 1.033 | 1.023 | 1.007 |
| | 3 | 10 | - | 0.791 | 0.904 |

1) 4 laboratories : WAK; RCH, SAL, TU
3 laboratories : WAK; SAL, TU

2) n = number of samples

2. Constant-bias model

The systematic errors or biases ($v_{.jk}$) between laboratory j and laboratory k according to the CB model were determined using eq. (A-24) from which relative percent biases (d) were derived according to eq. (3-19):

$$d = \frac{v_{.jk}}{0.5(y_{.j}+y_{.k})} \cdot 100\ (\%) \qquad (3\text{-}19)$$

The results for isotope abundance data with outliers included and for nuclide concentration data without outliers are given in tables 3.9 and 3.10 for those quantities (nuclides, U- and Pu-total) for which the relative bias is about 1 % or higher and the appropriate confidence level P is equal or higher than 95 %. In some cases values of $d < 1$ % and $P < 95$ % are given for comparison of results.

Table 3.9 shows that the U-236 measurements of RCH are about 1 % higher than those of the other laboratories. The Pu-238 determinations of TU deviate by 20 % to 36 % from those of the other 3 laboratories. This is due to the Pu-238 built-up by Cm-242 decay which depends on the date of analysis. The Cm-242 content had been determined by TU only and the TU data were subsequently corrected as of the date of fuel discharge. Apart from this it should be remembered that for the Pu-238 measurement of RCH a non-constant bias with $c_{RCH} = 0.956$ had been found, which nevertheless should cause only a minor difference.

The U-total determinations of WAK are about 2 % higher than those of the other laboratories. However, this result should be considered with caution since $c_{RCH} = 1.08$ was estimated with the non-constant-bias model.

On the other hand the Pu-total was measured by WAK about 2.2 % too low. This result is only slightly influenced by the fact that $c_{RCH}$, $c_{SAL}$ and $c_{TU}$ are about 2 % lower than $c_{WAK}$ of the NCB model (see table 3.8). Considering the mean and the range of the Pu-total values as measured by WAK ($1.125 \cdot 10^{-3}$g and $0.054 \cdot 10^{-3}$g respectively), the bias due to $c_{WAK} \neq 1.0$ can be estimated to be less than 0.1 % for this range of measured values.

For nuclide concentration data no comparative results of the non-constant-bias analysis exist, therefore the applicability of the constant-bias model cannot be checked and the results of it stand as such.

Table 3.10 shows that a strong bias of about 20 % exists for Pu-238 between TU and WAK on one side and RCH and SAL measurements on the other, which again is caused by Pu-238 built-up

Table 3.9: Percentage ratio (d)[1] of mean difference to mean content and level of confidence P (%) for paired comparison (see Grubbs' CBM, hypothesis $H_a$, section 3.1.3 and eq. (3-19)), outliers included. Nuclides refer to isotope abundance (w/o). Only those values are given for which P $\geq$ 95 % and d $\geq$ 1 %.

| quantity | n[2] | TU - WAK | | TU - RCH | | TU - SAL | | WAK - RCH | | WAK - SAL | | RCH - SAL | | signif.diff. in lab |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | d | P | d | P | d | P | d | P | d | P | d | P | |
| U-236 | 9 | | | - 0.92 | >98. | | | - 1.35 | >98 | | | 1.00 | >99. | RCH |
| Pu-238 | 9 | (-18.1 | 90.) | -36.5 | >99.99 | -22.0 | >99.99 | ( 1.33 | <90) | (- 3.93 | <90) | - 5.26 | >97 | TU |
| Pu-242 | 9 | | | 1.12 | >99.9 | | | 3.54 | >97. | | | | | |
| U total | 10 | - 2.23 | 99.99 | | | | | 1.42 | ∿93 | 1.88 | >99. | | | WAK |
| Pu total | 7 | 1.66 | >99.99 | | | | | - 3.34 | >98. | - 1.72 | >98. | | | WAK |

[1]
$$d = \frac{\frac{1}{n}\sum_{i=1}^{n}(y_{ij} - y_{ik})}{0.5(y_{.j} + y_{.k})} \cdot 100 \ (\%)$$

[2] n = number of samples

from Cm-242 decay taken into account only for TU measurements. However, no explanation for the lack of bias between TU and WAK data can be given, which amounted to - 18 % for the isotope abundance data. Moreover, the WAK measurements of Pu-239, Pu-240 and Pu-241 are about 4 %, 5 % and 3.5 % lower than those of TU, RCH and SAL, respectively, with relevant confidence levels greater than 99 %. Since these biases are not encountered with the isotope abundance data a systematic error must have been introduced by the data transformation from isotope abundance to nuclide concentration, i.e. by the bias of U-total and/or Pu-total. The bias cannot be caused by a biased burn-up determination, since the burn-up determined by TU had been used for data transformations of all four laboratories.

Minor biases at lower confidence levels are found for U-234, U-236 and Pu-242 in the measurements of SAL, RCH and SAL respectively.

### 3. Analysis of variances

The significance of systematic errors of isotope abundance data was evaluated by testing hypothesis $H_a$ (see 3.1.2 and eq. (A-16)). Differences in the laboratory biases at a significance level $\alpha = 0.05$ were found for U-236, Pu-239, Pu-240, Pu-241, Pu-242 and for Pu-total. These findings agree only partly with the results of the CB model, where in addition biases were detected for Pu-238 and U-total, but none in the measurements of Pu-239, Pu-240, Pu-241. The discrepancy is probably due to the use of different decay corrections and outlier criteria.

### 3.3.4 Some examples of the application of ICT to ICE data

As mentioned in chapter 3.2.2 and more explicitly demonstrated in chapter A.4 there exist different approaches to determine the parameters of a linear regression $Y=b_o + b_1 \cdot X$ in case the measurements of both variables X and Y bear random errors. In the Isotope Correlation Experiment the method of minimum distances (eq.(A-46)) and Deming's method (eq.(A-46)) was used.

For both methods the coordinates of a point $(\overline{x}_i, \overline{y}_i)$ were determined as the means of the values of batch i as measured by the four laboratories (or three in case of missing measurements). The variances $s^2(x_i)$ and $s^2(y_i)$ of the $x_i$ and $y_i$ values, respectively are used for the determination of the weights of point $(\overline{x}_i, \overline{y}_i)$ according to equations (A-48) and (A-50).

Results of some linear isotope regressions $Y = b_o + b_1 \cdot X$ based on the method of minimum distance involving nuclide concentrations and/or

Table 3.10: Percentage ratio (d)[1] of mean difference to mean concentration and level of confidence (P) for paired comparison (see GRUBBS CBM, hypothesis $H_a$, section 3.1.3 and eq. (3-19)), outliers excluded according to the criterion of GRUBBS at $\alpha = 0.05$ . Nuclide concentration data in units of (atoms/IMA). Only those values are given for which $P \geq 95$ % and $d \geq 1$ %.

| isotope | TU - WAK | | | TU - RCH | | | TU - SAL | | | WAK - RCH | | | WAK - SAL | | | RCH - SAL | | | sign.diff. in lab. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | d | P | n[2] | d | P | n | d | P | n | d | P | n | d | P | n | d | P | n | |
| U-234 | | | | | | | - 9.9 | >95. | 5 | | | | 4.9 | <95. | 5 | - 5.7 | 95. | 7 | (SAL) |
| U-236 | | | | - 0.8 | >90. | 7 | | | | - 1.5 | >95. | 7 | | | | 1.3 | 99.9 | 7 | (RCH) |
| Pu-238 | | | | -22.6 | 99.9 | 7 | -24.3 | 99.9 | 9 | -18.7 | 99.9 | 6 | | | | - 4.6 | 98. | 5 | |
| Pu-239 | 4.4 | 99.9 | 10 | | | | | | | - 5.7 | 99. | 7 | - 3.7 | 99.9 | 10 | | | | WAK |
| Pu-240 | 4.0 | 99.9 | 10 | | | | | | | - 5.2 | 99. | 7 | - 3.5 | 99.9 | 10 | | | | WAK |
| Pu-241 | 3.9 | 99.9 | 10 | | | | | | | - 4.7 | 98. | 7 | - 3.2 | 99.9 | 10 | | | | WAK |
| Pu-242 | | | | | | | 2.0 | 98. | 9 | | | | 2.1 | ∿95. | 9 | 2.4 | >90. | | (SAL) |

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[1] $$d = \frac{\frac{1}{n}\sum_{i=1}^{n}(y_{ij} - y_{ik})}{0.5 \cdot (y_{.j} + y_{.k})} \cdot 100 \ (\%)$$

[2] n = number of samples

Table 3.11: Calculated correlations for isotopic relations based on results from 4 laboratories. Nuclides refer to nuclide concentration data, outliers included. Estimated regression equation $Y = b_o + b_1 \cdot X$ by method of minimum distance, n = number of points, R = correlation coefficient.

| Y | X | n | $b_o$ | $b_1$ | R | $\chi_c^2$ | error direction |
|---|---|---|---|---|---|---|---|
| D235 | vs.Ft | 10 | $0.19\underline{0}$[1] | $0.16\underline{3}$ | 0.969 | - | x,y[2] |
| U-236 | vs.D235 | 10 | -0.582 | 334. | 0.979 | 9.44 | y |
| Pu/U | vs.D235 | 10 | $4.92x10^{-4}$ | 0.0121 | 0.948 | 1.76 | y |
| Pu/U | vs.Ft | 10 | 0.00297 | 0.00191 | 0.953 | 1.60 | y |
| Pu/U | vs.Cs-134/137 | 9 | $0.007\underline{89}$ | $5.68x10^{-4}$ | 0.398 | 14.42 | y |
| Pu-239 | vs.Ft | 10 | 0.00387 | $3.38x10^{-4}$ | 0.605 | 2.8 | y |
| Pu-240 | vs.Ft | 10 | $7.60x10^{-5}$ | $6.29x10^{-4}$ | 0.954 | 3.04 | y |
| Pu-241 | vs.Ft | 10 | $-5.71x10^{-5}$ | $3.77x10^{-4}$ | 0.965 | 3.28 | y |
| Pu-242 | vs.Ft | 10 | $-5.14x10^{-4}$ | $3.03x10^{-4}$ | 0.994 | 5.6 | y |
| Pu-241/239 | vs.Pu-240/239 | 10 | $-0.028\underline{7}$ | $0.61\underline{8}$ | 0.991 | 2.96 | x,y |
| Pu-240/239 | vs.U-235/238 | 10 | $0.61\underline{9}$ | $-21.\underline{4}$ | 0.937 | 23.12* | x,y |
| Pu-241/240 | vs.Pu-240/239 | 10 | $0.4\underline{10}$ | $0.3\underline{45}$ | 0.752 | 24.16* | x,y |
| Pu-242/241 | vs.Pu-240/239 | 10 | $-0.30\underline{9}$ | 1.68 | 0.994 | 1.28 | x,y |
| Pu-242/240 | vs.Pu-240 | 10 | $-0.0\underline{842}$ | $14\underline{5}.$ | 0.952 | 1.92 | x,y |
| Pu-242/240 | vs.Ft | 10 | -0.0324 | 0.0769 | 0.986 | 4.72 | y |

* $\chi_c^2 > \chi^2 \; (0.05, 8) = 15.51$

[1] underlined digits: discrepancy between method of minimum distance and Deming's method.

[2] Individual errors unknown. The $\chi^2$-values are calculated using an adjusted weight value for all points. These values can therefore not be applied to interpret the goodness-of-fit.

isotope ratios are given in table 3.11 where the variables Y , X , the number of samples (n), the regression parameters $b_o$ and $b_1$ , the correlation coefficient (R), the goodness of fit parameter ($\chi_c^2$), and the variable with which the error is associated are listed.

The regression parameters ($b_o$ , $b_1$) calculated by use of Deming's method differ only slightly from those of table 3.11. To illustrate, the digits which differ are underlined in the table.

## Correlation coefficient

The correlation coefficient (R) is statistically significant from zero at a significance level $\alpha = 0.05(0.001)$ when it exceeds the value of 0.666(0.898) for n = 9 samples and of 0.632(0.872) for n = 10 . Thus, the variables X and Y of all correlations are correlated at a high significance level except for those of Pu/U versus Cs-134/Cs-137 (R = 0.398), Pu-239 versus $F_t$ (R = 0.605) and of Pu-241/Pu-240 versus Pu-240/Pu-239 (R = 0.752). This is probably due to the high interlaboratory coefficient of variation of Pu/U, Pu-239 and Pu-241/240.

## Goodness of fit

The goodness of fit of the points $(\overline{x}_i, \overline{y}_i)$ to the estimated regression line had been tested by comparing the values of $\chi_c^2$ of table 3.11 with the appropriate $\chi^2$ distribution value (see chapter A.4.2) which amounts to $\chi^2(\alpha,\nu) = 15.51$ at the significance level $\alpha = 0.05$ and $\nu = n-2 = 8$ degrees of freedom. $\chi_c^2 > 15.51$ is encountered for the regressions of Pu-240/Pu-239 on U-235/U-238 and Pu-241/Pu-240 on Pu-240/239. The correlation coefficient of the first regression, R = 0.937, is significantly different to zero at $\alpha < 0.001$ indicating that the assumption of the linear model might not be correct. In contrast, R = 0.752 of the second regression points to a rather weak correlation suggesting a strong scatter of the data points around the regression line.

### 3.3.5 Summary of the results obtained with ICT

1. An internal consistency check revealing measurement errors and outlying batches can be performed with success.

2. Random errors estimated by use of appropriate correlations assuming the error is in the Y variable only compare with those calculated by the Grubbs constant-bias method. In case individual measurement errors will be known an improvement of the random error estimation by ICT is to be expected since then it is possible to split off the random errors in both X and Y variable portions.

3. Both Deming's method and the method of minimum distances give nearly identical results for the parameters of a regression line.

4. Isotope correlations based on theoretical calculations give results as precise as analytical measurements (see appendix C).

## 4. Material balance of uranium and plutonium isotopes

The aim of the reprocessing input analyses is to establish a material balance. Usually this material balance is made for a reprocessing campaign comprised of many fuel assemblies of a reactor reload.

### 4.1 Methods of material balance

Several methods have been described (1), (2) which will be compared by using the results of this experiment. As emphasis is given to the methodological aspect rather than to the performance of the individual laboratories the averages of the results as obtained by the laboratories are used (table 2.9). In the Annex (C and D) evaluations are described following the method developed by the CEA, Cadarache and using the transportable data bank of CEN, Mol. In both cases different levels of the quality of an analytical laboratory are considered.

The applied method of measuring the reprocessing input at the WAK plant is the volumetric method. From the concentration of each element, the volume and density of the solution of the accountability tank and the dilution factor of the samples the mass of each nuclide is calculated.

If ICT is used to measure the mass of the Pu and U isotopes, the initial fuel weight has to be used. Correlations determining the Pu/U ratio (as originally proposed by BNWL) or the concentration of an individual nuclide as related to the initial metal atoms, IMA (as used in reactor physics and elaborated by the European Institute for Transuranium Elements) eliminate the concentration determination of nuclides in the solution by determining the ratio of each nuclide to the most abundant nuclide i.e. U-238.

This principle follows from the gravimetric method (sometimes referred to as the Pu/U ratio method). Computer codes, such as the often-used ORIGEN and the approach taken by the CEA described in this report, use the initial fuel weight, Uo as well.

There is an important difference, Δ (s. eq. 4-1) between the first method and the others. The volumetric method measures only the material dissolved ready to enter the reprocessing process, whereas the other methods determine the input of the spent fuel to the reprocessing plant. The difference, Δ consists of possible head-end losses and measurement errors in the initial fuel weight, Uo and in the accountability tank content. In order to balance the weight of the spent fuel with Uo, the burn-up, Ft has to be known.

$$U_o = (U+Pu+TPu+\Delta)/(1-Ft/100) \tag{4-1}$$

In this equation the sum of the masses of U, Pu and transplutonides TPu of the spent fuel, corrected for the burn-up, as obtained by Nd-148 analyses, has to balance the initial fuel amount Uo when the above described difference Δ is considered.

The available data is used to compare the different input analysis methods according to their accuracy, effort, information required, tamper resistance and timeliness.

For the comparison only the most "popular" correlations were selected. (In table 4.1 each variable X is correlated with each variable Y). The variable Y comprises isotopic concentrations (atoms/IMA) or the ratio Pu/U. The variable X uses information obtained by less costly measurements than the information of the variable Y, i.e. isotopic ratios or the Cm-244 concentrations.

| X | versus | Y |
|---|---|---|
| D-U-235 | | U -235 IMA |
| Pu-242/240 | | Pu-239 IMA |
| 100 - Pu-239* | | Pu-240 IMA |
| Pu-(242•239)/(240•240)** | | Pu-241 IMA |
| Cm-244 | | Pu/U |
| Cs-134/137 | | |
| Xe-132/131 | | |

$* \ 100 - \frac{100 \text{ Pu-239}}{\text{Pu}}$ (a/o) $\quad ** \ \frac{\text{Pu-242}}{\text{Pu-240}} \cdot \frac{\text{Pu-239}}{\text{Pu-240}}$

Table 4.1: Correlations used for the comparison. (All are linear except Cm-244 IMA, which is quadratic.)

| Method | U-235 | Pu-239 | Pu-240 | Pu-241 | Pu/U |
|---|---|---|---|---|---|
| Isotope correlations: | | | | | |
| X=D-U-235 | 0.4 | 1.1(1) | 1.0(1) | 1.3 | 1.0(1) |
| Pu-242/240 | 1.9 | 1.2(2) | 1.5 | 1.9 | 1.6 |
| Cm-244 IMA | 0.9 | 1.2(1) | 1.1(1) | 1.6 | 1.1 |
| Xe-132/131 | 3.1(2) | 1.1(2) | 2.7(2) | 2.9(2) | 2.0(2) |
| Cs-134/137 | 3.7 | 1.3 | 2.4 | 2.6 | 1.7 |
| 100 - Pu-239 (a/o) | 1.2 | 1.0(2) | 0.9(2) | 1.8 | 1.7 |
| Pu-(242•239)/(240•240) | 2.8 | 1.6 | 1.8 | 2.2 | 1.6 |
| Theor.calc. IC, CEA | | | | | 0.75 |
| ANOVA | 0.4(1) | 1.4 | 1.3 | 1.3 | 1.3 |
| Grubbs analysis: RCH | 0.4 | * | 2.8 | 3.0 | 2.8 |
| SAL | 0.5 | 1.2 | 0.7 | 1.0 | 0.7 |
| TU | 0.3 | 0.5 | 0.6 | 1.0 | 1.9 |
| WAK | 1.0 | 1.5 | 1.8 | 0.7 | 5.4 |

*) negative variance

Table 4.2: Mean variation coefficients, V(%), of nuclide concentrations as evaluated by isotope correlations, by analysis of variances (ANOVA), by Grubbs' analysis and by theoretical calculations. The first method is based on an interbatch comparison, whereas ANOVA and Grubbs' analysis are on an interlaboratory comparison. For detailed explanation see the paragraph headed 'variation coefficients'. The number of excluded outliers is in brackets.

| Method | U-235 | Pu-239 | Pu-240 | Pu-241 | Pu/U |
|---|---|---|---|---|---|
| Isotope correlations: | | | | | |
| X=D-U-235 | + 0.3 | + 1.3 | + 0.7 | - 0.5 | + 1.0 |
| Pu-242/240 | - 0.2 | + 0.3 | + 0.02 | - 0.06 | + 0.3 |
| Cm-244 IMA | - 0.5 | + 1.0 | + 0.9 | + 0.7 | + 0.9 |
| Xe-132/131 | - 1.6 | + 0.3 | + 0.8 | + 0.9 | + 0.4 |
| Cs-134/137 | - 3.4 | + 1.3 | + 2.3 | + 2.8 | + 1.6 |
| 100 - Pu-239 (a/o) | - 0.4 | + 0.8 | + 0.7 | + 0.1 | + 0.7 |
| Pu-(242•239)/240•240) | - 0.7 | - 0.2 | - 0.6 | - 0.9 | - 0.3 |
| Theor.calc. IC, CEA | + 5.0 | + 0.4 | - 1.4 | - 6.6 | + 0.7 |
| Volume/concentration | - 0.7 | - 0.8 | - 0.9 | - 0.8 | - 0.8 |

Table 4.3: Bias (%) of the methods based on the Pu/U ratio method for 10 input batches. (Difference observed for the volume/concentration method is caused by unmeasured head-end losses etc.)

## 4.2 Comparison of different methods

### Accuracy

The variation coefficients and the biases obtained for the total campaign are determined for the isotope correlation technique and the other methods.

The data of the tables 4.2 and 4.3 are calculated after application of Grubbs' outlier criterion at 1% level of significance. The excluded values are:

sample 90 (RCH) of U-235 and U-235/238
sample 93 (SAL) of Pu-242/241.

The historical data so far collected in various data banks do not match well with those of the experiment. Therefore, in order to estimate the amount of the nuclides, $N_i$ by isotope correlations, the data have been arbitrarily split into two groups of 5 batches each, using one group for the determination of the regression line $Y = b_o + b_1 \cdot X$ from which the values $N_i = y_i$ of the other 5 batches are calculated using the analytical data of the X variable averaged over the four laboratories (table 2.9). Then groups 1 and 2 are exchanged and the procedure is repeated.

### Variation coefficient

Mean variation coefficients are estimated by isotope correlations, the analysis of variances (ANOVA), Grubbs' analysis and by theoretical calculations (table 4.2). It should be noted that for isotope correlations these values are based on an interbatch comparison whereas for ANOVA and Grubbs' analysis they are based on an interlaboratory comparison.

For isotope correlations which are based on the averaged values of table 2.9 the variation coefficients are calculated according to equation (4-2), which is an ad hoc definition:

$$V(ICT) = \sqrt{\frac{s^2_{y.x}\ (1+\frac{1}{n})}{y.}} \cdot 100\ (\%) \qquad (4\text{-}2)$$

where $s^2_{y.x}$ is determined by use of equation (A-51) and y. is the mean of the ten y batch values.

The variation coefficients labeled 'ANOVA' are derived the following way. For each batch mean averaged over the four laboratories a a variation coefficient $V_i/\sqrt{4}$ is calculated. A mean variation coefficient, V (ANOVA) is then determined from the ten batch mean variation coefficients according to eq. (4-3):

$$V\ (ANOVA) = \sqrt{\frac{\sum_{i=1}^{10} V_i^2/4}{10}} \qquad (4\text{-}3)$$

where the $V_i$ stem from table (2.10). Bartlett's test revealed that except for U-235 the variances corresponding to the $V_i$ are homogeneous and therefore a mean value, V may be calculated, although minor systematic errors, i.e. biases among laboratories exist which may result in slightly overestimated variation coefficients by this method.

The variation coefficients of Grubbs' analysis are taken from table 3.5.

The variation coefficient V (theor. calc.) stems from appendix C, table C.5:

$$V\ (theor.\ calc.) = \sqrt{\frac{\sum_{i=1}^{5} V_i^2}{5}} \qquad (4\text{-}4)$$

where the $V_i$ are the variation coefficients of the five Pu/U mean values determined from correlations h and $\delta$.

The Grubbs analysis shows the errors associated with the individual laboratories. From this it becomes evident, that the accuracy of the ICT compares well with these results. Therefore it can be concluded that given the state of the analytical technique at the time of the experiment, ICT is as accurate direct measurements.

Comparing the isotope correlations among themselves one can observe that the correlations determining the Pu/U ratio show no advantage over correlations determining the concentration of uranium and plutonium nuclides in the fuel. On the otherhand one should note that the correlations determining the isotope concentrations (IMA) possess the advantage of checking the isotopic composition of the fuel. For the xenon isotope correlation (Xe-132/131) two analyses are excluded. The results differ considerably from the correlation predictions. This could have one of two causes: the xenon samples are not analysed properly or the samples taken from those two input batches are not representative of the fuel batch (it should be born in mind that any portion of the spent fuel still satisfies the isotope correlation, even if it is not representative of the fuel batch). The outliers observed for the other correlations reflect that some of the Pu analyses are doubtful. (There exists a bias between the laboratories of the IAEA and EURATOM on one side and the WAK and IRCH on the other side).

## Bias

The bias (table 4.3) is determined as the relative difference of the total amount of the major heavy nuclides, $N_i$ determined by the gravimetric method, GR and by the other methods. For example for ICT the bias is calculated by

$$\text{bias} = 100 \cdot (\sum_i N_i(GR) - \sum_i N_i(ICT))/\sum_i N_i(GR) \quad (\%) \qquad (4\text{-}5)$$

When the ten batches are summed up, the biases between the methods become apparent. The comparison is based on the Pu/U ratio method according to equation (4-1).

The differences observed for the volume/-concentration method is the $\Delta$ , which consist of head-end losses and measurement errors. Since the isotope correlation technique is based on the initial fuel amount, Uo this systematic error component should not be conserved. Nevertheless some correlations show larger biases. In agreement with our earlier observation the correlation Pu-242/240 gives the best results.

## Effort

Comparing the effort the volume/concentration and the Pu/U ratio method of course require more analytical work than the analyses of isotope ratios needed for ICT. Here again one can distinguish between the isotope ratio measurement of uranium and plutonium isotopes, which is made by thermal ionisation mass-spectrometry, whereas the Xe-132/131 ratio is determined by the simpler gas mass-spectrometry. The measurement of the Cs-134/137 ratio is even easier performed by Ge(Li) $\gamma$-spectrometry. The concentration of Cm-244 was measured by $\alpha$-spectrometry. A determination by neutron interrogation seems feasible.

## Information

Information needed for each method is routinely reported and is available to the safeguards authorities. For the volume/ concentration method the fuel history has not to be known. All the other methods have to rely on the fresh fuel weight, Uo. Cm-244 and the Cs-134/137 correlations have to be corrected for decay in order to compare data of different campaigns. Information on the irradiation history is needed (s. table 4.4).

## Timeliness

The present safeguards practice foresees a re-measurement of duplicate samples by the safeguards laboratory. Difficulties in transporting samples have caused long delays in the analyses.

Correlations based on Xe-132/131, Cs-134/137 and Cm-244 IMA could be applied more timely. The measurements are possible to be automated or performed by the inspectors themselves at the plant.

## Tamper resistance

Methods relying on earlier verified information are more resistant against tampering than those where all the measurements have to be made at the time of the input determination. In this sense the volume/concentration method is less favourable, because all its information relies on new measurements. In contrary the other methods use the earlier verified fuel weight and - in case of ICT - verified historical data. The same applies to the reactor physics calculations, however, this approach as well as shortlived radioactive isotopes need information on the irradiation history. In the approach by the CEA experimental data are used together with general design information and the irradiation history to establish isotope function for the particular reactor.

The sources of information needed to establish a material balance according to each method are different. Reactor physics calculations can be made completely independent from the analysis of the input solution. The other extreme would be the volumetric method, where no historical information is needed. All other methods require a mix of informations from different sources (table 4.4).

| Method | Source of information<br>isotope analysis | U/Pu conc. | Pu/U ratio | vol. density | init. weight | reactor design | power histogram | cooling time |
|---|---|---|---|---|---|---|---|---|
| volumetric | + | + | + | + | - | - | - | - |
| gravimetric | + | - | + | - | + | - | - | - |
| ICT U,Pu isotopes | + | - | - | - | + | - | - | - |
| ICT Xe isotopes | + | - | - | - | + | - | - | - |
| ICT Cm-244, Cs-134/137 | + | - | - | - | + | - | + | + |
| theor. calculated IC (CEA) | + | - | - | - | + | + | + | + |
| reactor physics calculations | - | - | - | - | + | + | + | + |

Table 4.4: Source of information required by each method

## 5. Conclusions

It should be emphasized that the experiment was conducted under normal plant operating conditions. This includes the safeguards inspection and the input analyses as well. No additional experimental effort was needed at the plant.

It has to be pointed out, that the experiment was confined to only ten batches and that the burn-up range was narrow.

In order to evaluate the experiment access to the fabrication data and to the fuel history became necessary. Through the cooperation of the fuel fabricator and the reactor operator this information was easily obtained.

It was surprising for the group to find that no established procedure existed to compare verification measurements of three or four labs. The analytical data were chequed for outliers using the Dixon and the Grubbs outlier criterion and by the isotope correlation technique. Random errors and systematic errors, i.e. biases were evaluated by application of the analysis of variances, Grubbs' constant-bias model, Jaech's non-constant-bias model, and by the isotope correlation technique including theoretical calculations and regression analysis. Finally the mass balances of uranium and of plutonium were set up.

The most important result is that the accuracy in determining the masses of U and Pu and their isotopic composition by ICT is comparable to the accuracy of the direct analyses based on mass-spectrometric isotope dilution. However, it must be noted that the quality of the analytical work could be improved when compared with the potential accuracy of this type of analysis.

The application of the heavy isotope correlation technique procedures at reprocessing plants is feasible and does not put extra burden on plant operators. Information required by this technique is readily available. Outliers can be detected by ICT as well as by other statistical techniques.

For this particular fuel the group did not have access to historical data of earlier campaigns. Therefore the campaign was splitted into two sets, each treated like historical data. In such a situation theoretically calculated correlations offer an alternative.

For consistency checks ICT is superior to parallel measurements. For such evaluation the data set of a single laboratory is sufficient compared to the measurements necessary for the interlaboratory comparison.

Encouraging results have been obtained on correlations based on the isotope ratio of Xe-132/131 and Cs-134/137 and of the Cm-244 concentration. Considering the potential of measuring these nuclides insitu by the inspector when compared to the time consuming transport of samples to central laboratories in order to measure heavy isotope ratios, this new type of correlation opens up the possibility of timely detecting diversion.

Pu/U based correlations compared to the Pu-IMA correlation exhibit no advantage concerning accuracy. It should also be pointed out that the Pu-IMA correlations are isotope specific.

During the experiment several shortcomings were observed, which should be avoided in the follow-up experiment:

- An analysis quality-control program between the plant operator and the safeguards laboratory is needed. The quantitative analysis of Pu expecially has to be improved compared to the performance of ICE.
- The head-end losses (shearing losses, residues, analyses of hulls) have to be quantified.
- In order to check the representativity of the sample dilutions of independent samples have to be analysed.
- If no historical data are on hand care should be taken to select samples covering a large range of burn-up.
- Following the ISO recommandations the Dixon criterion should be used for outlier detection.

The follow-up experiment could be enlarged in order to compare with other techniques under development (NDT neutron interrogation, etc.) or to test new concepts (mass balance of Pu on the basis of Pu-240 etc.) in a well characterized campaign.

## 6. Previous publications

During the evaluation of the ICE several publications appeared on this subject. Some use a slightly different data base. This report should be considered as the final information.

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1. ESARDA SYMPOSIUM, Proc. p. 180 (1979)

(2) H.J. Arenz, G. Hough, L. Koch: Experience for Safeguards Gained in the Isotope Correlation Experiment.
2. ESARDA SYMPOSIUM, Proc. p. 339 (1980)

(3) S. Schoof, W.L. Zijp: How Good are Isotope Correlationships Compared to Conventional Statistical Techniques.
2. ESARDA SYMPOSIUM, Proc. p. 342 (1980)

(4) C. Beets, P. Bemelmans, F. Franssen, S. Schoof: Head-End Fissile Material Balance of a Reprocessing Campaign: An On-Site Evaluation Procedure.
2. ESARDA SYMPOSIUM, Proc. p. 347 (1980)

(5) L. Koch: The Isotope Correlation Experiment.
2. ESARDA SYMPOSIUM, Proc. p. 392 (1980)

(6) L. Koch, K. Kammerichs, S. Schoof: The Potential of Fission Product and Transplutonium Correlations in the Verification of the Reprocessing Input.
3. ESARDA SYMPOSIUM, Proc. p. 175 (1981)

(7) L. Koch, S. Schoof: An Example of Material Accounting and Verification of Reprocessing Input.
22. INMM-Meeting, July 13-15, Proc. (1981)

## 7. References

### 7.1 References chapter 2

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7. Int. Mass Spec. Conf. Proc. Vol. 7, 1052 (1976)

(2) L. Koch, B. Brandalise, Annali di Chimica, 67, 767 (1977)

(3) S.F. Marsh, T. Abernathey, J.E. Rein, Report LA-5568 issued March 1974 (Rev. April 1977)

(4) D.H. Smith et al.: Instruction Manual for ORNL Tandem High Abundance Sensitivity Mass Spectrometer, ORNL/TM-5485

(5) L. Koch, IAEA-SM-231/4 (1978)

### 7.2 References chapter 3

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(2) F.E.Grubbs, G.Beck: Extension of sample sizes and percentage points for significance tests of outlying observations.
Technometrics 14, p. 847-854 (1972)

(3) F.E.Grubbs: On estimating precision of measuring instruments and product variability.
J. Amer. Statist. Assoc. 43, p. 243-264 (1948)

(4) F.E.Grubbs: Errors of measurement, precision, accuracy and the statistical comparison of measuring instruments.
Technometrics 15, p. 53-66 (1973)

(5) J.L.Jaech: Large sample tests for Grubbs' estimators of instrument precision with more than two instruments.
Technometrics 18, p. 127-133 (1976)

(6) J.L.Jaech: Errors of measurement with more than two measurement methods.
Nuclear Materials Management Journal IV, p. 38-41 (winter 1976)

(7) J.L.Jaech: A program to estimate measurement error in nondestructive evaluation of reactor fuel element quality.
Technometrics 6, p. 293-300 (1964)

(8) J.L.Jaech: Extension of Grubbs' method when relative biases are not constant.
Nuclear Materials Management Journal, p. 76-80 (spring 1979)

(9) J.Bouchard, A.Giacometti, M.Robin: Reprocessing plant input controls based on reactor data.
Paper presented at the 1st ESARDA Symposium on Safeguards and Nuclear Material Management, Brussels (April 1979)

(10) B.A. Napier and C.L. Timmerman: Developing Isotopic Functions.
Paper presented at the Symposium on the Isotopic Correlation and its Application to the Nuclear Fuel Cycle, Stresa, Italy (May 1978)

### 7.3 References chapter 4

(1) L. Koch, IAEA-SM-231/4 (1978)

(2) L. Koch, M. Bresesti, INMM Vol. IV, III, 498 (1975)

## Appendix A

## Mathematical description of the statistical methods used with the data evaluation of ICE

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This is a more extended description of the methods mentioned in chapter 3. For convenience equation numbers of chapter 3 are also given if available.

### A.1 Analysis of variances

The fixed effect model (i.e. model I) with one measurement per batch and per laboratory and without interaction was used:

$$y_{ij} = \mu + b_i + a_j + e_{ij} \qquad \text{(A-1)} \quad \text{(3-1)}$$

$i = 1,\ldots,n$ denoting batches

$j = 1,\ldots,m$ denoting laboratories

$y_{ij}$ = value of sample or batch $i$ as measured by laboratory $j$

$\mu$ = overall mean

$\mu + b_i$ = "true" value of batch $i$

$a_j$ = bias of laboratory $j$

$e_{ij}$ = random error associated with $y_{ij}$

The following conditions are assumed:

1) $\sum_{j=1}^{m} a_j = 0$ (A-2) (3-2)

2) $\sum_{i=1}^{n} b_i = 0$ (A-3) (3-3)

3) $e_{ij}$ are independent and $N(0,\sigma_e^2)$

Under these conditions the following least squares estimates are obtained:

$$\hat{\mu} = y_{..} \qquad \text{(A-4)}$$

$$\hat{a}_j = y_{.j} - y_{..} \qquad \text{(A-5)}$$

$$\hat{b}_i = y_{i.} - y_{..} \qquad \text{(A-6)}$$

$$s_e^2 = \frac{\sum_{j=1}^{m} \sum_{i=1}^{n} (y_{ij} - y_{i.} - y_{.j} + y_{..})^2}{(m-1) \cdot (n-1)} \qquad \text{(A-7)}$$

where the above notations have been defined the usual way:

$$y_{..} = \frac{1}{n \cdot m} \cdot \sum_{j=1}^{m} \sum_{i=1}^{n} y_{ij} \qquad \text{(A-8)}$$

$$y_{i.} = \frac{1}{m} \cdot \sum_{j=1}^{m} y_{ij} \qquad \text{(A-9)}$$

$$y_{.j} = \frac{1}{n} \cdot \sum_{i=1}^{n} y_{ij} \qquad \text{(A-10)}$$

and where $s_e^2$ is the estimate of $\sigma_e^2$.

Model (A-1) assumes that there is no significant interaction between laboratory and batch effect, which means the model is additive with respect to $a_j$ and $b_i$ for all $j = 1,\ldots,m$ and $i = 1,\ldots,n$ or $s_{ab}^2 = 0$, where $s_{ab}^2$ is the variance due to interaction. If $s_{ab}^2 > 0$, which can be evaluated by a test proposed by Tukey(1), then the residual mean square ($MS_r$) of table A.1 will not longer be equal to $s_e^2 + s_{ab}^2$. In order to evaluate $s_e^2$ and thus $s_{ab}^2$ replicate analyses are needed. The model then should be that of a two-way layout with interaction.

During the course of data evaluation the interlaboratory variance ($s_{IL}^2$), defined as the mean sum of squares within groups of the one-way analysis of variance model was calculated:

$$s_{IL}^2 = \frac{\sum_{i=1}^{n} \sum_{j=1}^{m_n} (y_{ij} - y_{i.})^2}{n \cdot (m_n - 1)} \qquad \text{(A-11)}$$

where $m_n$ equals 4 or for missing measurements 3.

From equation (A-11) the interlaboratory coefficient of variation ($V_{IL}$) was calculated:

$$V_{IL} = \frac{s_{IL}}{y_{..}} \cdot 100 \ (\%) \qquad \text{(A-12)}$$

Table A.1: Analysis of variances for the two-way layout with one observation per cell

| Source of variation | Sum of squares | Degrees of freedom | Mean squares | Expected mean squares |
|---|---|---|---|---|
| laboratory | $SS_a = n \sum_{j=1}^{m} (y_{.j} - y_{..})^2$ | $\nu_a = m-1$ | $MS_a = \frac{SS_a}{\nu_a}$ | $s_e^2 + \frac{n}{m-1} \sum_{j=1}^{m} a_j^2$ |
| batches | $SS_b = m \sum_{i=1}^{n} (y_{i.} - y_{..})^2$ | $\nu_b = n-1$ | $MS_b = \frac{SS_b}{\nu_b}$ | $s_e^2 + \frac{m}{n-1} \sum_{i=1}^{n} b_i^2$ |
| residual | $SS_r = \sum_i \sum_j (y_{ij} - y_{i.} - y_{.j} + y_{..})^2$ | $\nu_r = (m-1)\ (n-1)$ | $MS_r = \frac{SS_r}{\nu_r}$ | $s_e^2$ |

Similarly the interbatch coefficient of variation ($V_{IB}$) was defined as

$$V_{IB} = \frac{1}{y_{..}} \cdot \sqrt{\frac{\sum_{i=1}^{n} (y_{i.} - y_{..})^2}{n-1}} \cdot 100\ (\%) \qquad \text{(A-13)}$$

The interlab variance ($s_{IL}^2$) is related to the random error variance ($s_e^2$) defined by equation (A-7) in the following way, taking equations (A-5) to (A-10) into account.

$$(m-1) \cdot (n-1) \cdot s_e^2 = \sum_i \sum_j \{(y_{ij} - y_{i.}) - (y_{.j} - y_{..})\}^2$$

$$\begin{aligned}(m-1) \cdot (n-1) \cdot s_e^2 = & \sum_i \sum_j (y_{ij} - y_{i.})^2 \\ & - 2\sum_{ij}\sum (y_{ij} - y_{..} - y_{i.} + y_{..})(y_{.j} - y_{..}) \\ & + n\sum_j (y_{.j} - y_{..})^2\end{aligned}$$

$$\begin{aligned}(m-1) \cdot (n-1) \cdot s_e^2 = & \ n \cdot (m-1) \cdot s_{IL}^2 - 2\sum_{ij}\sum (y_{ij} - y_{..}) \cdot a_j \\ & + 2\sum_{ij}\sum b_i \cdot a_j + n\sum_j a_j^2 \qquad \text{(A-14)}\end{aligned}$$

The second term of the right hand side of equation (A-14) equals zero and the third term vanishes if there is no interaction, thus equation (A-15) results:

$$s_e^2 = \frac{n}{n-1} s_{IL}^2 + \frac{n}{(m-1)\ (n-1)} \sum_j a_j^2 \qquad \text{(A-15)}$$

If there are no significant laboratory biases, i.e. all $a_j = 0$ or hypothesis $H_a$ (see below) is accepted, than $s_{IL}^2$ provides a measure of $s_e^2$.

The hypotheses to be tested are:

1. Hypothesis $H_a$: all $a_j = 0$, i.e. no significant laboratory biases exist.
The F-test of $H_a$ at a significance level $\alpha$ consists of rejecting $H_a$ if

$$\frac{MS_a}{MS_r} > F\ (\alpha; \nu_a, \nu_r) \qquad \text{(A-16)}$$

where $MS_a$, $MS_r$, $\nu_a$, $\nu_r$ are calculated according to table A.1.

2. Hypothesis $H_b$: all $b_i = 0$ or

$$\sigma_b^2 = \frac{1}{n-1} \sum_{i=1}^{n} b_i^2 = 0,$$

i.e. differences in batch means ($\mu + b_i$) are statistically insignificant. Once again, hypothesis $H_b$ is rejected, if

$$F_b = \frac{MS_b}{MS_r} > F\ (\alpha; \nu_b, \nu_r) \qquad \text{(A-17)}$$

using the F-statistics at a significance level $\alpha$. $MS_b$, $MS_r$, $\nu_b$, $\nu_r$ are calculated according to table A.1.

Only under the condition that the variation in batch means ($MS_b$) exceeds the random error variance ($MS_r$) by a certain amount is it worthwhile to use the measurement data of a nuclide content or isotope abundance ratio for subsequent isotope correlations. Either raising the precision of the measurement or increasing the batch variation will solve the problem where $H_b$ cannot be rejected.

The parameter $MS_b$ depends on the inter-batch variation coefficient ($V_{IB}$) taking eq. (A-13) into account:

$$MS_b = m \cdot y_{..}^2 \cdot V_{IB}^2, \qquad \text{(A-18)}$$

where $y_{..}$ is the overall mean defined in eq. (A-8).

On the other hand, $MS_r$ is related to the interlaboratory variation coefficient ($V_{IL}$) via eq. (A-19) which can be derived from equations (A-7), (A-12) and (A-15) under the assumptions that no significant laboratory biases exist and there is no interaction between batch and laboratory effect.

$$MS_r = \frac{n}{n-1} \cdot y_{..}^2 \quad V_{IL}^2 \qquad \text{(A-19)}$$

Thus, for checking the applicability of nuclide data to isotope correlations the parameter $F_b$

$$F_b = \frac{m(n-1)}{n} \cdot \frac{V_{IB}^2}{V_{IL}^2} \qquad \text{(A-20) (3-18)}$$

has to be tested according to inequality (A-17).

## A.2 Grubbs' constant-bias model

The Grubbs constant-bias$^{(2,3)}$ (CB) model assumes independency between bias and batch value, it may be written as

$$y_{ij} = x_i + a_j + e_{ij} \qquad \text{(A-21) (3-4)}$$

$i = 1,\dots,n$ denoting batches

$j = 1,\dots,m$ denoting laboratories

$y_{ij}$ = value of batch $i$ as measured by laboratory $j$

$x_i$ = "true" value of batch $i$

$a_j$ = bias of laboratory $j$

$e_{ij}$ = random error associated with $y_{ij}$

The following assumptions are made:

1) $e_{ij}$ are independent and $N(0,\sigma_{e_j}^2)$

2) $x_i$ and $e_{ij}$ are statistically independent, i.e. $E\,(x_i \cdot e_{ij}) = 0$

One of Grubbs' methods for solving equation (A-21) consists of calculating the $m(m-1)/2$ columns of differences between lab $j$ and lab $k$ where $j,k = 1,\dots,m$, but $j < k$. Each column contains $n$ differences $v_{ijk}$

$$v_{ijk} = y_{ij} - y_{ik} = a_j - a_k + e_{ij} - e_{ik} \qquad i = 1,\dots,n \qquad \text{(A-22)}$$

the variance of which is denoted by $V_{jk}$ and given in equation (A-23).

$$V_{jk} = \frac{\sum_{i=1}^{n} (v_{ijk} - v_{.jk})^2}{n-1} \qquad \text{(A-23)}$$

where $v_{.jk}$ is the mean bias between lab. $j$ and lab. $k$:

$$v_{.jk} = \frac{1}{n} \sum_{i=1}^{n} v_{ijk} \qquad \text{(A-24)}$$

The estimated random error variance or imprecision of the $j$-th laboratory is then:

$$s_{e_j}^2 = \frac{1}{m-1} \Big\{ \sum_{\substack{l=1 \\ l \neq j}}^{m} V_{jl} - \frac{1}{m-2} \sum_{k=1}^{m-1} \sum_{\substack{l=k+1 \\ k,l \neq j}}^{m} V_{kl} \Big\}$$

$$j = 1,\dots,m \qquad \text{(A-25)}$$

The sampling variance of the precision estimate ($s_{e_j}^2$) was derived by Grubbs$^{(2)}$ to be as follows:

$$\operatorname{var}(s_{e_j}^2) = \frac{2}{n-1} s_{e_j}^4 + \frac{4}{(n-1)\cdot(m-1)^2} \Big\{ s_{e_j}^2 \sum_{\substack{l=1 \\ l \neq j}}^{m} s_{e_l}^2$$

$$+ \frac{1}{(m-2)^2} \sum_{k=1}^{m-1} \sum_{\substack{l=k+1 \\ k,l \neq j}}^{m} s_{e_k}^2 \cdot s_{e_l}^2 \Big\} \qquad \text{(A-26)}$$

At least $m = 3$ laboratories are needed in order to get estimates (A-26) free of batch variance $s_x^2$. For $m = 2$ $\operatorname{var}(s_{e_j}^2)$ increases with increasing $s_x^2$.$^{(2)}$ An interesting approach for the reduction of dependency on $s_x^2$ is proposed in appendix B.

As already stated in chapter 3, section 3.1.3, absolute biases cannot be estimated.

Nevertheless, it is possible to derive from equation (A-22) the relative bias between lab j and lab k, which is given in equation (A-27).

$$\widehat{(a_j - a_k)} = v_{.jk} \qquad \text{(A-27)}$$

Several hypotheses can be tested when applying Grubbs' analysis:

1. Hypothesis $H_a$: $a_j = a_k$ ,

i.e. there is no significant bias between lab j and lab k. This can be tested with the Student-t test, it corresponds to the well known method of comparison of paired data which requires the calculation of the test parameter $t_o$:

$$t_o\ (n-1, a_j=a_k) = \frac{v_{.jk}\ \sqrt{n}}{V_{jk}} \qquad \text{(A-28)}$$

where $v_{.jk}$ is to be calculated by equation (A-24).

One of three possible results is to be accepted at a significance level $\alpha$:(3)

1) $a_j < a_k$ if $t_o < t_{1-\alpha}$

2) $a_j = a_k$ if $-t_{1-\alpha/2} \leq t_o \leq t_{1-\alpha/2}$

and

3) $a_j > a_k$ if $t_o > t_{1-\alpha}$.

2. Hypotheses about the $s^2_{e_j}$ :

hypothesis $H_o$: all $s^2_{e_j}$ are equal

or hypothesis $H_1$: all but one $s^2_{e_j}$ are equal

These hypotheses may be tested using tests proposed by Grubbs(3) and by Jaech(4,5). Various examples are given in those references.

## A.3 Non-constant-bias model

Grubbs' constant-bias model had been extended by Jaech(6,7) to cover data evaluations when relative biases among laboratories depend linearly on batch magnitude. The mathematical model for the non-constant-bias (NCB) model is of the form:

$$y_{ij} = a_j + c_j \cdot x_i + e_{ij} \qquad \text{(A-29)} \quad \text{(3-7)}$$

where

$i$ = 1,...,n denoting batches

$j$ = 1,...,m denoting laboratories

$y_{ij}$ = value of batch i as measured by laboratory j

$x_i$ = "true" but unknown value of batch i

$e_{ij}$ = random error associated with $y_{ij}$, assumed to be independent and $N(0,\sigma^2_{e_j})$

$a_j, c_j$ = parameters describing the bias of lab. j in the following way:

$a_j = 0,\ c_j = 1$ : no bias of lab j

$a_j \neq 0,\ c_j = 1$ : constant bias

$c_j \neq 1$ : bias depends linearily on batch magnitude

Since absolute biases cannot be estimated, constraints on $a_j$, $c_j$ have to be made. One of the conditions proposed by Jaech (6) is:

$$a_1 = 0 \quad \text{and} \quad c_1 = 1, \qquad \text{(A-30)} \quad \text{(3-8)}$$

i.e. the measurement bias of laboratory 1 is arbitrarily fixed to be zero, against which the biases of the other laboratories are related. Under this condition the relative biases $c_j/c_1$ and $a_j - a_1 \cdot c_j/c_1$ are calculated which however are independent of which laboratory was chosen as reference, whereas the estimate $s^2_x$ (eq. A-38) does depend on the choice of the reference laboratory.

The statistical evaluation of the parameters of the NCB model is based on laboratory means $y_{.j}$, j = 1,...,m (eq. (A-10)), its variance $s^2_j$ and the m(m-1)/2 covariances $s_{jk}$ between all possible laboratory pairs, where

$$s^2_j = \sum_{i=1}^{n} (y_{ij} - y_{.j})^2/(n-1) \qquad j=1,\ldots,m \qquad \text{(A-31)}$$

$$s_{jk} = \sum_{i=1}^{n} (y_{ij} - y_{.j}) \cdot (y_{ik} - y_{.k})/(n-1)$$

$$j,\ k=1,\ldots,m \text{ but } j \neq k \qquad \text{(A-32)}$$

These parameters have the expected values:

$$E\ (y_{.j}) = a_j + c_j \cdot x_. \qquad j = 1,\ldots,m \qquad \text{(A-33)}$$

$$E\,(s_j^2) \doteq c_j^2 \cdot \sigma_x^2 + \sigma_{e_j}^2 \qquad j = 1,\ldots,m \qquad \text{(A-34)}$$

$$E\,(s_{jk}) = c_j \cdot c_k \cdot \sigma_x^2 \qquad j,k = 1,\ldots,m \text{ but } j \neq k \qquad \text{(A-35)}$$

where $x_{\bullet}$ is the mean of the batches $x_i$, $i = 1,..n$, considered to be a random sample population with variance $\sigma_x^2$.

Taking the logarithm of equation (A-35) yields equation (A-36)

$$\ln E\,(s_{jk}) = \ln c_j + \ln c_k + \ln \sigma_x^2 \qquad \text{(A-36)}$$

The least squares estimates of the parameters of the model (A-29) are then derived from equations (A-33), (A-34), and (A-36):

$$\hat{c}_j = \Big(\prod_{k \neq 1,j}^{m} s_{jk}/s_{1k}\Big)^{1/(m-2)} \qquad j = 2,\ldots,m \qquad \text{(A-37)}$$

$$s_x^2 = \Big(\prod_{\substack{j=2,k=3\\ j<k}}^{m} s_{1j} \cdot s_{1k}/s_{jk}\Big)^{2/(m-1)(m-2)} \qquad \text{(A-38)}$$

$$s_{e_1}^2 = s_1^2 - s_x^2 \qquad \text{(A-39)}$$

$$s_{e_j}^2 = s_j^2 - \hat{c}_j \cdot s_x^2 \qquad j = 2,..,m \qquad \text{(A-40)}$$

$$\hat{a}_j = y_{.j} - \hat{c}_j \cdot y_{.1} \qquad j = 2,..,m \qquad \text{(A-41)}$$

$$\hat{x}_{\bullet} = y_{.1} \qquad \text{(A-42)}$$

The variance of the imprecision $s_{e_j}^2$ which is given in ref. (6) together with the variances of the other parameters reads as follows, assuming normality:

$$\text{var}(s_{e_j}^2) \simeq \frac{2}{n-1}\, s_{e_j}^4 + \frac{4}{(n-1)\cdot(m-1)^2}\, c_j^4 \Big\{\frac{(m-3)\cdot(m-1)}{(m-2)^2}\, \frac{s_{e_j}^2}{c_j^2} \sum_{\substack{l=1\\ l\neq j}}^{m} \frac{s_{e_l}^2}{c_l^2} + \frac{1}{(m-2)^2} \sum_{l=1}^{m-1} \sum_{k=l+1}^{m} \frac{s_{e_l}^2}{c_l^2} \cdot \frac{s_{e_k}^2}{c_k^2}\Big\} \qquad \text{(A-43)}$$

If one considers all $c_j = 1$, this estimate corresponds to equation (A-26) of the CB model.

Procedures for testing various hypotheses about $s_{e_j}^2$ and $c_j$ using Chi-square-tests are given in reference (6). They had not been used with data evaluation of ICE-1.

## A.4 Special aspects of regression analysis used with the isotope correlation technique

As pointed out in chapter 3, sect. 3.2.2 regression analysis is one tool for solving relationships such as

$$Y = \sum_{i=0}^{k} b_i \cdot X^i \qquad \text{(A-44) (3-9)}$$

where X and Y stand for quantities such as isotope abundance or nuclide concentration and/or isotope abundance ratio, Pu/U and burn-up.

The problem of solving equation (A-44) for the regression parameters $b_i$ is done by minimizing the sum (SS) of squared and occasionally weighted residuals from which the $b_i$ are then derived:

$$SS = \sum_{i=1}^{n} w_i \cdot res_i^2 \qquad \text{(A-45) (3-11)}$$

where the residual ($res_i$) is defined as the distance between the measured point $(x_i, y_i)$ and the calculated point $(x_i^{calc}, y_i^{calc})$ on the regression curve (A-44). $w_i$ is the weight of point $(x_i, y_i)$.

Several approaches have been proposed for the determination of the residuals and of the parameters $b_o$, $b_1$ in case of a linear regression function (A-44) which will be described briefly.

### A.4.1.1 Minimum distance or orthogonal regression line

If the residuals ($res_i$) are presumed to be perpendicular to the regression line the sum of squares (SS) reads as follows:

$$SS = \sum_{i=1}^{n} w_i \cdot res_i^2 \qquad \text{(A-46)}$$

where

$$res_i^2 = \frac{(x_i - x_i^{calc})^2}{s_x^2} + \frac{(y_i - y_i^{calc})^2}{s_y^2}, \qquad \text{(A-47)}$$

$w_i$ is the weight of $res_i$ and is defined as

$$w_i = \frac{2}{\frac{s^2(x_i)}{s_x^2} + \frac{s^2(y_i)}{s_y^2}} \qquad \text{(A-48)}$$

$s^2(x_i), s^2(y_i)$ are the measurement error variances of the measured values $x_i$ and $y_i$, respectively.

$s_x^2$ , $s_y^2$ are scaling factors which are identical to the overall variance of the x and y values, respectively.

Equation (A-47) means that the residuals ($res_i$) are calculated from the residuals in the X and Y directions after transforming them according to the scale transformation factors. These residuals ($res_i$) are then weighted with weights $w_i$ which depend on the random error variances of the $x_i$ and $y_i$ values according to equation (A-48).

The parameters $b_o$, $b_1$ of the regression line are estimated from the minimum sum of squares with respect to $b_o$ and $b_1$, i.e. the derivatives d SS/d $b_o$ and d SS/d $b_1$ are set equal to zero, from which the estimates $\hat{b}_o$ and $\hat{b}_1$ are then determined as well as the variances and other statistical parameters needed. More information can be found in references (8) and (9).

### A.4.1.2 Demings approach

Demings method$^{(10)}$ consists of weighting the residuals in the X and Y directions individually which results in equation (A-49) for the sum of squares:

$$SS = \sum_{i=1}^{n} \{w_{ix} \cdot (x_i - x_i^{calc})^2 + w_{iy} \; (y_i - y_i^{calc})^2\} \qquad \text{(A-49)}$$

where the weights $w_{ix}$ and $w_{iy}$ are taken as inversely proportional to the measurement error variance of the measured values $x_i$ and $y_i$ respectively, i.e.

$$w_{ix} = \frac{1}{s^2(x_i)} \qquad \text{(A-50)}$$

$$w_{iy} = \frac{1}{s^2(y_i)}$$

Equation (A-49) implies that the angle between residuals, taken as the distance between measured point $(x_i,y_i)$ and its calculated value $(x_i^{calc},y_i^{calc})$, and the regression line is not fixed as in the case of minimum distances but depends on changing weights $w_{ix}$ and $w_{iy}$. Thus, solving equation (A-49) for minimum SS cannot be done by simply equating to zero the derivatives of SS with respect to $b_o$ and $b_1$ . The method used here is that of the Lagrange Multipliers. The application to regression analysis is well described in reference (10).

It should be noted that Deming's approach is not restricted to linear regression functions.

Some special cases of Deming's sum of squares (eq. (A-49)) may be distinguished:

1) $s^2(x_i) = 0$ and $s^2(y_i) = \text{const.}$ for all i,

or $s^2(x_i) = \text{const.}$ and $s^2(y_i) = 0$ for all i,

this is the classical approach of unweighted least squares where fixed errors are in either Y or X direction only.

2) $s^2(x_i) = 0$ and $s^2(y_i) \neq 0$

or $s^2(x_i) \neq 0$ and $s^2(y_i) = 0$

individually specified errors in either Y or X direction.

3) $s^2(x_i) \,/\, s^2(y_i) = \text{const.}$ for all i

a) $s^2(x_i)$ (and therefore $s^2(y_i)$) are not constant for all i.

b) $s^2(x_i)$ (and therefore $s^2(y_i)$) are constant for all i.

This approach has also been used with the isotope correlation technique$^{(11)}$.

### A.4.2 Goodness of fit

The least squares value of SS serves as a measure of the goodness of fit between the assumed regression function and the data points since it is known that $SS_{min}$ follows a Chi-square-distribution for $\nu = n - k'$ degrees of freedom, where n = number of points to be fitted and k' = number of regression parameters to be estimated (k' = 2 for a straight line).

Values of $SS_{min}$ larger than $\chi^2(\nu)$ mean that either the assumed regression model is not appropriate or the specified measurement errors $s(x_i)$, $s(y_i)$ are too small.

### A.4.3 Estimation of random error variances

It has been shown for the classical approach of constant errors in the Y direction only that regression analysis provides a biased estimate of the random error variance(12).

If $s^2_{y.x}$ denotes the mean sum of squares about regression, i.e.

$$s^2_{y.x} = \frac{SS}{n-2} = \frac{\sum_{i=1}^{n} res_i^2}{n - 2} \qquad (A-51)$$

and if the measurement exhibits a constant bias (a) the random error variance $(s^2_{e_j})$ as defined by the Grubbs constant-bias model (eq.(A-21)) may be estimated by ICT through equation (A-52) whereby neglecting subscripts j denoting the laboratory:

$$s^2_e = s^2_{y.x} \cdot (1 + \frac{1}{n}) - \frac{n}{n-1} \cdot a^2 \qquad (A-52)$$

If the measurement is unbiased (a = 0), the quantity $s^2_{y.x}(1 + \frac{1}{n})$ obtained by isotope correlations yields an unbiased estimate of $s^2_e$ .

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## Appendix B

## Grubbs analysis and paired comparisons

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The model assumptions made by Grubbs in his first contribution to the problem of estimation of precision [1] are widely known, but are repeated here for the purpose of defining a notation:

$$x_{ij} = X_i + e_{ij} \qquad (1)$$

$i = 1,2,\ldots,n$ denoting items

$j = 1,2,\ldots,m$ denoting laboratories or measurement techniques

$x$ measured values

$X$ true but unobserved values

$e$ random errors

$$E(e_{ij}) = \mu_{e_j} \qquad (2)$$

$$E(e_{ij}e_{kl}) = \sigma^2_{e_j} \text{ for } j = l \text{ and } i = k$$
$$= E(e_j)\,E(e_l) \text{ otherwise} \qquad (3)$$

$$E(Xe_{ij}) = E(X)\;E(e_j) \qquad (4)$$

A more convenient notation for the same model would be:

$$x_{ij} = a_j + X_i + e_{ij} \qquad (5)$$

$a_j$ denoting an additive "bias"

$$E(e_{ij}) = 0 \qquad (6)$$

$$E(e_{ij}e_{kl}) = \sigma^2_{e_j} \text{ for } j = l \text{ and } i = k \qquad (7)$$
$$= 0 \text{ otherwise}$$

$$E(Xe_{ij}) = 0 \qquad (8)$$

This latter notation will be used in subsequent expressions. Estimates for $\sigma^2_{e_j}$ are usually obtained by two methods:

$$\text{Method 1: } \hat{\sigma}^2_{e_j} = \text{var}(x_j) - \overline{\text{cov}}(x_k x_l) \quad k \neq l \qquad (9)$$

$$\text{whereby } \overline{\text{cov}}\,(x_k x_l) = \frac{1}{m(m-1)} \sum_{\substack{k,l\\k\neq l}} \text{cov}(x_k x_l) \qquad (10)$$
$$= \hat{\sigma}^2_x$$

An estimator for $\sigma^2_x$ (process variance) is thus the mean of the covariances between all pairs of laboratories. It is easily seen that when $m = 2$ the method 1 error variance estimator reduces to

$$\hat{\sigma}^2_{e_1} = \text{var}(x_1) - \text{cov}(x_1 x_2)\;. \qquad (11)$$

A second method was proposed for when $m > 2$.

$$\text{Method 2: } \hat{\sigma}^2_{e_j} = \text{var}(x_j) - 2\,\overline{\text{cov}}(x_j x_k) + \overline{\text{cov}}(x_k x_l)$$
$$k,\, l \neq j \quad k \neq l \qquad (12)$$

Method 1 has been shown to be superior over method 2 in terms of efficiency (sampling variance of the estimators) for $m = 3$ if

$$\sigma^2_x < \frac{\max\limits_j(\sigma^4_{e_j})}{\min\limits_j(\sigma^2_{e_j})} \qquad (13)$$

which in the most restrictive case means

$$\sigma^2_x < \max_j(\sigma^2_{e_j})\;. \qquad (14)$$

An additional inequality should be considered: even ignoring available laboratory 3 data, using only laboratory 1 and laboratory 2 data, method 1 is more efficient if

$$\sigma^2_x < \sigma^2_{e_3}\;. \qquad (15)$$

Every estimate, then, involves a decision about method selection and numbers of laboratories used per method in order to choose the most efficient estimator. A small example illustrates this situation:

$\sigma^2_{e_1} = 1$

$\sigma^2_{e_2} = 2$

$\sigma^2_{e_3} = 4$

$\sigma^2_x = 3$

In this case the best estimates are obtained by method 1 rather than method 2 because:

$$\sigma_x^2 = 3 < \frac{\max_j(\sigma_{e_j}^4)}{\min_j(\sigma_{e_j}^2)} = \frac{\sigma_{e_3}^4}{\sigma_{e_1}^2} = \frac{16}{1} = 16$$

and

$\sigma_{e_1}^2$ is best estimated

by $\hat{\sigma}_{e_1}^2 = \mathrm{var}(x_1) - \mathrm{cov}(x_1x_2)$

because $\sigma_x^2 < \sigma_{e_3}^2$

and $\sigma_{e_2}^2$

by $\hat{\sigma}_{e_2}^2 = \mathrm{var}(x_2) - \mathrm{cov}(x_1x_2)$

because $\sigma_x^2 < \sigma_{e_3}^2$

but $\sigma_{e_3}^2$

by $\hat{\sigma}_{e_3}^2 = \mathrm{var}(x_3) - \dfrac{\mathrm{cov}(x_1x_3) + \mathrm{cov}(x_2x_3) + \mathrm{cov}(x_1x_2)}{3}$

because $\sigma_x^2 > \sigma_{e_2}^2 > \sigma_{e_1}^2$.

If $\sigma_x^2 = 5$ method 2 would have to be chosen for all estimates of $\sigma_{e_j}^2$ because

$$\sigma_x^2 = 5 > \max_j(\sigma_{e_j}^2) = \sigma_{e_3}^2 = 4 .$$

Similar inequalities for $m > 3$ have not yet been developed. But, such inequalities can be replaced by calculation of the sampling variance of the estimates obtained by different methods and different subsets of laboratories and using the decision rule to choose the estimate with the minimum sampling variance.

The statistical background for these inequalities can be found in [1] equations (12), (13), (16), (18) and (23).

The application of the above equations to our example yields the following results:

Variance of estimates $\hat{\sigma}_e^2$ as a function of the combination of selected method and laboratories used ($n = 10$ assumed)

| Method | Laboratories Used | $\mathrm{var}(\hat{\sigma}_{e_1}^2)$ | $\mathrm{var}(\hat{\sigma}_{e_2}^2)$ | $\mathrm{var}(\hat{\sigma}_{e_3}^2)$ |
|---|---|---|---|---|
| Method 1 | 1 and 2 | $\underline{1.44}$ | $\underline{2.11}$ | |
| | 1 and 3 | 2.33 | | 5.66 |
| | 2 and 3 | - | 3.77 | 6.44 |
| | 1,2 and 3 | 1.77 | 2.44 | $\underline{5.11}$ |
| Method 2 | 1,2 and 3 | 1.88 | 3.14 | 6.99 |

The underlined estimates show the minimum variance estimates. The method and laboratory optima are in accordance with the inequality criteria previously described. If the basic model is valid and if the process variance, $\sigma_x^2$, is small (in the same order of magnitude as the random error variances), the recommended procedure is then to examine the variance of all possible estimates and to choose the estimate with minimum estimator variance. The estimates of $\sigma_{e_j}^2$ and $\hat{\sigma}_x^2$ have to be substituted in the formulae for the variance of the estimates. If on the other hand no prior knowledge about the model aptness is available, or if the process variance is large compared to the random error variances, different approaches are recommended.

The first improvement is to allow for a non-additive bias, i.e. making no constraint on its value. The generalization of the previous model (5) is especially recommended for the determination of the random error variances of the element concentrations where a multiplicative bias due to sample dilution cannot be excluded.

The model could be formulated then as

$$x_{ij} = a_j + b_jX_i + e_{ij} . \qquad (16)$$

One has to be aware that the estimates of $\sigma_{e_j}^2$ obtained from the additive bias model could be misleading by as much as the value of $\mathrm{var}(b_j)$. Also results will be misleading if the bias, $a_j$, has shifts which are unaccounted for by calculations assuming a constant bias over all items.

The extension of the model (1) to model (16) should especially be chosen if no strong protection against the possibility of a relative bias, $b_j$, can be formulated. To illustrate the effect of ignoring a relative bias though it is present, consider:

$$x_{ij} = a_j + b_j X_i + e_{ij}$$

$$= a_j + X_i + \{e_{ij} + X_i(b_j - 1)\} \quad (17)$$

and denote $\{e_{ij} + X_i(b_j - 1)\} = e'_{ij}$

so that $x_{ij} = a_j + X_i + e'_{ij}$ (18)

Assumption (8) $E(Xe_{ij}) = 0$ is strongly violated since

$$E(Xe'_{ij}) = \sigma_x^2 (b_j - 1)^2 \quad (19)$$

and the estimators (9) or (12) have expected values

$$E(\hat{\sigma}^2_{e'_j}) = \sigma^2_{e_j} + \sigma_x^2 (b_j - 1)^2.$$

They are thus biased by

$$\sigma_x^2 (b_j - 1)^2.$$

An example shows the importance of the correct model specification. The random error in the Pu-concentration measurement for the ICE batches was estimated for the IAEA laboratory (SAL) with the constant-bias model as 0.83 % relative standard deviation.

The non-constant bias $b_j$ was determined for SAL to be 1.017 relative to WAK which was assumed to be the base with $b_1 = 1$ in the bias determination. The effect of this apparently very small (< 2 %) relative bias propagates quite strongly in the estimate of the random error of SAL. If one disregards this non-constant bias one would commit a systematic error in the estimate of about 6.5 % of the more correct variance estimate.

The random error relative standard deviation was estimated with the non-constant-bias model to be 0.37 % for SAL with a mean of 1.50 g/kg. The process standard deviation was estimated to be 5.8 % relative standard deviation with roughly the same mean of 1.47 g/kg.

$$\hat{\sigma}^2_{e_{SAL}} = \left(\frac{0.37 \times 1.5}{100}\right)^2 = 3.08 \times 10^{-5}$$

$$\hat{\sigma}^2_x = \left(\frac{5.8 \times 1.47}{100}\right)^2 = 7.27 \times 10^{-3}$$

$$\hat{\sigma}^2_x (1 - b_{SAL})^2 = 7.27 \text{x} 10^{-3} \text{x} (1 - 1.017)^2 = 2.01 \text{x} 10^{-6}$$

$$\frac{\hat{\sigma}^2_x (1 - b_{SAL})^2 \times 100}{\hat{\sigma}^2_{e_{SAL}}} = 6.5 \%$$

This means that the estimate for $\sigma^2_{e_{SAL}}$ will be systematically 6.5 % too large if the non-constant bias component is disregarded. Compared to the uncertainty (sampling error) associated with the estimate, this error is relatively small, but this smallness is due only to the relatively small process variance. The data on the whole campaign with a relative process standard deviation of 21 % compared to 5.8 % for ICE would yield a comparable overestimate of $\sigma^2_{e_{SAL}}$ of 83 % of the correct estimate.

Considering the effect of neglecting possible multiplicate bias components it is always advisable to use a non-constant-bias model as long as the non-constant bias can be estimated with relatively high precision. This is the case in situations of large $\hat{\sigma}^2_x$. The effect of neglecting this non-constant bias is strongest in such situations.

Numerous estimation techniques for the relative biases can be found in the literature 2/, 3/, 4/.

It is quite obvious that all current techniques yield only the ratios of relative biases or the products of relative biases and true values in the absence of constraints on the true values such as constraining their variance to a certain value.

The estimators proposed by Jaech 2/ are

$$\hat{b}_j = \left(\prod_{k\neq 1,j}^{m} \frac{\text{cov}(x_k x_j)}{\text{cov}(x_1 x_j)}\right)^{1/(m-2)} \qquad \text{for } j > 1 \quad (20)$$

$$\hat{b}_j = 1 \qquad \text{for } j = 1$$

and for

$$\hat{\sigma}^2_x b_1^2 = \hat{\sigma}^2_x = \left(\prod_{\substack{j=3 \\ k<j,\ \neq 1}}^{m} \frac{\text{cov}(x_1 x_j)\,\text{cov}(x_1 x_k)}{\text{cov}(x_k x_j)}\right)^{2/(m-1)(m-2)} \quad (21)$$

and for

$$\hat{\sigma}^2_{e_j} = \text{var}(x_j) - \hat{b}_j^2 \hat{\sigma}^2_x . \quad (22)$$

These estimators are unfortunately applicable only for $m > 2$.

For $m \geq 2$ an estimator for $b_j/b_k$ was developed by Wald 5/:

$$\left(\frac{\hat{b}_j}{b_k}\right) = \frac{\bar{x}_j^{(1)} - \bar{x}_j^{(2)}}{\bar{x}_k^{(1)} - \bar{x}_k^{(2)}} \quad (23)$$

whereby

$$\bar{x}_j^{(1)} = \frac{2}{n} \sum_{i=1}^{n/2} x_{ij} \quad \text{and} \quad \bar{x}_j^{(2)} = \frac{2}{n} \sum_{i=n/2+1}^{n} x_{ij}$$

for even $n$ . The $x_{ij}$ are sorted in sequence of $\bar{x}_i$ .

For uneven $n$ one observation has to be dropped. The rationale behind this and similar estimators is clear if the estimator is developed in terms of the right hand side of the model equation (16)

$$\left(\frac{\hat{b}_j}{b_k}\right) = \frac{(a_j + b_j\bar{X}^{(1)} + \bar{e}_j^{(1)}) - (a_j + b_j\bar{X}^{(2)} + \bar{e}_j^{(2)})}{(a_k + b_k\bar{X}^{(1)} + \bar{e}_k^{(1)}) - (a_k + b_k\bar{X}^{(2)} + \bar{e}_k^{(2)})} \tag{24}$$

$$= \frac{b_j(\bar{X}^{(1)} - \bar{X}^{(2)}) + \bar{e}_j^{(1)} - \bar{e}_j^{(2)}}{b_k(\bar{X}^{(1)} - \bar{X}^{(2)}) + \bar{e}_k^{(1)} - \bar{e}_j^{(2)}} \; . \tag{25}$$

If we can assume

$$E(\bar{e}_j^{(1)}) = E(\bar{e}_j^{(2)}) = E(\bar{e}_k^{(1)}) = E(\bar{e}_k^{(2)}) = 0 \tag{26}$$

then

$$E\left(\frac{\hat{b}_j}{b_k}\right) = \frac{b_j}{b_k} \; . \tag{27}$$

Assumption (26) is crucial. If the variance of the true values is considerably larger than the error variances (26) will usually hold. Otherwise the sorting sequence of the observed values will reflect the sorting sequence of the random errors rather than the one of the true values so that

$$E(\bar{e}_j^{(1)}) < 0 < E(\bar{e}_j^{(2)})$$

and (25) will be biased.

Random allocation of observed values to one of the two groups on the other hand - which would make assumption (26) far more likely for small process variances - has the undesired effect that

$$E(\bar{X}^{(1)} - \bar{X}^{(2)}) = 0 \tag{28}$$

so that (24) will be an indeterminate form. Nevertheless, if assumption (26) holds, which it will if $\sigma_x^2 \gg \sigma_{e_j}^2$ , then the estimator (23) is useful and can replace estimator (20) for the two laboratory situations. The estimator (22) for $\hat{\sigma}_{e_j}^2$ and estimator (21) for $\hat{\sigma}_x^2$ would be used in the same way as for the $m > 2$ situation.

The two defined estimators allow for a relative bias effect and thus provide an improved estimator for $\sigma_{e_j}^2$, but they still suffer from large sampling variances. Such large variances will frequently cause negative and operationally useless estimates.

One remedy against these undesirable large sampling variances is a transformation which effects a reduction in process variance and an increase in random error variance of the transformed values.

Consider again that the $x_{ij}$ values could be sorted in ascending sequence of the true values $X_i$ so that for any pair in the sorted sequence $x_{1j}, x_{kj}$

$$1 < k \text{ if } X_1 < X_k$$

$$\text{and} \quad x'_{ij} = x_{ij} - x_{(i-1)j} \quad \text{for } i > 1 \tag{29}$$

$$= \text{missing} \quad \text{for } i = 1 \; .$$

In the ideal case of equally spaced true values $X_i$ the variance of the first differences of the true values would vanish since

$$\sigma_{x'}^2 = 0 \qquad \text{if} \tag{30}$$

$$X' = X_i - X_{i-n} = \text{constant} \tag{31}$$

and

$$\sigma_{e'_j}^2 = 2\sigma_{e_j}^2 \; . \tag{32}$$

Under these ideal conditions inequality (14) would always suggest to use method 1 estimators (9) with $m = 2$ improved by the bias removal obtained by (22). The reduction $\sigma_x^2 - \sigma_{x'}^2$ is a function of the parameters of the distribution of $X$ and obviously of the type of distribution itself and primarily of the sample size $n$ since

$$\lim_{n \to \infty} \left| x_i - x_{i-1} \right| = 0 \; . \tag{33}$$

It can, however, be estimated by

$$\hat{\sigma}_x^2 - \hat{\sigma}_{x'}^2 \tag{34}$$

and $\sigma_{x'}^2$ can be checked for

$$\hat{\sigma}_{x'}^2 < 2 \max_j (\hat{\sigma}_{e_j}^2) = \hat{\sigma}_{e'_j}^2 \tag{35}$$

to decide which estimation technique is likely to produce the most efficient results.

For practical purposes it is of utmost importance to establish (prior to computing first differences) a sorting sequence which is completely independent of the random errors, otherwise autocorrelation terms cov($e_{ij}$ $e_{(i-1)j}$) will not vanish and will bias the estimates. It is suggested that for the calculation of $\hat{\sigma}^2_{e_j}$ the sorting sequence is established by the $x_{ik}$, $k \neq j$ and vice versa, since $E(e_j\ e_k) = 0$ per assumption (7). Hence, any "bias" in sorting by $x_{ik}$ will not propagate in $E(e_{ij}\ e_{(i-1)j})$.

Practical experience already shows that small sample sizes as e.g. n = 10 for ICE suggest the recommended estimation of $\hat{\sigma}^2_{e_j}$ with method 1, m = 2 and a transformation (29). An example will illustrate the reduction in sampling variance obtained with the estimator based on $x'_{ij} = x_{ij} - x_{(i-1)j}$. The data for this example are contained in the table of results. The sampling variance of the Pu-239 wt.% determination as obtained by Grubbs' method 2 with constant bias taking the results of SAL, WAK and TU simultaneously into consideration can be computed by formula (14) of 1/

$$\mathrm{var}(\hat{\sigma}^2_{e_j}) = \frac{2}{n-1}\sigma^4_{e_j} + \frac{1}{n-1}(\sigma^2_{e_1}\sigma^2_{e_2} + \sigma^2_{e_1}\sigma^2_{e_3} + \sigma^2_{e_2}\sigma^2_{e_3}).$$

Substituting $\hat{\sigma}^2_{e_j}$ estimated by Grubbs' method 2 for $\sigma^2_{e_j}$:

$$\hat{\sigma}^2_{e_{TU}} = 0.011$$

$$\hat{\sigma}^2_{e_{SAL}} = 0.064$$

$$\hat{\sigma}^2_{e_{WAK}} = 0.031$$

the variance of $\hat{\sigma}^2_{e_{TU}}$ is then obtained by

$$\mathrm{var}(\hat{\sigma}^2_{e_{TU}}) = \frac{2}{9}\,0.011^2 + \frac{1}{9}\,(0.011 \times 0.064 + 0.011 \times 0.031 + 0.064 \times 0.031)$$

$$\mathrm{var}(\hat{\sigma}^2_{e_{TU}}) = 3.63 \times 10^{-4}.$$

The process variance estimate $\hat{\sigma}^2_x = 1.25$, whereas the variance estimate of the first differences $\hat{\sigma}^2_{x'} = 0.013$ and since x' has a random error of $2\sigma^2_{e_j}$ (so that $x'' = \frac{x'}{\sqrt{2}}$ with $\mathrm{var}(x'') = \frac{\mathrm{var}(x')}{2}$ has a random error of $\sigma^2_{e_j}$), the process variance to be used for the calculation of var($\hat{\sigma}^2_{e_{TU}}$) using the first difference method is 0.0065.

$$\hat{\sigma}^2_{e_{TU}} = \mathrm{var}(x_{TU}) - \mathrm{cov}(x_{TU}x_{WAK})$$

then has a variance according to formula (5) of 1/ of

$$\mathrm{var}(\hat{\sigma}^2_{e_{TU}}) = \frac{2}{n-1}\sigma^4_{e_{TU}} + \frac{1}{n-1}(\sigma^2_x\sigma^2_{e_{TU}} + \sigma^2_x\sigma^2_{e_{WAK}} + \sigma^2_{e_{TU}}\sigma^2_{e_{WAK}})$$

$$= \frac{2}{9}\,0.111^2 + \frac{1}{9}\,(0.0065 \times 0.011 + 0.0065 \times 0.031 + 0.031 \times 0.011)$$

$$= 9.5 \times 10^{-5}$$

which is only ∿ 1/4 of the previous estimate of $3.63 \times 10^{-4}$.

It is pointed out that for the estimate var ($\hat{\sigma}^2_{e_{TU}}$) = $9.5 \times 10^{-5}$ the estimates $\hat{\sigma}^2_{e_j}$ from Grubbs' method 2 were used in order to show the reduction in sampling variance solely as a function of the reduction of $\hat{\sigma}^2_x$ by using $\hat{\sigma}^2_{x''}$ instead.

This means that the precision of our estimate obtained by the first difference method using only two laboratories is, in terms of its variance, 4 times as good as the estimate obtained with the original data using all three laboratories. This means again that the random error variance estimates obtained with the first difference method which we would obtain if we would repeat the ICE experiment over and over again (in a completely controlled way so that only the random errors vary from repetition to repetition) would cluster around the true value of $\sigma^2_{e_j}$. But the resulting variability of the estimates would be only 1/4 of the variance of the estimates of Grubbs' method 2 on the original data. This could definitely be considered an improvement.

A further problem which was not yet considered is the estimation of var (a). This estimate is of utmost importance for practical safeguards as well as for the laboratories since either possible diversion or problems with the sample treatment are reflected in this estimate.

A recent contribution $\underline{6}/$ even suggests to base the rejection or acceptance of interlaboratory differences primarily on tests of observed differences against empirically-established distribution functions of differences.

An estimate of $\sigma^2_a$ for the constant-bias model is obtained by

$$\hat{\sigma}^2_a = \frac{1}{m-1} \sum_{j=1}^{m} (\overline{x}_{.j} - \overline{x}_{..})^2 - \frac{1}{mn} \sum_j \hat{\sigma}^2_{e_j} \quad (36)$$

This estimate is to be understood as the variance of a random variate, i.e. the bias $a_j$ is a sample out of a population of biases with mean $\mu_a$ and standard deviation $\sigma_a$ for which $\hat{\sigma}_a$ is an estimate. If independent estimates for the bias variance for a population a' exist, $\sigma^2_a=\sigma^2_{a'}$, could be tested, thus estimating the probability that the current sample of biases is drawn from a defined population of biases. If this probability is smaller than a set level of significance one could conclude that either the bias populations are different or that the true values are different. This conclusion however cannot be made without estimator (36) so that the random variance estimation is indispensable for this conclusion. Reference $\underline{6}/$ seems to neglect the random error component in the acceptance test of interlaboratory mean differences. A mean difference of two laboratories with very high precision has obviously more weight in terms of acceptance or rejection as the difference between laboratories with very low precision, which is not taken into account in $\underline{6}/$. Rather than testing absolute mean differences testing of $\hat{\sigma}^2_a$ is therefore recommended since $\hat{\sigma}^2_a$ is corrected for the precision component.

For the case of the non-constant-bias model equation (16) estimates of $\sigma^2_a$ cannot be made without constraints like $\Sigma a = 0$ or similar constraints. Only estimates for the additive biases plus a non-constant shift like, e.g.

$$\text{est}(a_j + b_j X_k)$$

can be obtained whereas for the constant-bias model estimates like

$$\text{est}(a_j + X_k)$$

were possible. This will be shown later in the context of the ANOVA approach.

As an alternative, estimates for $\sigma^2_{\frac{a}{\bar{b}}}$ could be obtained if one transforms

$$x'_{ij} = x_{ij}/b_j, \quad (37)$$

estimates $\hat{\sigma}^2_{e'_j}$ and then applies estimator (36). The same testing procedure can then be applied as for the constant-bias model.

## Analysis of Variance

The model equation (5) which reads

$$x_{ij} = a_j + X_i + e_{ij}$$

could also be written as

$$x_{ij} = \sum_{k=1}^{m+n} c_{ki} d_k + e_{ij} \quad (38)$$

whereby

$$c_{ki} = 1 \quad \text{if} \quad k = j \quad \text{or} \quad k = m + i$$

$$= 0 \quad \text{otherwise.}$$

Then e.g.

$$d_1 = a_1 \quad (39)$$

and

$$d_{m+1} = X_1 \quad (40)$$

and

$$x_{ij} = d_j + d_{m+i} + e_{ij} \quad (41)$$

$$= a_j + X_i + e_{ij}.$$

The vector of unknown parameters $\underline{d}$ can be estimated by leat squares if the matrix of coefficients C would have rank m + n. But as it can be readily seen C has rank m + n - 1 so that no unique least squares solution for $\hat{d}$ exists.

Rewriting (reparametrization of) equation (38) as

$$x_{ij} = \sum_{k=1}^{m+n-1} c_{ki} d_k + e_{ij}$$

solves this difficulty but the parameters d assume a different meaning

e.g. $\quad d_1 = a_1 + X_n \quad (43)$

and $\quad d_{m+1} = X_1 - X_n \quad (44)$

but $\quad x_{ij} = d_j + d_{m+i} + e_{ij}$

$$= a_j + X_n + X_i - X_n + e_{ij}$$

$$= a_j + X_i + e_{ij} \quad .$$

The traditional ANOVA approach consists in estimating the mean square (MS) of the biases a and of X and of the error term which is assumed to be homogeneous over the laboratories.

The above defined dummy variable approach allows non-orthogonal designs (with missing values) as well as providing a capability for obtaining estimates for $\sigma^2_{e_j}$ rather than only an estimate for a pooled random error variance.

These estimates for $\sigma^2_{e_j}$ were developed by K. Stewart 7/ and are well described in this reference. The basic rationale behind them is that each $x_{ij}$ is predicted by $\hat{x}_{ij}$ after estimates for $\underline{d}$ are obtained.

Each residual $r_{ij} = x_{ij} - \hat{x}_{ij}$ is expressed as a linear combination of all $x_{ij}$

i.e. $$r_{ij} = \sum_i \sum_j w_{ij} x_{ij}$$

$$= \sum_i \sum_j w_{ij}(a_j + X_i + e_{ij}) \quad (46)$$

and each $\sum_i r^2_{ij}$ can be expressed as a linear function of all $\sigma^2_{e_j}$,

i.e. $$\sum_i r^2_{ij} = \sum_j w_j \sigma^2_{e_j} \quad . \quad (47)$$

The resultant system of equations is then solved for the unknowns $\sigma^2_{e_j}$ thereby obtaining estimates $\hat{\sigma}^2_{e_j}$.

These estimates can be shown to be the same as the Grubbs estimates 12/ for the orthogonal case but are obviously different in the non-orthogonal case. Hence, the same sampling variance problems exist for the orthogonal case. But it is advisable to check for a non-orthogonal application if the decrease in sampling variance of $\sigma^2_{e_j}$ due to using all information, rather than dropping a complete row vector of observations if only one element is missing as it would have to be done for estimator (12), compensates for neglecting inequalities (13) and (15).

Estimates $\hat{\sigma}^2_a$ from model (42) can be obtained by equation (36). This equation applies the standard technique of equating the expected mean squares (EMS) with the computed mean squares (MS) and solving for the unknown variance components.

Rewriting (42) for the non-constant bias case is possible if one sets

$$C_{ki} = 1 \text{ if } k = j$$

$$= 0 \text{ if } k \neq j \text{ and } k \leq m$$

$$= b_j \text{ if } k = m + i$$

$$= 0 \text{ if } k \neq m + i \text{ and } k > m$$

E.g. for an experiment with 3 laboratories and 3 observations the design matrix assumes then the form

$$c = \begin{matrix} 1 & 0 & 0 & b_1 & 0 & 0 \\ 1 & 0 & 0 & 0 & b_1 & 0 \\ 1 & 0 & 0 & 0 & 0 & b_1 \\ 0 & 1 & 0 & b_2 & 0 & 0 \\ 0 & 1 & 0 & 0 & b_2 & 0 \\ 0 & 1 & 0 & 0 & 0 & b_2 \\ 0 & 0 & 1 & b_3 & 0 & 0 \\ 0 & 0 & 1 & 0 & b_3 & 0 \\ 0 & 0 & 1 & 0 & 0 & b_3 \end{matrix}$$

and is of rank $m + n - 1 = 5$. If the last column would be dropped then

$d_1$ would estimate $a_1 + b_1 Y_3$

$d_2$ would estimate $a_2 + b_2 Y_3$

$d_3$ would estimate $a_3 + b_3 Y_3$

$d_4$ would estimate $Y_1 - Y_3$

$d_5$ would estimate $Y_2 - Y_3$

and e.g.

$$\hat{x}_{12} = d_1 + b_1 d_5$$

$$= a_1 + b_1 Y_3 + b_1(Y_2 - Y_3)$$

$$= a_1 + b_1 Y_2 .$$

Equating expected mean squares with computed mean squares yields, in this case, no estimates for $\sigma^2_a$ and $\sigma^2_x$ due to the non-constant coefficients $b_j$.

The estimates $r_{ij} = x_{ij} - \hat{x}_{ij}$ can nevertheless always be obtained and used for purposes of outlier testing.

The ANOVA approach is hence only recommended for outlier testing but does not add any new estimation techniques at all in the orthogonal case. For the non-orthogonal case (missing values) ANOVA might reduce the sampling variance of the variance components estimates but the statistical apparatus would have yet to be developed especially for the non-constant-bias model.

The first recommendation is to apply the non-constant-bias model for $\sigma^2_x > \sigma^2_{e_j}$. It is further recommended to estimate within this model using the original data and first differences in order to determine the estimators with the smallest sampling variance. Finally, it is recommended that outliers be tested by using the residual method and to exclude the outliers after they have been explained by extraneous sources.

## Outlier detection

Numerous outlier detection methods are to be found in the literature. However, each method determines outliers as extreme unlikely samples given that a certain model is true. In our case outliers would then have to be obviously determined as extreme unlikely samples given that model (5) or model (16) holds.

Since with each of the two models predictions of observed values $\hat{x}_{ij}$ are possible the residuals $r_{ij} = | x_{ij} - \hat{x}_{ij} |$ are the obvious quantities to be tested.

The variance of $r_{ij}$ can again be estimated from the $\hat{\sigma}^2_{e_j}$, since each $r_{ij}$ can be expressed as a linear function of all observed values, each of which $x_{ij}$ has a variance $\sigma^2_{e_j}$.

If one wants to perform a simultaneous test on all residuals then $\alpha' = 1 - (1-\alpha)^{1/nm}$ has to be computed if $\alpha$ is overall type I error, i.e. the probability of detecting one or more outliers among the n x m cases when indeed no true outlier exists. Each residual has to be tested then against the $100(1-\alpha'/2)$ percentile point of the distribution of $r_{ij}$.

Normalization of the residuals

$$r'_{ij} = \frac{r_{ij}}{\hat{\sigma}_{r_{ij}}}$$

allows testing $r'_{ij}$ against Student's t distribution with $df = (n-1)(m-1) - 1$ if the df for $\hat{\sigma}_{r_{ij}} = (n-1)(m-1) - 1$ which is only the case if $\hat{\sigma}_{e_1} = \hat{\sigma}_{e_2} = \ldots . \hat{\sigma}_{e_m}$. If this is not the case then an approximation for the df for small nm should be used. The application of Satterthwaite's formula to (47) after solving for the coefficients $w_j$ and after using again Satterthwaite's formula to determine the df for $\hat{\sigma}_{e_j}$ could be recommended.

The same method as just outlined could be used for the non-constant-bias model. This outlier test was proposed in reference $\underline{7}/$.

## Summary of recommendations

Such a summary contains first the recommendation to apply the non-constant-bias model for $\sigma^2_x > \sigma^2_{e_j}$. Further, it is recommended to estimate within this model using the original data and with the first differences in order to determine the estimators with the smallest sampling variance. Finally, is the recommendation to test for outliers by the residual method.

One should be aware that the rejection of outliers is a protection against a type of diversion strategy, which consists of an intentional inflation of precision by reporting outlying results, so that tests on mean differences between operator and inspector become less sensitive. Therefore, it is recommended to base precision estimates always on data excluding outliers and tests on mean differences between operator and inspector on data including them.

## Results

The attached table of results is a condensed representation of the evaluation. The estimates are obtained after the outliers are excluded. The outliers are tested against the constant-bias model and not against the respective model in order to have the same data set for both models after the exclusion of the outliers. The estimates for the constant-bias model are obtained by the ANOVA approach by solving (47) for $\sigma^2_{e_j}$ thus obtaining $\hat{\sigma}^2_{e_j}$.

The estimates for the random error standard deviations for the non-constant-bias model are obtained as follows: For all three pairs of laboratories (TU-WAK, TU-SAL, SAL-WAK) estimates by formula (22) are obtained. For each laboratory are thus two estimates for $\hat{\sigma}^2_{e_j}$ available. The mean value of these two estimates per laboratory is shown for the non-constant-bias model in the table. In formula (22) $var(x_j)$ was replaced by $var(x'_j)/2$ and $\hat{\sigma}^2_x$ was estimated by $cov(x'_k x'_j)/2$, whereby $x'_k x'_j$ are denoting first differences as defined in (29).

Process standard deviations $\hat{\sigma}_x$ and $\hat{\sigma}_{x'}$, are computed by (21).

Asterisks in the column 'Criterion (35)' denote the superiority of the first difference approach by inequality (35) and likewise for column 'Criterion (13)'. Negative estimates for $\hat{\sigma}^2_{x'}$, can obviously be applied without difficulties in these criteria. They suggest the application of the first difference approach.

Estimates for $\sigma_a$ are possible only for the constant-bias model and are computed by ANOVA.

It should be noted that the constant-bias model using the original data yields 17 % negative estimates due to large sampling variances whereas the first difference method improved by the generalization due to the inclusion of a non-constant bias term yields only 4 % negative estimates.

This improvement becomes even stronger if one checks the corresponding results on the whole campaign due to the fact that $\sigma_{x'}/\sigma_x$ is among other things a function of n (number of batches).

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Table B.1

Outliers as Screened by the Constant-Bias Model on the 5 % Level of the Overall Type I Error

| Element/Isotope | Laboratory | Batch |
|---|---|---|
| U-235 | TU | 9 |
| U-235/U-238 | TU | 9 |
| Pu-238 | WAK | 7 |
| Pu-238 | WAK | 2 |
| Pu-240 | WAK | 2 |
| Pu-242 | SAL | 8 |
| Pu-238/Pu-239 | WAK | 7 |
| Pu-238/Pu-239 | WAK | 2 |
| Pu-240/Pu-239 | WAK | 2 |
| Pu-242/Pu-239 | SAL | 8 |

Table B.2

Estimates After Outliers Are Removed
Data as Reported in 4th ICE Newsletter, Pu and Pu Isotopes Decay Corrected

| | Constant Bias Model Using Original Data | | | | Non-constant Bias Model Using 1st Differences | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\hat{\sigma}_{e_j}*100/\bar{X}_j$ | | | $\hat{\sigma}_a*100/\bar{X}..$ | $\hat{\sigma}_{e_j}*100/\bar{X}_j$ | | | $(\frac{b_{SAL}}{b_{WAK}})$ | $(\frac{b_{TU}}{b_{WAK}})$ | $\hat{\sigma}_x*100/\bar{X}..$ | $\hat{\sigma}_{x'}*100/\bar{X}$ | Criterion (35) | Criterion (13) |
| | TU | SAL | WAK | | TU | SAL | WAK | | | | | | |
| Pu-Conc | 0.5 | 0.83 | 0.77 | 1.13 | 0.96 | 0.37 | 0.40 | 1.02 | 1.01 | 5.8 | 2.3 | | * |
| Pu/U | not estimated | | | | 0.91 | 0.87 | 0.87 | 1.08 | | 3.9 | 0.5 | * | |
| Pu-238 | 8.64 | 3.99 | 4.52 | 8.96 | 9.00 | 12.25 | 5.72 | 2.93 | 2.54 | | • | * | |
| Pu-239 | 0.18 | 0.43 | 0.30 | 0.10 | 0.27 | 0.46 | 0.26 | 0.94 | 0.97 | 1.9 | 0.2 | * | |
| Pu-240 | 0.15 | 0.47 | 0.28 | • | 0.41 | 0.44 | 0.51 | 0.98 | 1.06 | 1.6 | 0.6 | | |
| Pu-241 | 0.29 | 1.05 | 0.41 | 0.13 | 0.57 | 0.82 | 0.49 | 0.84 | 0.82 | 2.2 | • | * | |
| Pu-242 | • | 4.78 | 0.93 | 2.59 | 2.51 | 2.63 | 4.24 | 1.07 | 1.40 | 8.0 | 0.8 | * | |
| Pu-240/Pu-239 | • | 0.46 | 0.21 | 0.07 | 0.36 | 0.45 | 0.23 | 0.95 | 1.02 | 3.4 | 0.3 | * | |
| Pu-241/Pu-239 | 0.41 | 0.58 | 1.14 | 0.06 | • | 0.84 | 0.14 | 0.86 | 0.87 | 4.1 | 1.4 | | * |
| Pu-242/Pu-239 | • | 1.30 | 4.98 | 2.79 | 2.00 | 4.11 | 4.91 | 1.06 | 1.34 | 9.8 | • | * | |
| Pu-238/Pu-239 | 8.69 | 4.29 | 4.01 | 9.00 | 9.28 | 10.74 | 6.54 | 1.08 | 2.28 | 5.5 | 1.9 | * | |
| U-Conc | • | 1.05 | 1.13 | 1.10 | 0.35 | 1.78 | 0.79 | 1.05 | 1.06 | 6.7 | 2.1 | | * |
| U-234 | 11.01 | • | 21.61 | 5.22 | 6.12 | 10.70 | 4.52 | 2.22 | 1.82 | 7.1 | • | * | |
| U-235 | 0.65 | 0.52 | 0.76 | 0.96 | 1.10 | • | 1.04 | 1.08 | 0.91 | 6.8 | 2.7 | | * |
| U-236 | 1.37 | • | 1.48 | • | 1.21 | 1.35 | 0.72 | 0.97 | 1.17 | 1.7 | 2.6 | * | |
| U-238 | 0.02 | • | 0.03 | • | 0.02 | 0.02 | 0.02 | 1.34 | 1.10 | 0.1 | • | * | |
| U-234/U-238 | 11.01 | • | 21.61 | 5.22 | 4.90 | 13.62 | 4.67 | 2.22 | 1.83 | 7.3 | • | * | |
| U-235/U-238 | 0.66 | 0.53 | 0.77 | 0.97 | 1.06 | • | 1.01 | 1.07 | 0.91 | 6.8 | 2.4 | | * |
| U-236/U-238 | 1.48 | • | 1.53 | • | 1.08 | 1.17 | 0.66 | 0.98 | 1.19 | 1.6 | 1.7 | * | |

• denotes negative estimates

## Appendix C

## Analysis of partial Obrigheim reprocessing data

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### Introduction

The ICE (Isotopic Correlation Experiment) was organized by ESARDA (European Safeguards Research and Development Association).

Samples taken from ten batches of the german reprocessing plant WAK (Karlsruhe) were analysed by four laboratories*. These ten batches correspond to five fuel bundles from the OBRIGHEIM reactor, each with burn-up close to 30 000 MWd/T.

The aims of this experiment were twofold. It was meant to check the consistency of analytical results and also to demonstrate the possibilities of Isotope Correlation Techniques in safeguarding the input of reprocessing plants. For this second purpose several laboratories received the analytical results and applied their own procedure of ICT.

As far as our role is concerned, we have, as usual, performed a complete set of calculations, compared these results with the measured values and then established an independent determination of the input balance from the measured isotopic ratios and calculated correlations. A comparison of the resulting input masses with those obtained by the volumetric method is also presented in this report.

### C.1 Brief recall of the french procedure for isotopic correlation

As indicated in previous papers /1/ /2/ /3/, we have used reactor physics calculation to determine correlation sets among final isotopic compositions of spent fuel and some parameters needed either for the input balance calculation or for the check of analytical results and coherence.

Concerning the input balance determination we use the following correlation sets:

A) For burn-up calculation : correlations based on isotopic measurements of uranium

$I = a(I,e) \times \Delta(U^5)$ ($^{235}U$ depletion)
$I = b(I,e) \times \Delta(U^6)$ ($^{236}U$ build-up)

B) For Pu/U ratio calculation : one correlation from the change in the uranium isotopic abundance and another one from the plutonium isotopic abundance

$$Pu/U = h(I,e) \times \Delta(U^5)$$

$$Pu/U = \delta(I,e) \times \frac{^{242}Pu \times {}^{239}Pu}{(^{240}Pu)^2}$$

- e is the initial fuel enrichment
- I is the burn-up.

Another set is used for internal consistency check in order to control the exactness of the initial enrichment of uranium and the type of bundle concerned.

These correlations combine the experimental Pu/U ratio and the isotopic compositions together with identification data given by the reactor (enrichment, bundle type,...).

### C.2 Obrigheim calculation

For neutron calculations, the fuel assembly was divided into two regions, the first one representing fuel pins and the second one the water holes.

A very simple multicell description was used without taking into account control rods or boron regulation.

All calculations were performed for a mean assembly.

In burn-up calculation we have assumed that keff = 1 for each successive step.

The procedure used is shown in figure 1. It is made up of the cell code APOLLO /4/ and the KAFKA system /5/ which includes the burn-up code EVOGENE.

* - WAK plant laboratory
- KfK reference laboratory (RCH)
- IAEA safeguards laboratory
- TU european laboratory

Only the following data were required:

- Type of assembly
- Number of fuel pins
- Cladding materials
- Approximate geometrical data
- Enrichment value
- Power history.

These data are normally available in the published literature for each reactor and most of it can be verified by using the checking correlations.

## C.3 Analysis of the results

Table C.1 shows the discrepancies between the analytical results obtained by the following laboratories: RCH, TU, WAK and IAEA.

For the $^{235}U$ depletion ($\Delta U^5$) only the analysis performed by TU on batch n° 94 stands out. This singularity does not exist for the $^{236}U$ measurement in the same analysis.

We can also note the large discrepancy existing for $^{242}Pu$, which is mainly caused by three analyses, in particular WAK n°86 and 90, IAEA n°93. We have already observed similar effects on other analysis campaigns.

For the $^{239}Pu/^{238}U$ ratios, which are not used in the correlation technique, there is a large discrepancy ($\sim$2.7 %) characterized by a systematic underevaluation by WAK.

Values of the main isotopic ratios versus burn-up were obtained from the preceding calculation.

Using the calculated burn-up from KWU, the values for each fuel assembly (two batches) were then compared with the analysis results.

In table C.2 we show the direct comparison of the mean values of experimental results with the calculated values for each fuel assembly reprocessed.

However the calculated values can only be considered for the assembly as a whole. Thus the comparisons must be made by combining the measured results of both batches corresponding to the same assembly.

The discrepancies are larger than in table C.1 because all of the calculations refer to the fuel assembly burn-up. In addition each half assembly does not have the exact same burn-up, because the burn-up distribution is sensitive to the radial orientation of the assembly.

We can note that the assembly reprocessed in batches 92 and 93 seems to represent an underestimated prediction of the burn-up.

The mean discrepancies shown in table C.2 are quite similar to those obtained for other reactors in previous studies.

## C.4 Input mass balance determination

After the direct comparison of measured results and calculated values discussed in the last section, we have obtained the burn-up and Pu/U ratios by using the correlation method. This allows us to calculate the input masses by the gravimetric method.

### A) Burn-up determination

We use two correlation functions to obtain the burn-up:

$$I_a = a(I,e)\ \Delta U^5$$
$$I_b = b(I,e)\ \Delta U^6$$

a(I,e) and b(I,e) are obtained from the calculation procedure described above.

The burn-up values reached are shown in table C.3. We can note that they are quite different for the two batches of a given assembly. This difference can easily be attributed to the fact that the assembly has been divided into two parts by separating the fuel pins which have not been irradiated in the same conditions due to the flux shape in the core.

Usually the discrepancy found between the burn-up predicted by the reactor operators and the burn-up calculated from the correlation set is about $(I - I_R)/I_R = - 3\ \% \pm 2\ \%$ *. We obtain here - 3.4 % ± 2.6 % which is in agreement with the usual results. Furthermore it is possible that the assembly reprocessed in batches 92 and 93 has an underestimated burn-up. The best estimate would be around 28 000 MWd/tm.

### B) Pu/U ratio determination

Two calculated correlations have been used to obtain the Pu/U ratios :

$$Pu/U = h(\bar{I},e)\ \Delta U^5$$

$$Pu/U = \delta(\bar{I},e)\ \frac{^{239}Pu \times {}^{242}Pu}{(^{240}Pu)^2}$$

---

* : This systematic error may be due to several reasons including the theoretical value of the energy released by fission.

where $\bar{I}$ is the mean burn-up obtained from the correlations $I_a$ and $I_b$ indicated above.

Table C.4 shows the Pu/U ratios measured by each laboratory. We can note that a rather large discrepancy of about two per cent occurs between the different laboratory results.

As for the burn-up, Pu/U ratios are given for each assembly as a whole.

The following table C.5 shows the Pu/U ratios which were calculated by the correlation method and we give the discrepancies among the mean measured values.

The very low, 0.1 % mean discrepancy results from a compensation of larger deviations. It must be taken into consideration that the correlation values are always within the limits of analytical result scattering and seem to be more accurate.

C) Determination of the input masses

First of all, we must underline the fact that the input balance determination has only been calculated for a part of the campaign. Therefore, we cannot include rinsing operations in this determination.

The relationships giving the input masses are shown here :

$$M_U^f = M_U^i \times \frac{1 - \bar{I}}{1 + \overline{(\frac{Pu}{U})}}$$

$$M_{Pu}^f = \overline{(\frac{Pu}{U})} \times M_U^f$$

- $M_U^i$ is the initial uranium mass for a whole assembly
- $M_U^f$ and $M_{Pu}^f$ are the final uranium and plutonium masses.

The burn-up values $(\bar{I})$ come from the mean of $I_a$ and $I_b$ (see table C.3).

The Pu/U ratios come from the mean of $\frac{Pu}{U}h$ and $\frac{Pu}{U}\delta$ given by the correlations (see table C.5).

As $\bar{I}$ and $\overline{Pu/U}$, both given by the correlation technique, concern a whole assembly reprocessed, we thus calculate the input masses for each whole assembly.

The uranium and plutonium input masses are shown in tables C.6 and C.7.

In the first three columns we give the input masses obtained from the volumetric method using the analytical results of each laboratory.

In the fourth column we give the input masses obtained from the gravimetric method. This method uses the calculated correlations which in turn use the mean values of measured isotopic ratios as indicated in the previous section (without excluding any of the analytical results). Although some of the analytical results may seem doubtful we have decided, nevertheless, to include them.

We have summarized in table C.8 the discrepancies between the input masses obtained with the volumetric method and those obtained with the gravimetric method.

As can be read in the tables, WAK's results are off the mean. They overestimate uranium masses and underestimate plutonium masses.

TU, IAEA and correlations results are rather consistent :

Mean U masses: 1319256 ± 7292 (± 0.55 % in 1 $\sigma$)

Mean Pu masses: 11487 ± 64 (± 0.56 % in 1 $\sigma$)

It is of interest to note in the third column of table C.8, that the correlation method gives a slight overestimation of uranium and plutonium masses. This may be attributed to the hold-up of the tanks which can only be taken into account when rinsing the unit or which would eventually disappear when considering a larger quantity of reprocessed fuel.

## C.5 Conclusion

We can note with confidence that the input gravimetric balance based on the correlation method and the classical volumetric balance used by the operators at WAK give identical results.

It is interesting to note that the correlation technique gives results as precise as analytical measurements.

Furthermore this method is independent of the Pu/U ratio measurements and of volume determinations.

Thus the correlation technique may be looked upon as an independent way to check the input balance in a reprocessing plant, as long as it is applied with a correct calculation procedure.

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KAFKA : Système modulaire pour le calcul des caractèristiques des combustibles irradiés dans les réacteurs de puissance.

| Batch number | $\Delta U^5$ | $\Delta U^6$ | $^{240}Pu/^{239}Pu$ | $^{242}Pu/^{239}Pu$ |
|---|---|---|---|---|
| 86 | 0.5 | 1.1 | 0.3 | 8.0 |
| 87 | 0.8 | 0.8 | 0.9 | 1.9 |
| 88 | 0.2 | 0.8 | 0.4 | 1.0 |
| 89 | 0.2 | 0.5 | 0.4 | 0.6 |
| 90 | 0.1 | 1.3 | 0.5 | 6.2 |
| 91 | 0.2 | 0.8 | 0.3 | 1.1 |
| 92 | 0.3 | 1.1 | 0.3 | 1.1 |
| 93 | 0.3 | 1.6 | 0.3 | 7.7 |
| 94 | 1.2(1) | 0.6 | 0.3 | 1.9 |
| 95 | 0.3 | 1.4 | 0.4 | 2.2 |
| Mean | 0.4 | 1.0 | 0.4 | 3.2 |

(1) TU measurement seems doubtful. Without it we reach 0.5 %.

Table C.1: DISCREPANCIES EXISTING BETWEEN THE ANALYTICAL RESULTS FOR THE PRINCIPAL ISOTOPIC RATIOS USED FOR ISOTOPIC CORRELATIONS

The means consider all the analyses done by the four laboratories. All results are in per cent.

| Batch | $\Delta U^5$ | $\Delta U^6$ | $Pu^9/U^8$ | $Pu^0/Pu^9$ | $Pu^2/Pu^9$ |
|---|---|---|---|---|---|
| 86 - 87 | -2.6±1.7 | -1.6±2.0 | -0.2±2.5 | -1.8±2.7 | -4.1±7.4 |
| 88 - 89 | -4.1±0.8 | -3.2±0.8 | -1.6±2.1 | -4.7±0.9 | -12.6±2.6 |
| 90 - 91 | -2.6±1.8 | -2.2±2.1 | -1.2±1.7 | -2.9±2.9 | -7.2±9.9 |
| 92 - 93 | +0.4±2.5 | +0.5±2.4 | -2.7±3.4 | +3.0±2.8 | +8.6±12. |
| 94 - 95 | -3.1±2.8 | -2.2±2.3 | -1.5±4.1 | -1.8±3.4 | -7.4±9.6 |
| Mean | -2.4±1.9 | -1.7±1.9 | -1.4±2.8 | -1.6±2.5 | -4.5±8.3 |

Table C.2: OBRIGHEIM : PARTIAL REPROCESSING CAMPAIGN

Comparison of mean analytical results and calculated values.

| Batch number | $I_a$ (%) | $\frac{I_a - I_R}{I_R}$ (%) | $I_b$ (%) | $\frac{I_b - I_R}{I_R}$ (%) | $\bar{I}$ (%) | $\frac{\bar{I} - I_R}{I_R}$ (%) |
|---|---|---|---|---|---|---|
| 86 | 2.89 | | 2.88 | | | |
| 87 | 3.02 | | 3.08 | | | |
| Tot | 2.95 | - 4.3 | 2.98 | - 3.5 | 2.966 | - 3.9 |
| 88 | 2.86 | | 2.88 | | | |
| 89 | 2.94 | | 2.92 | | | |
| Tot | 2.90 | - 6.2 | 2.90 | - 6.1 | 2.900 | - 6.1 |
| 90 | 3.01 | | 3.015 | | | |
| 91 | 2.84 | | 2.84 | | | |
| Tot | 2.93 | - 4.0 | 2.93 | - 4.0 | 2.926 | - 4.0 |
| 92 | 2.69 | | 2.71 | | | |
| 93 | 2.90 | | 2.91 | | | |
| Tot | 2.80 | + 8.0 | 2.81 | + 1.3 | 2.804 | + 1.0 |
| 94 | 2.62 | | 2.67 | | | |
| 95 | 2.83 | | 2.86 | | | |
| Tot | 2.72 | - 4.6 | 2.77 | - 3.1 | 2.746 | - 3.8 |
| Mean Discrepancies | | -3.66±2.60 | | -3.08±2.71 | | -3.36±2.62 |

Table C.3: OBRIGHEIM PARTIAL REPROCESSING CAMPAIGN

Burn-up determination

$I_R$ is the burn-up given by reactor; $I_a$ burn-up deduced from $\Delta U^5$; $I_b$ burn-up deduced from $\Delta U^6$.

| Batch number | RCH | WAK | TU | IAEA | Mean value ± 1 σ |
|---|---|---|---|---|---|
| 86<br>87 | | 0.800 | 0.916 | 0.884 | 0.8999<br>±0.0158 |
| 88<br>89 | | 0.871 | 0.886 | 0.873 | 0.8766<br>±0.0083 |
| 90<br>91 | 0.900 | 0.876 | 0.885 | 0.864 | 0.8813<br>±0.0154 |
| 92<br>93 | 0.870 | 0.833 | 0.851 | 0.851 | 0.8513<br>±0.0150 |
| 94<br>95 | 0.892 | 0.824 | 0.849 | 0.842 | 0.8514<br>±0.0288 |

Table C.4: OBRIGHEIM PARTIAL REPROCESSING CAMPAIGN

Pu/U ratios measured by assembly (%).

| Batch number | Pu/U by h | Discrepancies to mean analysis | Pu/U by δ | Discrepancies to mean analysis | Pu/U mean | Discrepancies to mean analysis |
|---|---|---|---|---|---|---|
| 86<br>87 | 0.888 | - 1.4 | 0.904 | + 0.5 | 0.8959 | - 0.44 |
| 88<br>89 | 0.875 | - 0.1 | 0.875 | - 0.2 | 0.8753 | - 0.15 |
| 90<br>91 | 0.882 | + 0.1 | 0.887 | + 0.6 | 0.8845 | + 0.36 |
| 92<br>93 | 0.867 | + 1.9 | 0.873 | + 2.5 | 0.8699 | + 2.18 |
| 94<br>95 | 0.844 | - 0.8 | 0.833 | - 2.2 | 0.8385 | - 1.52 |
| Mean | | -0.06±1.25 | | +0.24±1.69 | | +0.09±1.36 |

Table C.5: OBRIGHEIM PARTIAL REPROCESSING CAMPAIGN

Pu/U ratios determined by correlations (%).

| Batch number | TU | WAK | IAEA | Correlations |
|---|---|---|---|---|
| 86<br>87 | 259123 | 264295 | 261669 | 263800 |
| 88<br>89 | 262124 | 266533 | 262415 | 266500 |
| 90<br>91 | 261149 | 265744 | 263948 | 264390 |
| 92<br>93 | 264564 | 271434 | 264378 | 263880 |
| 94<br>95 | 263893 | 272428 | 271514 | 264420 |
| Total | 1310853 | 1340434 | 1323924 | 1322990 |
| Mean | 1325070 ± 1 % (1 σ) | | | 1322990 |

Table C.6: OBRIGHEIM PARTIAL INPUT MASS BALANCES OF THE REPROCESSING CAMPAIGN

a Uranium (g)

| Batch number | TU | WAK | IAEA | Correlations |
|---|---|---|---|---|
| 86<br>87 | 2373.1 | 2311.6 | 2313.0 | 2363.0 |
| 88<br>89 | 2322.6 | 2263.3 | 2289.4 | 2332.0 |
| 90<br>91 | 2311.2 | 2273.9 | 2279.3 | 2338.0 |
| 92<br>93 | 2251.9 | 2189.8 | 2249.6 | 2295.0 |
| 94<br>95 | 2240.2 | 2177.5 | 2286.9 | 2216.0 |
| Total | 11499 | 11216 | 11418 | 11544 |
| Mean | 11378 ± 1.3 % | | | 11544 |

Table C.7: OBRIGHEIM PARTIAL INPUT MASS BALANCES OF THE REPROCESSING CAMPAIGN

b Plutonium (g)

| Mass | TU (1) | IAEA (2) | Mean (1) + (2) | WAK (3) | Mean (1)+(2)+(3) |
|---|---|---|---|---|---|
| Uranium | - 0.92 | + 0.07 | -0.42±0.70 | + 1.32 | +0.16±1.12 |
| Plutonium | - 0.39 | - 1.09 | -0.74±0.50 | - 2.84 | -1.44±1.28 |
| Total | - 0.91 | + 0.06 | -0.43±0.69 | + 1.28 | +0.14±1.10 |

Table C.8: DISCREPANCIES BETWEEN VOLUMETRIC AND GRAVIMETRIC METHOD FOR THE PARTIAL INPUT MASSES BALANCE IN (%)

All discrepancies are reported to the gravimetric mass results $(\frac{V - G}{G})$.

| Batch number | U | U-235 | Pu | Pu-239 | Pu-240 | Pu-241 | Pu-242 |
|---|---|---|---|---|---|---|---|
| 86<br>87 | 263800 | 2414.6 | 2363 | 1350.0 | 564.6 | 326.1 | 122.3 |
| 88<br>89 | 266500 | 2435.3 | 2332 | 1331.6 | 557.4 | 322.1 | 120.9 |
| 90<br>91 | 264390 | 2463.1 | 2335 | 1342.6 | 556.0 | 321.0 | 118.4 |
| 92<br>93 | 263880 | 2785.0 | 2295 | 1370.1 | 525.6 | 301.3 | 98.1 |
| 94<br>95 | 264420 | 2691.0 | 2216 | 1307.6 | 513.5 | 295.1 | 99.8 |
| Total | 1322990 | 12789 | 11544 | 6701.9 | 2717.1 | 1565.6 | 559.5 |

Table C.9: OBRIGHEIM PARTIAL REPROCESSING CAMPAIGN

Masses (g) obtained by calculated correlations.

Remark added by the editors:

In order to compare the results obtained by the different approaches, the editors have requested a more detailed presentation of the results which are given in table C.9.

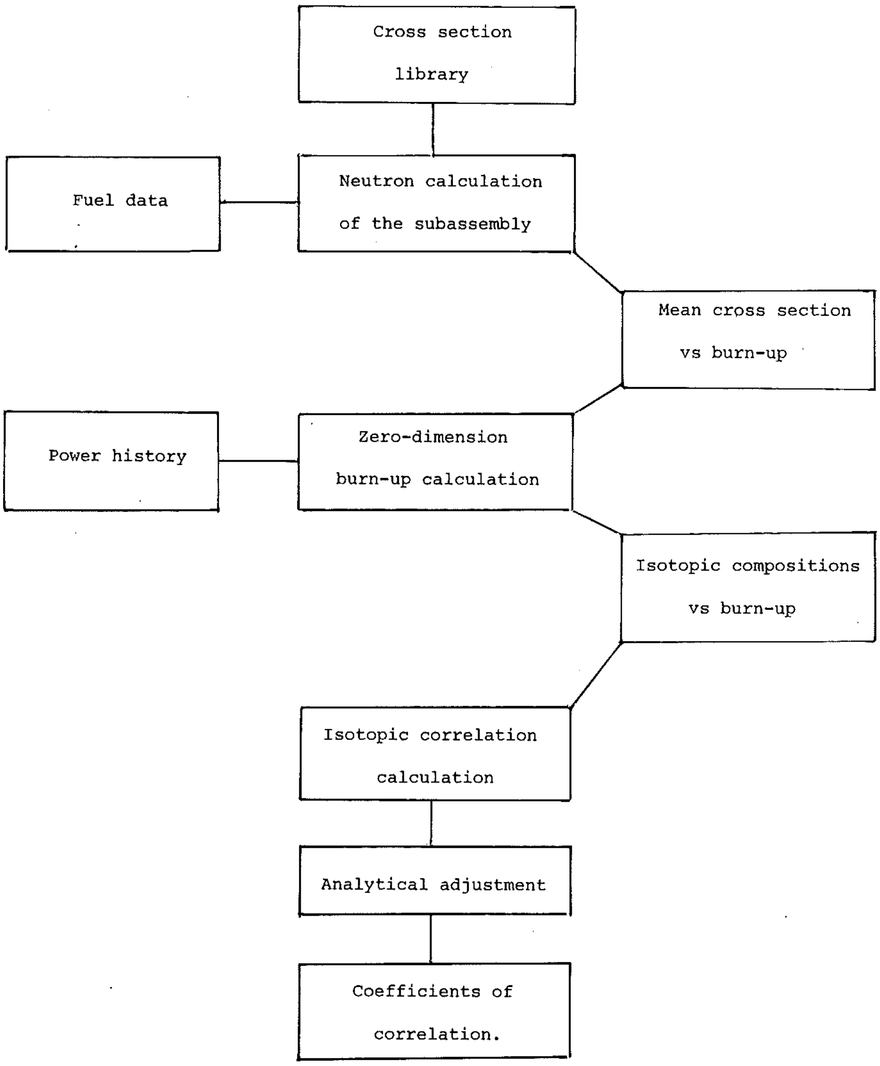

Figure 1: FLOW CHART OF THE CORRELATION CALCULATION

Appendix D

# Head-end fissile material balance of a reprocessing campaign: An on site evaluation procedure.*

C.Beets[1], P. Bemelmans[1], F. Franssen[1], S. Schoof[2]

[1] CEN/SCK, Safeguards Department, Mol-Belgium.
[2] KfK, Institut für Radiochemie, Karlsruhe.

## D.1 Introduction.

One of the purposes of the Isotope Correlation Experiment is to evaluate the benefits to be gained from an application of Isotopic Correlation Techniques in safeguards activities at a reprocessing plant. While other contributors discuss the evaluation of the data collected from the four involved laboratories by different statistical tools, this paper specifically considers the safeguards exercise from the point of view of the verification team.

In an actual safeguards situation, the verification team would not have four different sets of analytical measurements available, but would have to satisfy themselves that the operator's measurements are reliable and where there is doubt, to submit control samples for duplicate analysis by the reprocessor or for analysis by some referee laboratory and their choice, until they get a consistent set. They would then be in a position to establish a semi-independent material balance over the campaign.

The main tool that is available for chekking the reprocessor's data is the Isotope Correlation Technique, based on the relationships which exist between uranium depletion, plutonium build up and their isotopic compositions, and amongst the isotopic weight fractions themselves (1). These relationships can be applied in three ways:

- for internal data consistency verification in the campaign under way
- for consistency with well established relationships derived from the reprocessing of fuel from reactors of the same or like design ("historical data")
- for consistency with theoretical relationships established from reactor code computations.

In the present experiment, reactor code predictions were not released, and the historical PWR data (SENA, TRINO) available in the data bank of Mol proved unsuitable. The analysis therefore was restricted to the internal consistency verification.

Moreover, in order to simulate the actual safeguards situation, this consistency verification was deliberately confined to the reprocessor's data. When necessary, the IRCH figures were used as confirmation data.

At the end of the evaluation procedure, the material balances of uranium (total), uranium-235 and plutonium were compared to the averages derived from the three independent laboratories, TUI, SAL and IRCH, these averages being regarded as the best available independent estimates of the true values.

There are two features in the present experiment which are rather unfavourable to a sound application of the isotope correlation technique, namely :

- the range of burn ups is not broad (11 %)
- the investigated campaign bears upon 5 assemblies, whereas a full-size campaign would normally involve several scores of assemblies.

This state of affairs tends to obscure the correlations, sometimes even making them not significant and since the method relies on statistical decisions, well defined correlations are essential. Yet the differences between the material balances derived from the corrected WAK data and from the three independent laboratories were found to be compatible with the precisions and accuracies of the mass spectrometric determinations.

While the average of the three independent laboratories represents an analytical effort of 30 complete analyses (uranium, plutonium and isotopes) the described procedure based on the

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* Based on a paper contributed to the 2$^{nd}$ Annual Symposium on Safeguards and Nuclear Material Management, Edinburgh, 26th/28th March, 1980

Isotope Correlation Technique results in only four uranium concentration measurements being requested from the referee laboratory.

## D.2 Description of the procedure and results

### D.2.1 Reduction of the data to the shut down date.

The first step in the evaluation of the data is the correction of the plutonium total and its isotopic composition for Pu-241 decay: in order to make the data of different sources comparable, the data were all corrected to the shut-down date of 8 june 75. The decay half-life of 14.3 years was used for the Pu-241, while the decays of all the other isotopes were neglected.

### D.2.2 Reduction of the batch data into assembly data.

As a second step, because each assembly is shared out into two batches, the original batch data were pooled into five superbatches corresponding to the original five assemblies. The procedure eliminates any asymmetry introduced by the halving process and indeed resulted in improved correlations, especially where the uranium total and plutonium total are involved.

### D.2.3 Final uranium balance.

The result of the final uranium balance is presented in the table D.1 below.

TABLE D.1

U - final (kg)

WAK

| ASSEMBLY | DECLARED | REFEREE (IRCH) | ICT |
|---|---|---|---|
| 163 | 264.3 | - | 264.1 |
| 171 | 266.5 | - | 264.7 |
| 176 | 265.7 | - | 264.7 |
| 172 | 271.4 | 264.6 | 264.3 |
| 170 | 272.4 | 262.3 | 264.8 |
| TOTAL | 1340.3 | - | 1322.6 |

| ASSEMBLY | ACCEPTED | AVERAGE 3 INDEPENDENT LABS | DIFFERENCE |
|---|---|---|---|
| 168 | 264.3 | 262.5 | +1.8 |
| 171 | 266.5 | 263.3 | +3.2 |
| 176 | 265.7 | 262.5 | +3.2 |
| 172 | 264.3 | 264.5 | -0.2 |
| 170 | 264.8 | 263.1 | +1.7 |
| TOTAL | 1325.6 | 1315.9 | +9.7 |
| ESTIMATED σ | ±9 | ±5.3 | ±10 |
| ANALYTICAL EFFORT | 4 samples | 30 samples | |

The quantities are expressed in kilogrammes of total uranium and insignificant digits have been dropped. In the upper half of the table, the declared amounts of uranium are compared to the results of an approximate calculation (2) which relates the

$$\Delta U = U(o) - U(f)$$

to the uranium and plutonium isotopic data and to the Pu/U ratio through the formula :

$$\Delta U = 1.05\ U_o\ (U_o^{235} - U_f^{235} - U_f^{236})$$

$$+ U_f \times \frac{Pu}{U_f} \left[1 + 2.73\ (Pu^{240} + Pu^{241} + Pu^{242})\right]$$

where :

- the subscript (o) indicates initial values
- the subscript (f) indicates final measured values,
- the isotopic fractions are expressed in weight fractions (i.e., w/o divided by 100)
- and U and Pu quantities are in kg und in g, respectively.

When the WAK data are introduced into this formula and the resulting ΔU is subtracted from the initial uranium per assembly, the figures listed under the heading ICT are abtained. The measured uranium in the last two assemblies nrs. 172 and 170 are obviously high and the usual decision of the verification team would be to request a confirmation measurement either by the WAK itself or by the REFEREE laboratory. Here, accordingly the measurements of the REFEREE are listed for the two questionable cases and confirm the ICT results.

In the lower half of the table, under the heading "ACCEPTED", the measured data for the last two assemblies have been replaced by the ICT values. This column then, represents what the verification team would normally accept for total uranium inputs.

On the other hand, the best estimate of the actual inputs would, in principle, be obtained by averaging the results of the other three laboratories. The comparison of the two estimates reveals a slight systematic difference (0.75 % of the total input) which however is not to be ascribed to the Isotope Correlation Technique : a comparison of the four laboratory means (see under paragraph D.2.7, figure 4) gives a strong indication that the WAK laboratory is biassed high by something in the order of 5 kg. Further investigation of this bias is a matter for an interlaboratory comparison exercise.

### D.2.4 Consistency of uranium and plutonium isotopic abundances.

The evaluation of both the uranium-235 and the plutonium balances requires a reliable set of isotopic abundance data for at least the uranium-235 and if possible for other isotopes such as uranium-236 and plutonium-239 and -240. The consistency of the WAK uranium-235 and plutonium compositions was verified by correlating D-235 with U-236, with D-239*, and with the ratio Pu-240/239.

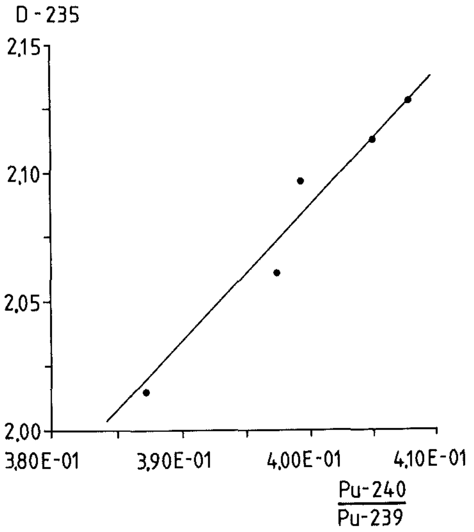

Figure 1. Correlation D-235 versus Pu-240/Pu-239 (WAK DATA)

The U-236 correlation, although a well-known one, proved inapplicable because this minor isotope was measured with only two significant digits. The best correlation was obtained with the isotopic ratio Pu-240/239 and is illustrated in the figure 1. Upon judging this diagramme and the others, it should be observed that the origin is not included and that the scales are very much enlarged.

On the basis of this correlation, no points were detected as outlying, and this was taken to indicate that both the uranium-235 and plutonium isotopic compositions were acceptable. It should be noted however that, owing to the reduced number of points, the correlation is somewhat loosely defined and that under these circumstances, the detection of an outlying measurement is not as efficient as it could be in a full-size campaign. Here, the situation being as it is, the set of WAK data has to be accepted as consistent. No additional analytical effort would be required.

### D.2.5 Uranium-235 balance.

The uranium-235 balance in g is established in the table D.2.

TABLE D.2

U-235 final (g)

| ASSEMBLY | U (kg) | WAK ACCEPTED U-235 (w/o) | WAK ACCEPTED U-235 (g) | AVERAGE 3 INDEPENDENT LABS | DIFFERENCE |
|---|---|---|---|---|---|
| 168 | 264.3 | 0.975 | 2577 | 2523 | + 54 |
| 171 | 266.5 | 1.005 | 2679 | 2641 | + 38 |
| 176 | 265.7 | 0.990 | 2631 | 2593 | + 38 |
| 172 | 264.3 | 1.040 | 2748 | 2776 | - 28 |
| 170 | 264.8 | 1.085 | 2873 | 2845 | + 28 |
| TOTAL | | | 13508 | 13378 | +130 |
| ESTIMATED σ | | | ±130 | ±75 | ±150 |
| ANALYTICAL EFFORT | | None | | 30 samples | |

Here, the accepted quantities of uranium total in kg are carried over from the table D.1, while the U-235 final enrichments in w/o measured by the WAK are accepted as such. The uranium-235 input per batch is expressed in grammes by

$$U_f^{235} = 10 \times U_f^{235} \times U_f$$

(g) (w/o) (kg)

Again the average of the other three laboratories is taken as the point of comparison and it is surprising to find a difference of 1 % again between the two balances.

### D.2.6 Consistency of Pu/U ratios with isotopic fractions.

The evaluation of the total plutonium input from each assembly is based on the total uranium established in the table D.1 and on accepted estimates of the Pu/U ratio.

Early recognized Pu/U indicators (3) include D-235, D-239 and Pu-240/239, the first one being known to be linear over the whole range of exposures.

The figures 2 and 3 represent the correlations of Pu/U with the plutonium isotopic ratio and with the D-235 respectively based on the WAK data after introduction of the revised $U_f$ values of the table D.1.

Again, the five Pu/U ratios must be regarded as acceptable, although the same remarks made in the paragraph D.2.4 can be repeated here. No additional analytical effort would be required.

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* The notation D-239 is used for 100 - Pu-239 in analogy to the D-235.

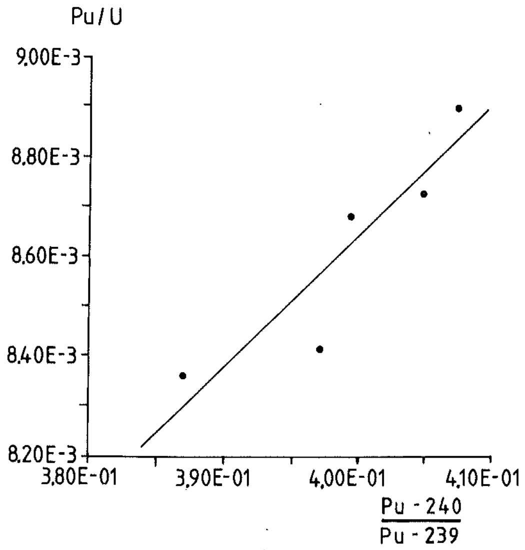

Figure 2. Correlation Pu/U versus Pu-240/Pu-239 (WAK DATA)

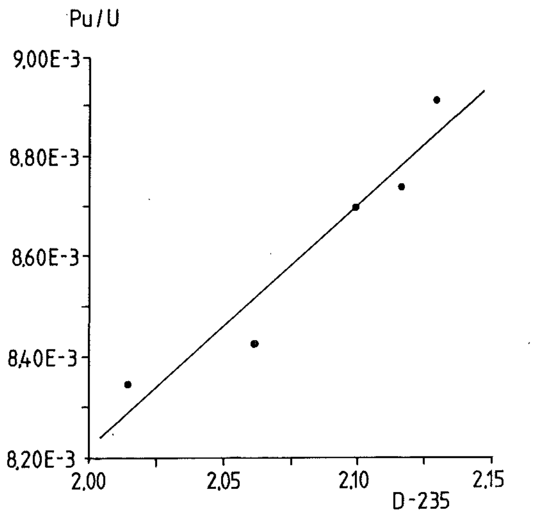

Figure 3. Correlation of the Pu/U ratio versus D-235 (WAK DATA)

D.2.7 Plutonium balance.

The plutonium input balance is presented in the table D.3 and simply consists of the sum of the five individual inputs determined by the reprocessor. The comparison with the average of the three independent laboratories reveals a discrepancy in the order of 200 g (1.8 % of the total input). This difference is due to a bias and can be corrected for provided either the magnitude of the bias is known beforehand or it is determined by submitting at least two samples by campaign to the referee laboratory.

A comparison of the four laboratory means for uranium total and plutonium total which is displayed in the figure 4, confirms that at least two of the participating laboratories are affected by systematic errors in the order of 40 g on the plutonium determination.

TABLE D.3

Pu total (g)

| ASSEMBLY | WAK ACCEPTED | AVERAGE 3 INDEPENDENT LABS | DIFFERENCE |
|---|---|---|---|
| 168 | 2348 | 2377 | - 29 |
| 171 | 2299 | 2323 | - 24 |
| 176 | 2310 | 2341 | - 31 |
| 172 | 2224 | 2283 | - 59 |
| 170 | 2211 | 2281 | - 70 |
| TOTAL | 11392 | 11605 | -213 |
| ESTIMATED σ | ±105 | ±60 | ±120 |
| ANALYTICAL EFFORT | None | 30 samples | |

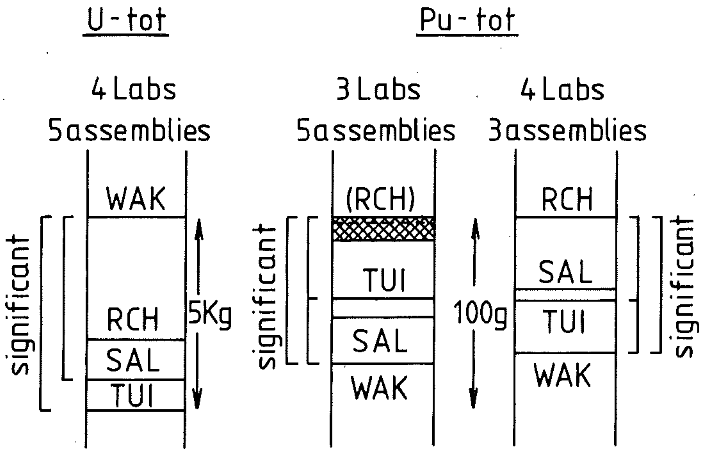

Figure 4. Comparison of laboratory means for U total and Pu total

## D.4 Conclusions

i) By a simple application of the Isotope Correlation Technique, it is possible to draw up a semi-independent fissile material balance of the head end of the reprocessing plant with a minimum of additional analytical effort.

ii) A limited number of simple linear correlations has been used, involving only the more important isotopes U-235, Pu-239 and Pu-240.

iii) Because the fabricators data refer to assemblies, it is recommended to pool the input batch data - in the present case two by two - in such a way as to apply the correlations to assembly data rather than fractions of assemblies.

iv) The accuracy and therefore the reliability of the results depend on the knowledge of the systematic discrepancies between the mass spectrometric laboratories.

v) Confirmation of the isotopic relationships by reactor code calculations would still enhance the confidence one can put in this technique.

## References

(1) D.E. Christensen, R.A. Schneider and K.B. Stewart, "Summary of Experience with the Use of Isotopic Correlation Safeguards Techniques", BNWL-SA-4274 (March 20, 1972) presented at the IAEA Working Group Meeting on the Use of Isotopic Composition Data in Safeguards, Vienna, Austria, April 10-14, 1972.

(2) French Contribution to the Resarch Coordination Meeting on Application of Isotopic Correlation Techniques to International Safeguards.
IAEA, Vienna 12-14 November 1979.

(3) C. Beets, editor "Contributions to the Joint Safeguards Experiment Mol IV at the Eurochemic Reprocessing Plant Mol-Belgium", BLG.486.