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The IDA-80 Measurement Evaluation Programme on Mass Spectrometric Isotope Dilution Analysis of Uranium and Plutonium

Volume I: Design and Results

W. Beyrich, W. Golly, G. Spannagel
Entwicklungsabteilung Kernmaterialsicherung
Institut für Datenverarbeitung in der Technik
Projekt Kernmaterialüberwachung

P. De Bièvre, W. Wolters
Central Bureau for Nuclear Measurements
JRC — Commission of the European Communities
Geel, Belgium

Kernforschungszentrum Karlsruhe

KERNFORSCHUNGSZENTRUM KARLSRUHE
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Kernforschungszentrum Karlsruhe

P. De Bièvre, W. Wolters
Central Bureau for Nuclear Measurements
JRC - Commission of the European Communities,
Geel, Belgium

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**Delegate of the Commission of the European Communities

Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

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Abstract

Guided jointly by CBNM and KfK, an analytical measurement evaluation programme has been carried out with the participation of 33 laboratories of 15 countries or international organizations under the auspices of ESARDA and with the support of IAEA. The main objective was the acquisition of basic data on the uncertainties involved in the mass spectrometric isotope dilution analysis as applied to the determination of uranium and plutonium in active feed solutions of reprocessing plants.

The element concentrations and isotopic compositions of all test materials used were determined by CBNM and NBS with high accuracy. The more than 60000 analytical data reported by the participating laboratories were evaluated by statistical methods applied mainly to the calculation of estimates of the variances for the different uncertainty components contributing to the total uncertainty of this analytical technique. Attention was given to such topics as sample ageing, influence of fission products, spike calibration, ion fractionation, Pu-241 decay correction, minor isotope measurement and errors in data transfer. Furthermore, the performance of the 'dried sample' technique and the 'in-situ' spiking method of undiluted samples of reprocessing fuel solution with U-235/Pu-242 metal alloy spikes, were tested successfully.

Considerable improvement of isotope dilution analysis in this safeguards relevant application during the last decade is shown as compared to the results obtained in the IDA-72 interlaboratory experiment, organized by KfK in 1972 on the same subject.

Das IDA-80 Meßprogramm zur Bewertung der massenspektrometrischen Isotopen-Verdünnungsanalyse von Uran und Plutonium

Vol. I: Auslegung und Ergebnisse

Zusammenfassung

Unter gemeinsamer Leitung der KfK/Karlsruhe und des ZBKM/Geel wurde ein analytisches Meßprogramm durchgeführt, an dem sich 33 Laboratorien aus 15 Ländern bzw. internationalen Organisationen beteiligten. Es stand unter der Schirmherrschaft der ESARDA und wurde von der IAEO unterstützt. Hauptziel der Untersuchungen war die Ermittlung der Meßunsicherheiten, die bei der Uran- und Plutoniumbestimmung in den Eingangslösungen von Wiederaufarbeitungsanlagen mittels massenspektrometrischer Isotopenverdünnungsanalyse auftreten.

Die Elementkonzentrationen sowie die Isotopenzusammensetzungen aller Testmaterialien wurden vom ZBKM/Geel und dem NBS/Washington mit hoher Genauigkeit bestimmt. Die Teilnehmerlaboratorien übermittelten über 60.000 analytische Daten. Sie wurden statistisch ausgewertet, vorwiegend hinsichtlich der Berechnung von Schätzwerten für die Varianzen der verschiedenen Fehlerkomponenten, die zur Gesamtunsicherheit dieser Meßmethode beitragen. Auch wurden der Einfluß von Spaltprodukten sowie Eichprobleme, Ionenfraktionierung, Pu-241 Zerfallskorrekturen, die Messung von Isotopen geringer Häufigkeit und Fehler bei der Datenübermittlung untersucht. Die Anwendung eingetrockneter Proben sowie die 'in-situ' Meßtechnik wurden erfolgreich erprobt. Bei letzterer werden unverdünnte Proben der Eingangslösung von Wiederaufarbeitungsanlagen unter Verwendung von U-235/Pu-242 Metall-Legierung als 'Spike'-Material analysiert.

Ein Vergleich mit den Ergebnissen des 1972 von der KfK organisierten Interlaborexperiments IDA-72 zeigt, daß seither erhebliche Fortschritte bei der Anwendung der Isotopenverdünnungsanalyse im Rahmen von Überwachungsmaßnahmen erzielt werden konnten.

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by
P. De Bièvre, M. Gallet, F. Hendrickx, W. Lycke, W. Wolters
JRC-CBNM, Geel, Belgium
K.R. Eberhardt, J.D. Fassett, J.W. Gramlich, L.A. Machlan
NBS, Washington, D.C., USA
E. Mainka, H. Wertenbach
KfK Karlsruhe, F.R.G.
KfK 3761/EUR 7991

Volume III:
"Compilation of Evaluation Data"
by
W. Beyrich, W. Golly, G. Spannagel
KfK Karlsruhe, F.R.G.
KfK 3762/EUR 7992

Preface

For nuclear safeguards, accurate determinations of fissile material in reprocessing input solutions are of key importance since they provide the basic information required for nuclear material accountancy and for control of reprocessing and consequently of the whole fuel cycle, especially with respect to plutonium. Up to now mass spectrometric isotope dilution analysis (IDA) has been universally accepted as the most accurate tool for this purpose.

In order to study applicability and results of this technique under routine conditions, an experiment had already been performed by the Safeguards Project of the Karlsruhe Nuclear Research Center in 1972 known as 'IDA-72'. It was carried out with the participation of 22 laboratories from 13 countries and international organizations. Satisfactory results were obtained in the determination of uranium. For plutonium, however, various error sources could be identified and many more uncertainty sources recognized.

With the results of this experiment in mind, a new version 'IDA-80' of this interlaboratory measurement evaluation programme was proposed some years ago. Under the auspices of the European Safeguards Research and Development Association (ESARDA) and supported by the International Atomic Energy Agency (IAEA), it was guided jointly by the Central Bureau for Nuclear Measurements (CBNM), an establishment of the Joint Research Centre of the Commission of the European Communities, at Geel, Belgium, and the Karlsruhe Nuclear Research Center (KfK) of the Federal Republic of Germany.

The interest in participation was again very high: in the end 33 laboratories of 15 countries or international organizations took part, underlining the importance which the community of measurement laboratories attaches to this type of intercomparisons*.

The reprocessing plant at Karlsruhe** (WAK) kindly made available samples taken from an actual production process for use in the programme.

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* Some further laboratories, interested in participating, had to withdraw for internal reasons.

** Wiederaufarbeitungsanlage Karlsruhe, Betriebsgesellschaft mbH.

Supported by the Institute for Radiochemistry (IRCh) of KfK, CBNM prepared the 749 test samples and, jointly with the National Bureau of Standards, Washington D.C., USA (NBS), established agreed certified values of high accuracy for the element concentrations and isotopic compositions of the test samples used. Furthermore, CBNM prepared the packing and - with the assistance of IAEA (for Eastern countries) - the transportation of the samples*.

Evaluation of the more than 60,000 analytical data generated, was performed by KfK, which also was responsible for the general organization and coordination of this world-wide undertaking.

In addition to the investigation of a number of uncertainty sources involved in isotope dilution analysis, studies of specific analytical techniques like the application of dried samples and the in-situ spiking of undiluted input solution with U-235/Pu-242 metal alloy spikes, were included in the IDA-80 programme, since they are of particular interest from the point of view of practical safeguards.

This extended programme loaded each participant with an average work load of about 17 man weeks. Its results were discussed in a Meeting of the Participants held at Karlsruhe in March 1984. The broad basis achieved by such extraordinary international participation backs up the results and conclusions of the IDA-80 programme in an indeed unique manner.

Their implications and consequences are considerable and should be examined carefully by the 'users' of the conclusions: plant control, and fissile material inventory responsibles, plant managers and Safeguards Authorities. The authors do not consider the implementation of the conclusions to be in their competence. They explicitly limit their responsibility to the production of the 'instant photographs' of the real state of the practice and making them available according to scientific criteria.

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*TransNuBel Co., Dessel, Belgium was charged with the actual transport to the different laboratories.

They hope that the results of IDA-80 are not only of interest for practical safeguards but also initiate an improvement in the performance of isotope dilution analysis of uranium and plutonium in general.

Wolfgang Beyrich	Paul De Bièvre
Karlsruhe Nuclear Research Center	Central Bureau for Nuclear Measurements

Karlsruhe/Geel, December 1984

Acknowledgement

The authors gratefully appreciate the valuable contributions and the excellent co-operation of all participating laboratories which made this programme possible. In particular, they would like to thank Rolf Berg of WAK Karlsruhe, for making available the reprocessing test materials.

The authors of KfK are indebted to Dr. Dipak Gupta, Leader of the Karlsruhe Safeguards Project at the time the Programme was started, for his encouraging interest and support.

The authors want to express their special thanks to Veronika Glienecke and Edith Wortmann for their diligent and kind assistance in the general organization of the programme as well as typing of the numerous notes, reports and tables, to Karlheinz Pfeffer for the preparation of drawings and to Gertrud Kronimus, Kevin Rosman and Roger Wellum for their help in correcting and wording the english versions of the manuscripts.

List of Participants

AERE - Atomic Energy Research Establishment
Chemistry Division
Harwell, Oxfordshire OX11 ORA, U.K.

E. Foster
M. E. Foy
R. Street

AGNS - Allied General Nuclear Services
P.O. Box 847
Barnwell, S.C. 29812/U.S.A.

J. Satkowski
G.D. Workman
G.A. Huff

ANL - Argonne National Laboratory
Analytical Chemistry Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, IL 60439/U.S.A.

E.L. Callis
D.L. Bowers

ANL - Argonne National Laboratory
P.O. Box 2528
Idaho Falls, Idaho 83401/U.S.A.

H.E. Keckler
M.T. Laug

AWRE - Atomic Weapons Research Establishment
Reading RG7 4PR
Aldermaston/U.K.

M. Morgan
P. Thompson
D. Soper

BAM - Bundesanstalt für Materialprüfung
Unter den Eichen 87
D-1000 Berlin 45, F.R.G.

W. Birke
K.-P. Ludwig
E. Santner
T. Tamberg
D. Thiele

BNFL - British Nuclear Fuels Ltd.
Windscale & Calder Works
Sellafield, Seascale
Cumbria CA 20 1PF/U.K.

J.C. Dalton
C.N. Ramsden
G.E. Taylor
D. Barnes
S.A. Sharpe

CBNM* - Central Bureau for Nuclear Measurements
Commission of the European Communities, Joint Research Centre
Steenweg naar Retie
B-2440 Geel, Belgium

G. Bortels
P. De Bièvre
M. Gallet
R. Geeraerts
K. Geerts
F. Hendrickx
E. Hens
W. Lycke
H. Prins
B. Uylenbroek
G. Van Baelen
A. Verbruggen
R. Werz
W.H. Wolters

CEA/RCP - Centre d'Etudes Atomiques
Laboratoire de Spectrométrie de Masse
Service R.C.P.
B.P. 12
F-91680 Bruyères le Châtel/France

H. Bassiere
A. Cherruault
A. Juery
D. Poupard

CEA/SCQ - Centre d'Etudes Atomiques
Service Contrôle Qualité
B.P. 12
F-91680 Bruyères le Châtel/France

Laboratoire des Actinides:
L. Charret
S. Gusmini
S. Parvillers

Laboratoire de Spectrométrie de Masse:
S. Deniaud
C. Leborgne

CEN - Centre d'Etudes Nucléaires Saclay
Section d'Etudes et d'Analyse Isotopique et Nucléaire
IRDI.DERDCA.DCAEA
B.P.2
F-91190 Gif-sur-Yvette/France

R. Hagemann
J. Cesario
M. Lucas
C. Chevalier

COGEMA - Compagnie Générale des Matières Nucléaires
Etablissement de Marcoule
B.P. 170
F-30200 Bagnols/Cèze, France

L. Baude
H. Lafon
J. Raimondi
J.P. Furgier
C. Manzi
A. Salles
J. Vialat
G. Verchere

ECN - Netherlands Energy Research Foundation
Westerduinweg 3
1755 ZG Petten (NH), The Netherlands

P.A. Deurloo
H. Haremaker
J.G. van Raaphorst

GE - General Electric Co.
Vallecitos Nuclear Center
P.O. Box 460
Pleasanton, CA 94566/U.S.A.

R.D. Reager
E.B. Mc Laughlin
J.A. Lindsey

IAEA - International Atomic Energy Agency
Safeguards Analytical Laboratory
P.O. Box 590
A-1011 Wien, Austria

S. Deron
D. Donohue
R. Fiedler
H. Swietly

IPEN - Instituto de Pesquisas Energêticas e Nucleares
Caixa Postal 11049 - Pinheiros
CEP 05508
São Paulo/Brazil

C. Rodrigues
S.S. Iyer
M.H. Kakazu
H.M. Shihomatsu
J.E. Sarkis
J.A. Seneda
I.M. Silva

JAERI - Japan Atomic Energy Research Institute
Tokai Research Establishment
Tokai-mura, Naka-gun, Ibaraki-ken 319-11/JAPAN

S. Okazaki
K. Gunji
N. Kono
N. Shinohara
M. Ouchi
H. Umezawa
H. Okashita
T. Komori
H. Natsume

KFA/ICT - Kernforschungsanlage Jülich GmbH
Institut für Chemische Technologie
Postfach 1913
D-5170 Jülich 1, F.R.G.

B.G. Brodda
D. Herz
H. Kirchner
G. Linse
B. Severit

KfK - Kernforschungszentrum Karlsruhe GmbH
Postfach 3640
D-7500 Karlsruhe 1, F.R.G.

Entwicklungsabteilung Kernmaterialsicherung (EKS)**:
W. Beyrich
W. Golly
W. Rust

Institut für Datenverarbeitung in der Technik (IDT)**:
R. Hulata
G. Spannagel

Institut für Radiochemie (IRCh):
M. Adam
E. Bolz
H. Deutsch
M. Friedrich
E. Gantner
R. Hauck
E. Mainka
M. Mostafa
H. Wertenbach

KRI - V.G. Khlopin Radium Institute
Roentgen 1
197022 Leningrad/U.S.S.R.

A.A. Lipovsky
B.N. Beljaev
A.V. Stepanov

KWU - Kraftwerk Union AG
Abt. R452
D-8757 Karlstein/Main, F.R.G.

R. Würtz

NBL - U.S. Department of Energy
New Brunswick Laboratory
9800 S. Cass Avenue, Bldg. 350
Argonne, Illinois 60439, U.S.A.

C.D. Bingham
C.G. Cacic
D.W. Crawford
M.A. Legel
J.M. Scarborough
N.M. Trahey

NBS* - National Bureau of Standards
Inorganic Analytical Research Div.
Room A25, Bldg. 221
Washington, D.C. 20234, U.S.A.

K.R. Eberhardt
J.D. Fassett
E.L. Garner
J.W. Gramlich
L.A. Machlan

NRIR - Nuclear Research Institute Rez
25068 Řež near Prague/CSSR

J. Moravec
F. Sus

ÖFZ - Österreichisches Forschungszentrum
Seibersdorf GmbH
Lenaugasse 10
A-1082 Wien/Austria

F. Pichlmayer
G. Falta
H. Lindauer
E. Klikovich

ORNL - Oak Ridge National Laboratory
P.O. Box Y, Bldg. 9735
Oak Ridge, TN 37830/U.S.A.

J.A. Carter

PNC - Power Reactor and Nuclear Fuel Development Corporation
9-13, 1-chome, Akasaka
Minato-ku
Tokyo, Japan 107

S. Watanabe
K. Ohnishi
Y. Wada
T. Hiyama
M. Takahashi

RNL - Risø National Laboratory
4000 Roskilde, Denmark

M. Mogensen
E. Larsen
T. Strauss
J. Funck

SCK/CEN - Studiecentrum voor Kernenergie/Centre d'Etude de l'Energie Nucléaire
Boeretang 200
B-2400 Mol, Belgium

P. De Regge
R. Boden

TUI - European Institute for Transuranium Elements
Commission of the European Communities, Joint Research Centre
D-7500 Karlsruhe 1, F.R.G.

L. Koch
R. Wellum
R. Molinet
M. Romkowski

UNI Helsinki - University of Helsinki
Department of Radiochemistry
Unioninkatu 35
SF-00170 Helsinki 17/Finland

M. Keinonen
O. Taivainen
J.K. Miettinen

WAK - Wiederaufarbeitungsanlage Karlsruhe
Betriebsgesellschaft mbH
Postfach 220
D-7514 Eggenstein-Leopoldshafen 2, F.R.G.

R. Berg
K.H. Henn
B. Himme
K.-D. Karnowski
K. Kohl
G. Smetak
P. Steinkuhle
B. Stojanik

WHC - Westinghouse Hanford Company
Hanford Engineering
Development Laboratory
P.O. Box 1970
Richland, WA 99352/U.S.A.

R.E. Brinson
M.W. Goheen
W.Y. Matsumoto
J.M. Ruggles

---

*Sample characterizing laboratory

**Evaluation team

Editorial Remark:

In order to facilitate typing and computer print-outs, the isotopes ^{238}U, ^{239}Pu etc. are written as U-238, Pu-239 etc.

1. Introduction

The IDA-72[1] interlaboratory experiment /1/, generated for the first time extensive data on the measurement uncertainties associated with isotope dilution analysis of uranium and plutonium. From their evaluation it became evident that the discrepancies between the results of different laboratories govern the measurement uncertainties much more than the within-laboratory reproducibilities - a situation which could only become clearly visible in an intercomparison experiment such as IDA-72. Because of the considerable consequences of that observation for practical safeguards, various interlaboratory measurement evaluation programmes on different analytical techniques used in safeguards were initiated over the next years /2-7/.

Basically, an analytical measurement evaluation programme consists of the distribution of identical samples for analysis amongst the participating laboratories and the evaluation of their measurement data using statistical methods. This allows the 'interlaboratory spread' of the measurements to be determined. If a picture of the accuracy achievements is wanted, the test samples must be carefully characterized with an overall uncertainty which is much smaller than the interlaboratory spread.

In order to obtain results which reflect the conditions of practical safeguards as closely as possible on the one hand and to allow a detailed evaluation on the other a distinction must be made between clear instructions for the analytical procedure and the liberty of the laboratory to choose those methods it uses in practical Safeguards[2]. For example, the laboratories can choose both mass spectrometry as well as alpha spectrometry for the determination of the Pu-238 isotope abundance, depending on their routine procedure, but had to perform the number of measurements according to the organizers' request.

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[1] The abbreviation 'IDA' stands for '<u>I</u>sotope <u>D</u>ilution <u>A</u>nalysis'.

[2] These aspects are discussed in more detail in /8/.

Hence, designing the IDA-80 programme, the following measures were taken attempting to generate data which reflect the conditions of practice as realistically as possible and allow an appropriate statistical evaluation:

1. the basic sample material was taken from an actual industrial reprocessing process in order to be of representative composition including all normal chemical and radioactive impurities.

2. exact instructions were given by the organizers on the number of repetitions to be made at each analytical step and on the method of data reporting, which had to be done on specifically prepared form sheets.

3. the participating laboratories were asked to perform the analyses using their routine procedures and not to invest extra efforts.

Extensive efforts were made to establish accurate values with certified uncertainties on all test samples used in the IDA-80 programme in order that they could serve in data evaluation as references. These procedures are described - together with the preparation of the IDA-80 samples in general - in Volume II of this Final Report /9/.

As far as the number of repetitions of the various steps of the analytical procedures were concerned, compromises had to be found between the work load for the participating laboratories and the statistical requirements. In general, three repetitions were considered as the smallest meaningful number.

In order to ensure uniform data treatment, the laboratories were asked to report the individual isotope ratio values for each mass spectrometric scan: eight per filament loading, in spite of the considerable work involved for both participating laboratories and the evaluation team. The participants followed this instruction without exception, although in some cases, it was not their routine measurement procedure.

The evaluation data derived from the reported isotope ratio values are listed and graphically presented in detail in Volume III of this Final Report /10/.

The participating laboratories were asked to provide, together with the measurement data themselves, some information on their methods of chemical sample preparation, their mass spectrometric equipment and the corrections they might have applied to their measurement data before reporting. Unfortunately, all details of this information can not be published since they would reveal the individual laboratory codes to a considerable extent.

The participants were requested to calculate, as part of the programme, the element concentrations and isotope abundances of uranium and plutonium in the test solutions. These 'declared values' probably represent very well the present state of practice[1]. It has to be noted however, that about 30 % of the laboratories mailed corrections of the originally reported data well before the deadline for such reasons as calculation errors, recalibration of working standards, mass discrimination corrections etc. to the evaluation team. This indicates to which extent in practice the uncertainties of declared values may be caused by such 'human errors'.

The evaluation team based its calculations on the corrected data, provided the laboratories reported these corrections before the deadline of July 1st, 1982. Therefore the evaluation results derived from these corrected data sets (which furthermore had to be cleaned from outlier values on statistical grounds) do not reflect any longer the actual state of practice but might be considered as 'target values' - achievable, but not yet reached in practice.

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[1] See Chapt. 3 of this Report

When confirming their participation, the laboratories were asked to indicate how long and how frequently they had been performing isotope dilution analyses of this kind. According to this information, two groups of laboratories can be distinguished in this paper: a group of 17 'more experienced' laboratories which claimed to have performed this type of analysis frequently or even continuously for more than five years and a second group consisting of the remaining 14 'less experienced' laboratories.

To avoid misunderstandings, it should be noted clearly that the IDA-80 programme - like all intercomparison programmes of this type - only aims at the estimation of the analytical uncertainties in the determination of the composition of the test solutions under consideration. Other error sources relevant for safeguards like insufficient sample representativity etc. are not the subject of this investigation.

2. Design of the programme

2.1 Objectives and general layout

Three main objectives were pursued with the IDA-80 programme:

1. the study of the capability and the limitations of isotope dilution analysis of uranium and plutonium as an analytical tool, in particular.

   - to demonstrate as realistically as possible the present status of within-laboratory reproducibility as well as the interlaboratory deviations of the analytical measurements under consideration;

   - to investigate as sources of uncertainties in the measurement technique
     a) the behaviour of diluted active input solutions
     b) the effect of fission products on the analytical procedure
     c) the spiking procedure
     d) the chemical sample preparation
     e) the isotope ratio determination by mass spectrometry.

2. to investigate possible improvements by the application of specific procedures such as

   - use of dried samples

   - use of a common spike solution

   - the 'in situ' spiking technique of undiluted sample material with metal alloy spike material /11, 12/.

3. the supplying of the participating laboratories with sufficiently detailed information in order to enable them not only to identify their performance within the international community, but also to detect as far as possible

specific sources of measurement uncertainties in their analytical work; i.e. in particular

- to determine in a uniform manner for each laboratory the reproducibility of its measurements
- to allow each participating laboratory to determine its bias.

A survey of the layout of the experiment is given in Fig. 1, and the approximate compositions of the test materials and spikes used are compiled in Tab. I.

A part of the undiluted feed solution 'A' taken at the reprocessing plant was diluted with nitric acid in a ratio of about 1:100 in order to obtain diluted solution 'B'.

This solution was used for the experimental parts 1.11, 1.12 and 1.2 (see Fig. 1). For part 1.11 it was furnished to the laboratories as a liquid and for part 1.12 as dried aliquot of exactly known mass. These samples had to be spiked by the laboratory itself using the laboratory's own spike material 'LOS'.

The samples for part 1.2 of the experiment were obtained from one common spiking procedure performed at CBNM with its mixed U-233/Pu-242 spike solution 'SUP'[1].

For part 1.3 of the programme some aliquots of the undiluted feed solution A were spiked with a U-235/Pu-242 metal spike 'MUP'[2] prepared at CBNM.

Contrary to the fission-product-containing basis materials used for part 1 of the programme, a fission-product-free reference solution 'R' also made

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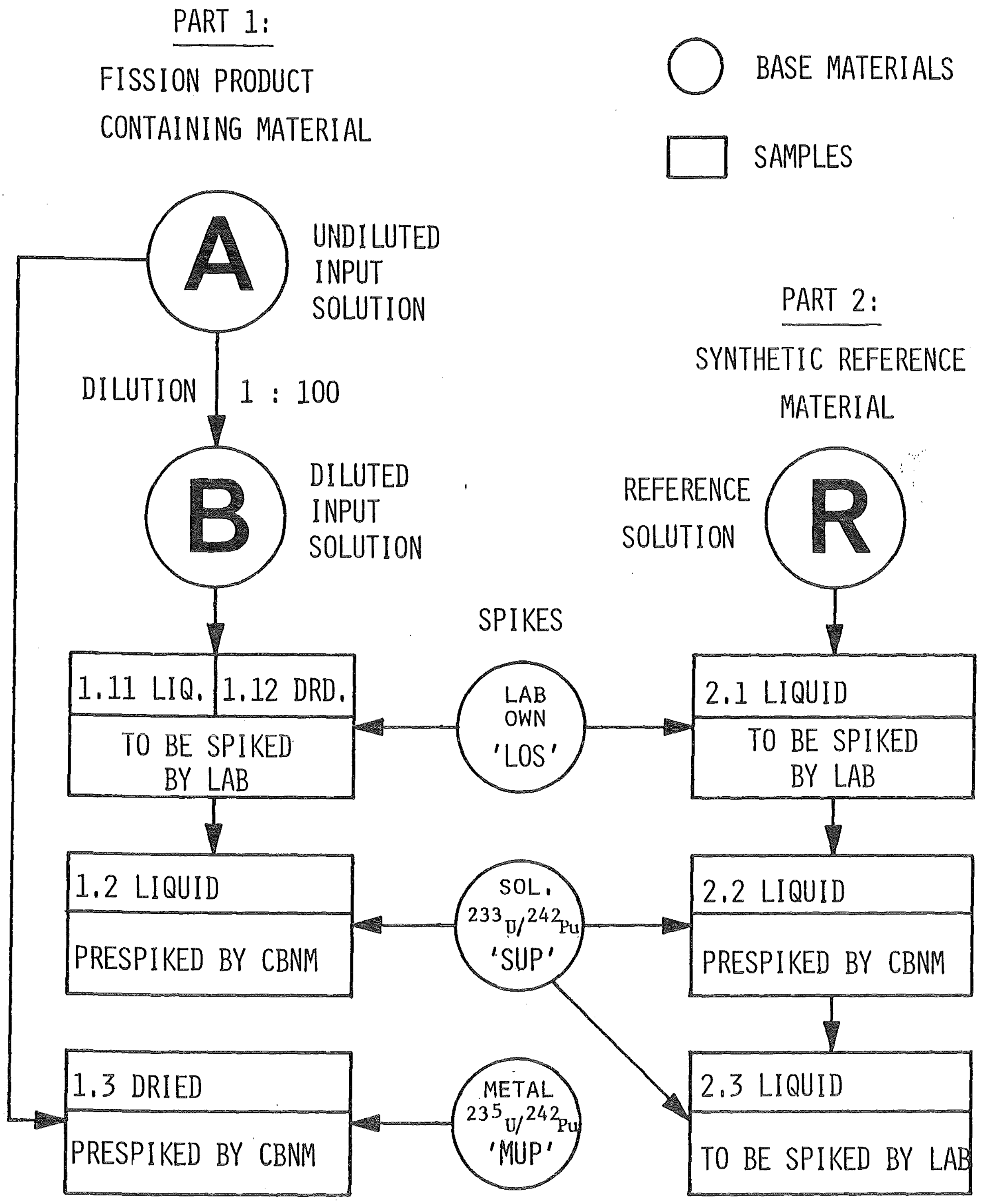
[1] The abbreviation 'SUP' stands for '(spike)solution uranium/plutonium'.

[2] The abbreviation 'MUP' stands for '(spike)metal uranium/plutonium'.



IDA-80/Fig. 1: Layout of the IDA-80 programme

IDA-80/TAB. I: APPROXIMATE COMPOSITIONS OF TEST MATERIALS[a]

	1	2	3	4	5	6	7	8
1	IDENTIFICATION		A	B	R	MUP	SUP	LOS
2	DESCRIPTION		UNDIL. FEED SOLUTION	DILUTED FEED SOLUTION	SYNTH. REFERENCE SOLUTION	METAL SPIKE	LIQUID SPIKE SOLUTION	LAB'S OWN SPIKE SOLUTION
3	USED IN PART		1.3	1.11 1.12 1.2	2.1 2.2 2.3	1.3	1.2 2.2 2.3	1.11 1.12 2.1
4	CONCENTRATION	MG U / G SOL.	170	2.05	1.72	99.7 WT-%	1.76	LABORATORIES OWN RESPONSIBILITY
5		µG PU / G SOL.	597	7.19	7.98	0.3 WT-%	6.28	
6	ISOTOPE COMPOSITION (WT-%)	U-233	-	-	-	-	99.70	
7		U-234	<0.01	<0.01	<0.01	0.78	0.24	
8		U-235	0.56	0.56	1.20	92.79	0.01	
9		U-236	0.18	0.18	<0.01	0.23	-	
10		U-238	99.25	99.25	98.78	6.20	0.05	
11		PU-238	0.21	0.21	0.12	1.00	0.99	
12		Pu-239	69.06	69.06	76.65	0.55	0.26	
13		PU-240	25.67	25.67	19.89	8.53	8.55	
14		PU-241	3.33	3.33	2.74	2.18	2.19	
15		PU-242	1.73	1.73	0.60	87.72	87.99	
16		PU-244	-	-	-	0.02	0.02	

a) FOR THE AGREED CERTIFIED VALUES REFER TO TAB. IV AND VOL. II /9/

at CBNM, was used for part 2 of the experiment. Supplied as a liquid, it had to be spiked by the laboratory using its own spike solution LOS (2.1) as well as the CBNM spike solution SUP (2.3).

In analogy to part 1.2, the samples for part 2.2 of the programme were obtained from one common spiking procedure performed at the CBNM with its 'SUP'- spike solution. These programme parts (1.2 and 2.2) are identical with the so-called 'Standard Experiment' of the IDA-72 programme /1/, thus permitting a direct comparison.

More detailed information on the uncertainty sources contributing to the total uncertainty of the isotope dilution technique was expected from comparisons between the results of different parts of the programme:

a) possible uncertainties introduced by lack of stability of a liquid diluted input solution ('ageing effects') should become visible by comparison of parts 1.11 and 1.12.

b) possible effects of fission products on the measurement procedures by comparison of parts 1.1 and 2.1 as well as 1.2 and 2.2

c) uncertainty introduced by the participant's own spike solutions by comparison of parts 2.1 and 2.3

d) uncertainties introduced by the participant's spiking procedures by comparison of parts 2.2 and 2.3.

Furthermore, it was of great interest to study in part 1.3 of the programme the results obtainable with the in-situ metal spiking technique mentioned. Since this method allows immediate fixing of the nuclear material content at the place and time of sampling and spiking without a previous dilution step, it is of particular interest for practical safeguards.

2.2 Preparation of samples

Detailed information on the preparation of the samples, their packing and transportation to the laboratories is given in Volume II of this Final Report /9/. In this Section, a summary is given.

Fig. 2 shows schematically the interrelation of the prepared samples.

The feed solution was sampled at WAK[1)] Karlsruhe in 19 glass vials of about 3 ml volume each on February 9, 1980 and delivered to the Institute for Radiochemistry (IRCh) of KfK, where sample preparation started immediately[2)].

Within a hot cell, the contents of the vials - a dark brown solution in which particles were observed - were collected in a glass vessel and filtered, resulting in test solution 'A'. Before filtering, some samples were taken for additional studies at IRCh on the influence of the particles[3)].

A fraction of solution A was diluted with 6 M HNO_3 in a ratio of about 1:100 by volume, resulting in a measured ratio of 1:82.78 by weight. This diluted input solution 'B' was transported in a tightly closed plastic bottle to CBNM for preparation of the samples for programme parts 1.1 and 1.2[4)].

From the remaining A-solution, 9 aliquots of about 1 ml each were taken and spiked with U-235/Pu-242 metal alloy spikes[3)]. After dilution with 6 M HNO_3, between 6 and 50 aliquots were taken from these spiked A-solution samples as indicated in Fig. 2. They were evaporated to dryness in glass vials with plastic stoppers for use in part 1.3 of the programme as samples 'AS'[5)].

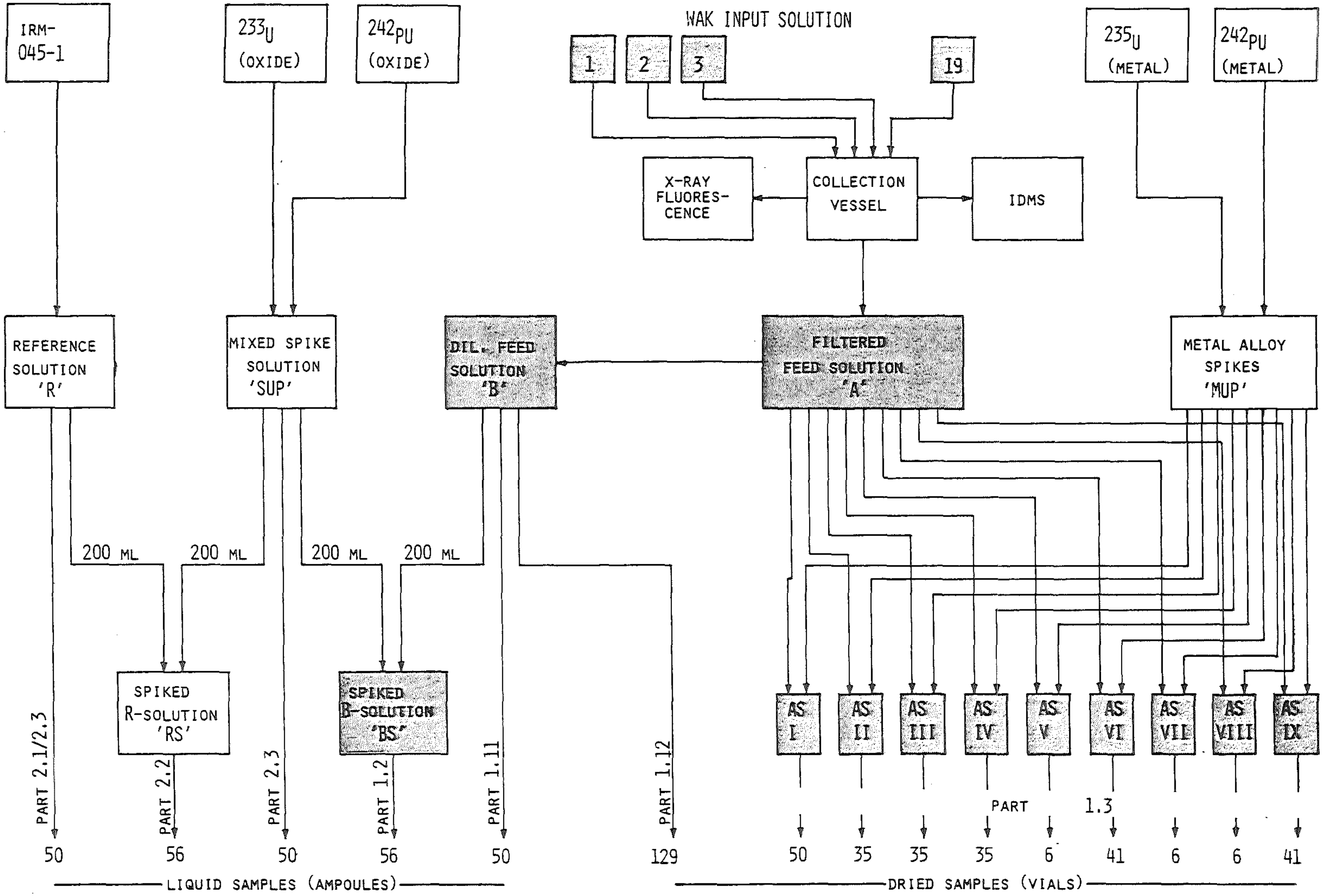
[1)] Wiederaufarbeitungsanlage Karlsruhe, Betriebsgesellschaft mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

[2)] FR 2 fuel; burn up 15 MWd/kg; Activity 7 Ci/l; Fission products 2.5 g/l. For approximate isotope compositions and element concentrations of U and Pu see Tab. I, column 3.

[3)] See Vol. II /9/.

[4)] For programme parts, refer to Fig. 1.

[5)] The letters 'S' and 'U' added to the symbols A, B and R of the test solutions refer to 'spiked' and 'unspiked' sample material.



(SHADED AREAS INDICATE MATERIALS CONTAINING FISSION PRODUCTS)

IDA-80/FIG. 2: INTERRELATION OF PREPARED SAMPLES

At CBNM, 50 aliquots of about 5 ml each were taken from the diluted feed solution B and sealed in glass ampoules for the studies of programme part 1.11. From the same material, 129 precisely weighed aliquots of about 1 ml each were taken, evaporated to dryness in glass vials and closed with screw caps for investigations of the dried sample technique in part 1.12 of the programme.

A weighed fraction of about 200 ml of the remaining solution B was mixed with a weighed fraction of about the same size of the U-233/Pu-242 mixed spike solution 'SUP' which had been prepared by CBNM from appropriate U_3O_8 and PuO_2 material. From the spiked solution B thus obtained, 56 aliquots of about 5 ml each were taken and shipped as liquids in sealed glass ampoules for use as samples 'BS' in programme part 1.2.

As indicated in the left hand side of Fig. 2, the synthetic reference solution 'R' for programme part 2 was made by CBNM from an existing parent solution. 50 ampoules were filled with about 10 ml of this reference solution and sealed for use in programme parts 2.1 and 2.3. For part 2.2 of the programme, a weighed fraction of about 200 ml of this solution was mixed with a weighed fraction of about the same amount of the SUP-spike solution. From this spiked reference solution 'RS', 56 aliquots of about 5 ml each were sealed in glass ampoules.

In total, each laboratory received 11 samples with information on the approximate compositions as shown in Tabs. II and III.

For shipment to the participating laboratories by road, sea or air, the glass ampoules and vials with the sample materials were carefully sealed in plastic bags and placed in specially manufactured lead and steel containers. The steel containers were packed into DOT 6M containers. No laboratory reported any transportation damage or surface contamination.

As described in Volume II of the Final Report /9/, the excessive administrative transportation requirements were in no relation at all to the extremely small amount of nuclear material shipped: about 300 form sheets had to be completed to transport a total amount of only about 3 g uranium and 12 mg plutonium to the participating laboratories.

IDA-80/TAB. II: SURVEY OF SAMPLES SUPPLIED PER LABORATORY

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16		
1 2	PART OF PROGRAM	SAMPLE DESCRIPTION	PHYSICAL STATE	APPROX. AMOUNT PER SAMPLE			APPROXIMATE ISOTOPE ABUNDANCES (%)									APPROX. DOSE RATE[a] (MREM/H) DISTANCE (CM)		
				VOLUME (ML)	U (MG)	PU (μG)	URANIUM				PLUTONIUM							
							233	235	236	238	238	239	240	241	242	0	10	50
3	1.11	BU	LIQUID	5	12	40	-	0.6	0.2	99	0.2	70	25	3	2	60	10	1
4	1.12	BU I, BU II, BU III	DRIED	-	3	10	-	0.6	0.2	99	0.2	70	25	3	2	120	20	1
5	1.2	BS	LIQUID	5	11	40 (20)[b]	44	0.3	0.1	55	0.6	38	17	3	42	30	5	0.5
6	1.3	3 VIALS OUT OF AS I TO AS VI	DRIED	-	8	25 (13)[b]	-	44	0.1	56	0.6	38	17	3	42	180	28	1.5
7	2.1[c]	RU	LIQUID	10	20	100	-	1	-	99	0.1	75	20	3	1	-	-	-
8	2.2	RS	LIQUID	5	10	45	50	0.5	-	49.5	0.5	38	14	3	44	-	-	-
9	2.3[d]	SUP	LIQUID	5	10	40	100	-	-	0.3	1	1	8	2	87	-	-	-

a) UPPER LIMITS MEASURED IN DIRECT CONTACT WITH THE SAMPLE AND AT A DISTANCE OF 10 AND 50 CM

b) VALUES IN BRACKETS INDICATE THE AMOUNTS OF PU ORIGINATING FROM SAMPLE SOLUTIONS A OR B FROM WHICH FISSION PRODUCT CONTENTS CAN BE DERIVED (SEE TABLE III)

c) FRACTION OF THE RU-SAMPLE MATERIAL SUPPLIED WITH PART 2.1 IS USED IN PART 2.3

d) FOR THE RU-MATERIAL NEEDED FOR THIS PART, REFER TO THE MATERIAL MENTIONED IN PART 2.1

NOTE: ALL AMOUNTS AND ABUNDANCES GIVEN IN THIS TABLE SHOULD BE CONSIDERED AS ROUGH APPROXIMATIONS ONLY.

IDA-80/TAB. III:
APPROXIMATE COMPOSITION OF γ-ACTIVE FISSION PRODUCTS IN TEST SOLUTIONS A AND B

ISOTOPE	μCI/μG PU
RU 106	0,06
SB 125	0,05
CS 134	0,17
CS 137	5,94
CS 144	0,04
EU 154	0,08
EU 155	0,04

2.3 Characterization of samples

For the test solutions used in the IDA-80 programme, 'agreed certified values' for the uranium and plutonium element concentrations as well as for the isotope abundances, were jointly established by CBNM Geel and NBS Washington. The methods, instruments and measurement procedures used, as well as the results obtained are described in detail in Volume II of the Final Report /9/. The key values - the isotope compositions and the element concentrations of uranium and plutonium in the A, B and R test solutions - are compiled in Tab. IV, the dilution ratios of the prespiked test solutions AS, BS and RS in Tab. V.

All measurements have been carefully corrected for isotope fractionation and for known instrument errors. For the major isotope abundance ratios and element concentrations, the relative difference between totally independent determinations by CBNM and NBS on the one side and the final certified value on the other side was smaller than 0.15 % (in most of the cases considerably better).

For all minor isotope abundances < 0.1 %, relative agreement was better than 1 %.

The uncertainties stated were established as follows:

a) at each institute (CBNM and NBS):
3 times the 'standard error' or 'standard deviation of the mean' ($\bar{s}$)

b) on the 'agreed certified values':

$$\sqrt{\frac{(3\bar{s})^2_{\text{CBNM}}+(3\bar{s})^2_{\text{NBS}}}{2}}$$

IDA-80/TAB. IV: AGREED CERTIFIED VALUES AND UNCERTAINTY RANGES OF TEST SOLUTIONS[a]

	1	2	3	4	5	6	7	8
1	ELEMENT OR TEST SOLUTION	CONCENTRATION		ISOTOPE ABUNDANCE (WEIGHT %)				
		$(\times 10^{16}\ \mathrm{AT}\ \frac{\text{PU-239}}{\text{G SOL}})$	(MG/G SOL.)					
2	URANIUM		ELEMENT	U-233	U-234	U-235	U-236	U-238
3	A		1.6966×10^{2} ± $.0012\times10^{2}$ (±0.071)	-	0.0087 ± .0001 (± 1.1)	0.5633 ± .0004 (± 0.071)	0.1783 ± .0014 (±0.79)	99.2497 ± .0015 (± 0.0015)
4	B		2.0491 ± .0019 (±0.093)	-	0.0087 ± .0001 (± 1.1)	0.5633 ± .0004 (± 0.071)	0.1783 ± .0014 (±0.79)	99.2497 ± .0015 (± 0.0015)
5	R		1.7154 ± .0017 (±0.099)	-	0.0089 ± .0001 (± 1.1)	1.2048 ± .0011 (±0.091)	0.0067 ± .0001 (±1.5)	98.7796 ± .0011 (± 0.0011)
6	PLUTONIUM[b]	PU-239	ELEMENT	PU-238	PU-239	PU-240	PU-241	PU-242
7	A	1.0391×10^{2} ± $.0031\times10^{2}$ (±0.30)	5.973×10^{-1} ± $.018\times10^{-1}$ (±0.30)	0.2070 ± .0017 (±0.82)	69.0631 ± .0254 (± 0.037)	25.6681 ± .0203 (± 0.079)	3.3352 ± .0053 (±0.16)	1.7266 ± .0044 (± 0.25)
8	B	1.2504 ± .0031 (±0.25)	7.193×10^{-3} ± $.018\times10^{-3}$ (±0.25)	0.2070 ± .0017 (±0.82)	69.0631 ± .0254 (± 0.037)	25.6681 ± .0203 (± 0.079)	3.3352 ± .0053 (±0.16)	1.7266 ± .0044 (± 0.25)
9	R	1.5414 ± .0037 (±0.24)	7.982×10^{-3} ± $.019\times10^{-3}$ (±0.24)	0.1153 ± .0028 (±2.4)	76.6542 ± .0161 (± 0.021)	19.8912 ± .0134 (± 0.067)	2.7440 ± .0091 (±0.33)	0.5953 ± .0012 (± 0.20)

a) UNCERTAINTY RANGES IN PERCENT ARE GIVEN IN BRACKETS. b) DATA VALID FOR FEBRUARY 9, 1980

IDA-80/TAB, V: AGREED DILUTION RATIOS FOR PRESPIKED TEST SOLUTIONS

	1	2	3	4	5
1	PRESPIKED TEST SOLUTION	URANIUM		PLUTONIUM	
2		ISOTOPE RATIO	DILUTION RATIO[a]	ISOTOPE RATIO	DILUTION RATIO[a]
3	AS I	$\frac{\text{U-235}}{\text{U-238}}$	0,92759 ± ,00024 (±0,026)	$\frac{\text{PU-242}}{\text{PU-239}}$	1,1022 ± ,0010 (±0,091)
4	AS II		0,90039 ± ,00044 (±0,049)		1,0701 ± ,0022 (±0,21)
5	AS IV		0,91032 ± ,00043 (±0,047)		1,0771 ± ,0014 (±0,13)
6	AS VI		0,91626 ± ,00034 (±0,037)		1,0839 ± ,0014 (±0,13)
7	BS	$\frac{\text{U-233}}{\text{U-238}}$	0,85242 ± ,00057 (±0,067)		1,0854 ± ,0013 (±0,12)
8	RS		1,05590 ± ,00089 (±0,084)		0,8979 ± ,0010 (±0,11)

a) UNCERTAINTY RANGES IN PERCENT ARE GIVEN IN BRACKETS

2.4 Reporting and general treatment of data

In order to ensure unique and complete reporting of measurement data, the laboratories were supplied with appropriate form sheets. An example is given in Fig. 3. Each of these form sheets contains all data regarding the mass spectrometric measurement of one filament loading ('run'). Besides general data on the origin and preparation of the sample, eight

IDA-80 DATA SHEET No.

A. MEASUREMENT CONCERNED:

(Please make no entry in this area)

- Programme part 1.11
- Laboratory code [*]
- Plutonium measurement
- B-solution, spiked with lab-own spike
-

1	.	1	1
		P	U
		B	L

Please make no entry in this area!

B. GENERAL DATA:

- BU-sample solution taken from ampoule no. ....
- Date of MS-measurement[+]: ....
- Date of chemical separation[+]: ....
- Date of BU-sample aliquotation[+]: ....
- Date of spike aliquotation[+]: ....
- Mass of BU-sample aliquot: ....(g)
- Mass of spike aliquot: ....(g)
-

C. ATOMIC RATIOS:

Report values after application of all corrections applied usually. If any outlier criterion is used, please put those values into brackets which would be rejected.

Scan No.	Pu-238/Pu-239[o]	Pu-240/Pu-239	Pu-241/Pu-239	Pu-242/Pu-239
	89	09	19	29
1	-			
2	-			
3	-			
4	-			
5	-			
6	-			
7	-			
8	-			

[*] Code number will be assigned after return of data sheet

[+] State date in the sequence day-month-year

[o] Determination of this ratio not requested

IDA-80/FIG. 3: DATA REPORTING SHEET (EXAMPLE) 'scan' values of the isotope ratios had to be reported.

The participants reported to the evaluation team at KfK more than 60 000 individual data, the majority being mass spectrometric scan values of isotope ratios. In order to reduce as far as possible errors due to data input into the computer, this work was done twice by two different persons and then checked for identity. Furthermore, different consistency checks were made. In particular, the Nalimov outlier criterion /13/ was applied to each set of reported scan values in order to detect erratic figures on the data sheets caused by writing mistakes.

Prior to statistical treatment the data were corrected for Pu-238 and Pu-241 decay to February 9, 1980 - the date of sampling at the reprocessing plant - as common reference date. This correction was based on the time intervals between this reference date and the date of mass spectrometric measurement at the participants laboratory[1].

Only six of the eight isotope ratio values were used for the evaluation itself. This was done in order to maintain an orthogonal structure even when one or two scan values of a run had to be omitted since the laboratory marked them as outliers. These six values were always the first six non-outlier values of the run, according to the judgement of the laboratory.

In the first stage of the evaluation, means and (relative) standard deviations were calculated for the determined isotope ratios, isotope abundances and concentrations for each participant. Since in general three mass spectrometer filament loadings were measured per sample, the 'laboratory mean' of an isotope ratio determination for instance is the mean value of three 'run means', each of the latter being the mean of six scan values. The run means of isotope ratios were used as the basis for the calculation of abundance and concentration data. In accordance with safeguards experience, they are given in weight % and gram element per gram solution, respectively. For some

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[1] This differs from the evaluation given in the Preliminary Evaluation Reports distributed to the laboratories, before the IDA-80 Participants' Meeting.

specific studies the use of Pu-239 concentration values was preferred[1].

After calculation of these data for the individual laboratories[2], estimates were derived in the second stage of evaluation for the 'scan', 'run' and 'between laboratory' variances by variance analyses based on the data of all laboratories. Generally, they are given as relative standard deviations (RSD) and describe average values of these error components. It should be noted that the values calculated in the different parts of the programme for the 'run' and 'between laboratory'[3] RSD's depend strongly on the contributing error sources according to the analytical procedure which was followed.

The application of variance analysis requires statistical homogeneity of the data population considered. In general, this condition is not fulfilled for data sets obtained in the present programmes and the application of outlier criteria becomes necessary. Evaluating the IDA-80 data, extreme laboratory mean values were excluded according to the Bartsch criterion /14/. For populations of the size under consideration, it rejects data which deviate from the mean of the group by more than four times the standard deviation[4]. After this procedure, the standard deviations of the laboratory mean values were checked for excessive values applying the outlier criterion of Dixon /15/, allowing a probability of only 1% that a value is rejected which in fact belongs to the group. When data rejection occurred the remaining group of laboratory mean values was again checked by the Bartsch criterion[5].

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[1] Because the uranium of all test solutions contains more than 98 % U-238, it is not meaningful to distinguish for uranium between element concentration and the concentration of the main isotope U-238.

[2] For data verification, each participating laboratory was supplied with the complete set of calculated data on isotope ratios, isotope abundances, element concentrations as well as the output of its reported data as stored in the computer of the evaluation team at KfK.

[3] In earlier interlaboratory programmes, the expression 'interlaboratory deviation' was often used for this uncertainty component.

[4] Mean value and standard deviation of the data group taken without the suspicious value.

[5] Data groups obtained in this way do not necessarily represent Gaussian distributions /16/. However, a more rigid rejection of measurement data for purely statistical reasons does not seem to be justified.

Instead of the 'grand mean' (the mean value of a group of laboratory means) the median value of the laboratory mean values is considered as the better estimate of the true value. This is because it remains unaffected by single excessive values in populations of the sizes considered here and, therefore is more reliable.

In some investigations, the term 'interlaboratory spread' is used. It denotes the relative standard deviation of a single value for a group of laboratory mean values.

For more details of the evaluation procedure, in particular individual evaluation data, their graphical presentation and the formulae used for their calculations, reference is made to Volume III of this Final Report /10/.

3. Methods and instruments used by the participants

3.1 Introductory remark

The information supplied by the laboratories on their analytical techniques and instrumentation cannot be presented in full detail, since this would reveal the laboratory codes to a considerable extent.

Attempts by the evaluation team to correlate certain analytical techniques with the corresponding performance data in a statistically significant way failed in almost all cases. Only in a few cases was some evidence for correlations observed. This will be mentioned in the following chapters in connection with the discussion of the subject concerned.

3.2 Pretreatment of Samples

The participants had been asked to report briefly which methods they used for redissolving the dried samples, for the redox procedure and for the element separation. These descriptions can be summarized as follows:

a) Redissolving of dried samples

The acidity of the nitric acid applied varies between 1.5 M and concentrated with a clear preference for 8M HNO_3. From those laboratories which measured the dried samples, 43%, 39%, and 18% used 8M HNO_3, less concentrated, and higher concentrated HNO_3, respectively. 57% of the laboratories reported heating of the samples between 'gently' and 'below boiling', a few of them reported evaporation to dryness prior to the actual redissolving.

Most laboratories repeated their procedure for redissolving several times and some added HF, H_2O_2 or waited up to a week for completion of the redissolution.

There was no significant difference in the techniques used by 'more experienced' and by 'less experienced' laboratories.

b) Redox procedure

A survey on the reported redox procedures is given with Fig. 4: Although the FeII/$NaNO_2$ and the $NH_2OH \cdot HCl/HNO_3$ methods are most often applied, neither is clearly preferred and other different techniques have also been described. In about 20% of the cases the use of $HClO_4$ is included. There is no indication that the 'more experienced' laboratories prefer any particular method.

c) Element separation

Fig. 4 also shows the techniques reported for element separation. The majority of the laboratories (about 80%) used anion exchange. Among the methods reported by the others, TTA extraction dominates.

3.3 Mass spectrometric measurements

Because four laboratories measured with two or even three instruments, a total of 36 mass spectrometers was used by the participants of the IDA-80 programme. Eight of these instruments were non-commercial, the others were different models of five manufacturers. As shown in Fig. 5[1], more than 60% of the spectrometers were brought into operation after the IDA-72 programme in 1972. Hence IDA-80 was performed on a rather new generation of instruments.

Four mass spectrometers (about 10%) were 2-stage and 3-stage instruments. Seven participants reported the use of Faraday cups for uranium ion detection, two of them also for the measurement of plutonium. In all the other cases, electron multipliers or ion pulse counting were applied.

For the acquisition and handling of the measurement data, about 50% of the laboratories reported fully computerized systems, about 30% semi-computerized ones. Approximately 20% of the laboratories evaluated manually strip-chart-produced spectra.

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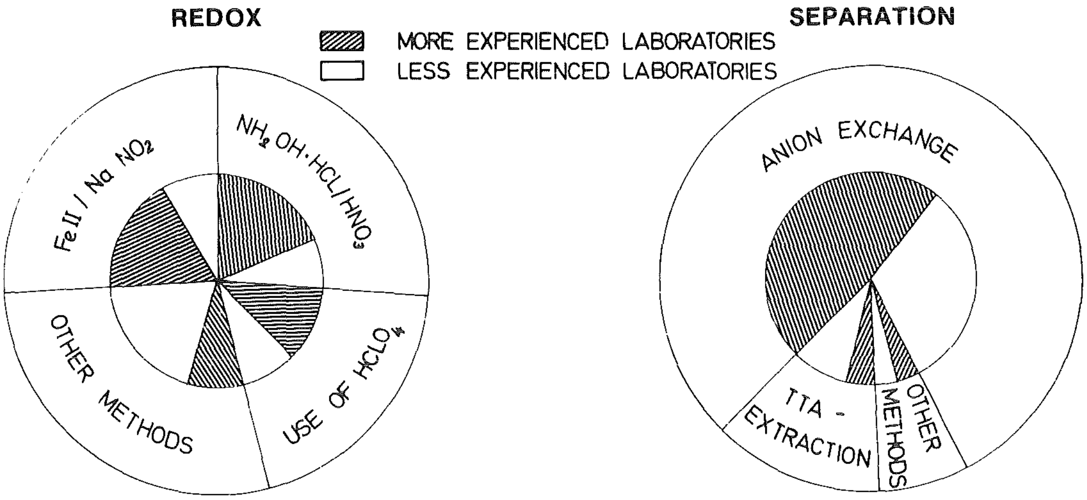
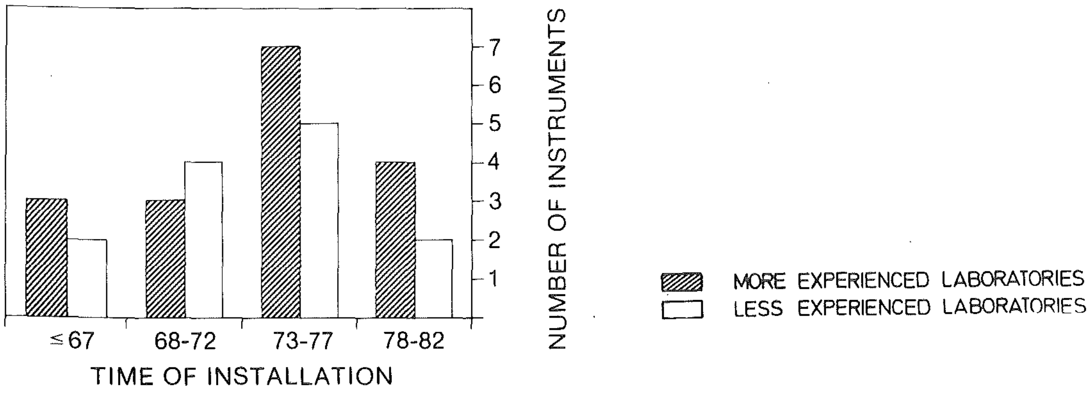
[1] Fig. 5 represents in total only 30 instruments, since six laboratories reported no data.



IDA-80/FIG. 4: METHODS OF SAMPLE PREPARATION REPORTED



IDA-80/FIG. 5: INSTALLATION TIME OF MASS SPECTROMETERS USED IN THE IDA-80 PROGRAMME

3.4 Application of outlier criteria and corrections

The participants had been asked to mark values of mass spectrometric scan ratios of isotopes which they would reject in routine operation and to describe the corrections applied to the measurement data before reporting to the evaluation team.

The application of outlier criteria is given in Fig. 6: Approximately one third of the participants applied the Dixon criterion; another third applied several other criteria mostly using a $k*\sigma$ level. About one third of the laboratories did not use outlier criteria or reported no information.

The corrections of measurement data were mainly concerned with the mass discrimination effect: 24 of the 31 laboratories (77%) reported that they applied corrections for this purpose. As shown in Tab. VI, the majority of laboratories calibrated with isotope reference material, to correct for all mass dependent bias effects, e.g. the bias component of isotope fractionation. Almost without exception NBS reference materials were used. However, from the reported measurement data there is no evidence, that the seven laboratories which made no corrections performed for this reason U-233/U-238 ratio determinations worse than the average.

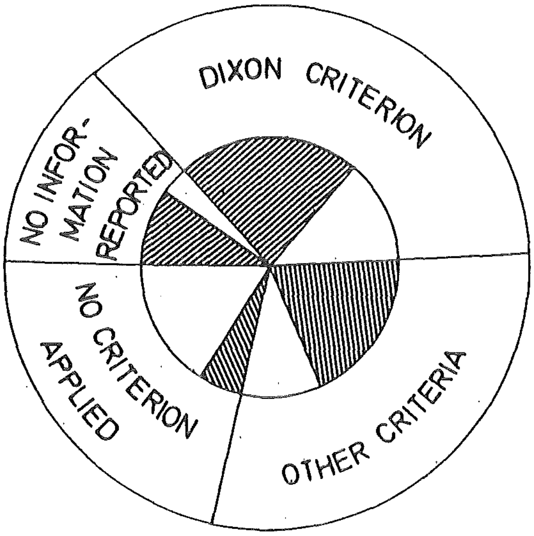
Other corrections mentioned by the laboratories concern background noise, zero shift of amplifiers, dead time of counting systems and beam fluctuations by the computer programme.

3.5 Determination of the Pu-238 isotope

Alpha spectrometry as well as mass spectrometry was used for Pu-238 determination in the IDA-80 programme. As shown in Fig. 7, 56% of the laboratories performing plutonium measurements applied alpha spectrometry, 26% used mass spectrometry. 8% of the participants reported results obtained by both methods and 10% of the laboratories did not measure the Pu-238 isotope

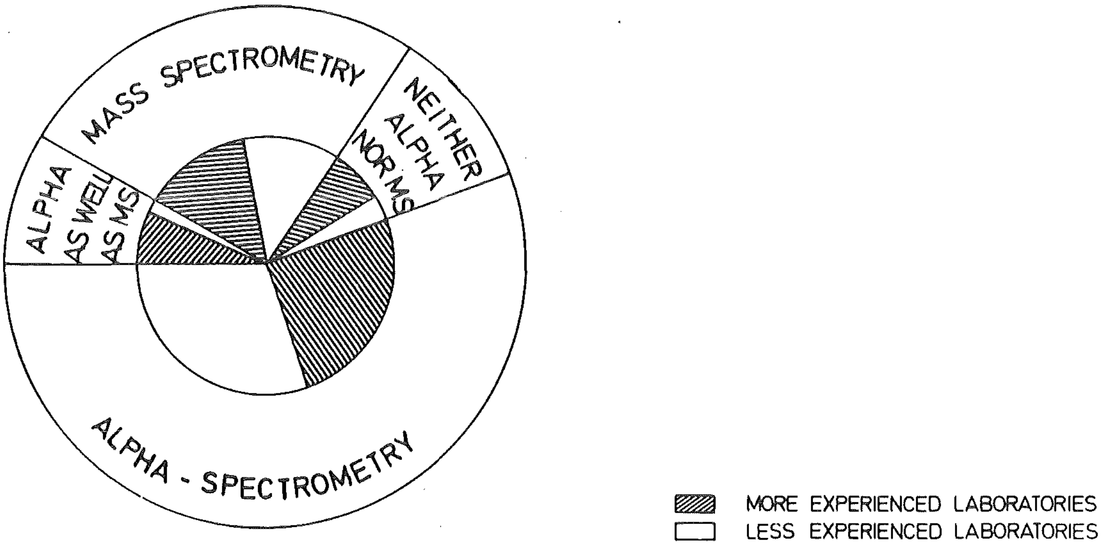
IDA-80/TAB. VI: MASS DISCRIMINATION CORRECTIONS APPLIED BY PARTICIPANTS

METHOD APPLIED	NUMBER (PERCENTAGE) OF LABS
CALIBRATION WITH STANDARDS	18 (58)
SQUARE ROOT OF MASS RATIO	2 (6)
METHOD NOT REPORTED	4 (13)
NO CORRECTION APPLIED	7 (23)



IDA-80/FIG. 6: OUTLIER CRITERIA APPLIED BY THE PARTICIPANTS at all, although Pu element determinations were requested. Neither the 'more experienced' nor the 'less experienced' laboratories prefer one of these two analytical techniques.

The results obtained in determining the Pu-238 abundance of the B and R test solutions by both methods are presented in Fig. 8. Arranged by increasing values, their relative deviations from the agreed certified values (see Tab. IV) are given[1]: Obviously, alpha spectrometry and mass spectrometry are both suitable for determining Pu-238 abundances in the investigated range of a few tenth of percent. The interlaboratory spread for the Pu-238 abundance values obtained by alpha spectrometry is about twice as high as that for mass spectrometric determination (calculated without exclusion of extreme values)[2][3].



IDA-80/FIG. 7: METHODS USED FOR THE DETERMINATION OF PU-238

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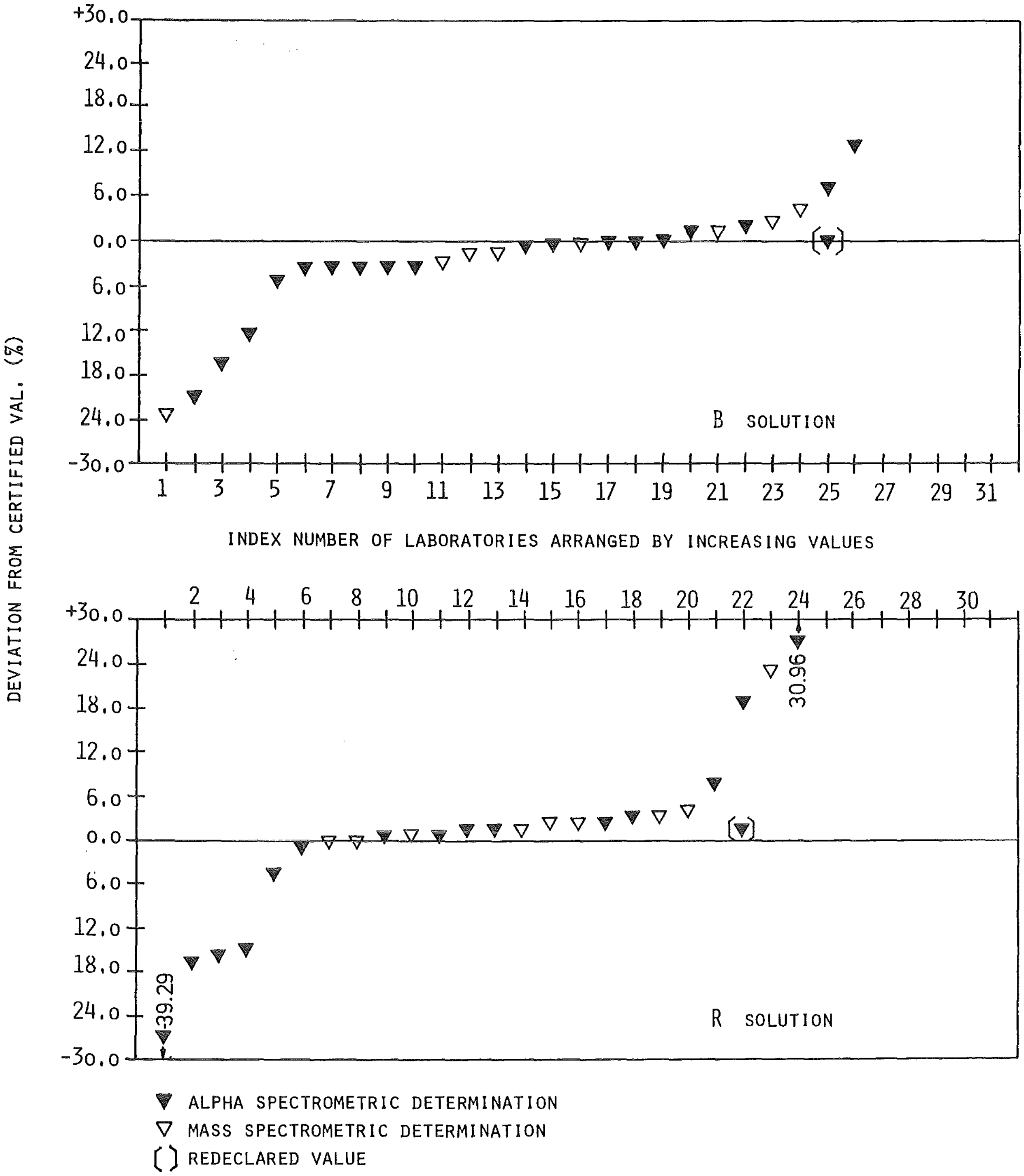
[1] Please note that - as a result of these means of presentation - the 'index number' of a laboratory's result differs from figure to figure and that these index numbers have no relation to the code numbers assigned to the participating laboratories in this programme.

[2] See Evaluation Sheets 54, 55, 61 and 62 in Vol. III /10/.

[3] The uncertainty components involved in alpha spectrometry were investigated in the AS-76 Programme /4/.



IDA-80/FIG. 8: PU-238 ABUNDANCE DETERMINATIONS
BY ALPHA- AND MASS SPECTROMETRY

According to the information reported, only one of the laboratories which determined the Pu-238 isotope by mass spectrometry used different instruments for plutonium and uranium measurements, thus avoiding any U-238 memory effect.

4. Element concentration values and isotope abundances reported by the participants

As already mentioned, the participants were requested to report the element concentrations and isotope abundances of uranium and plutonium in the diluted reprocessing feed solution B and the synthetic reference solution R (see Tab. I).

In figures 9 to 18 the relative deviations of the reported results from the agreed certified values are presented ordered in sequence of increasing values[1]. The shaded areas indicate the $\pm 3\bar{s}$ uncertainty ranges of the agreed certified values. In Tab. VII, the positioning of the reported values with respect to the uncertainty ranges of the agreed certified values is considered.

Two different symbols are used in the figures. They indicate the degree of experience the laboratories had in this type of analysis, according to their own statements made before the performance of the measurements: Points indicate frequent or even continuous analytical work in this field for more than five years ('more experienced' laboratories), circles indicate 'less experienced' laboratories.

In order to meet conditions of practical safeguards as near as possible, the laboratories were asked to report the results of the element concentration determinations as gram uranium (or plutonium) per gram sample solution and isotope abundances in weight percent. All the plutonium data were requested to be corrected for radioactive decay to February 9, 1980 used as common reference day[2]. On purpose, no specific values were recommended for the physical constants needed in the calculations.

In some cases, the laboratories supplied second results corrected for very different reasons such as calculation errors, recalibration of working standards or mass discrimination corrections, several weeks or months after the first result but before the final deadline for data acceptance. In such cases, the first result reported is used and the second (corrected) one is given additionally within brackets.

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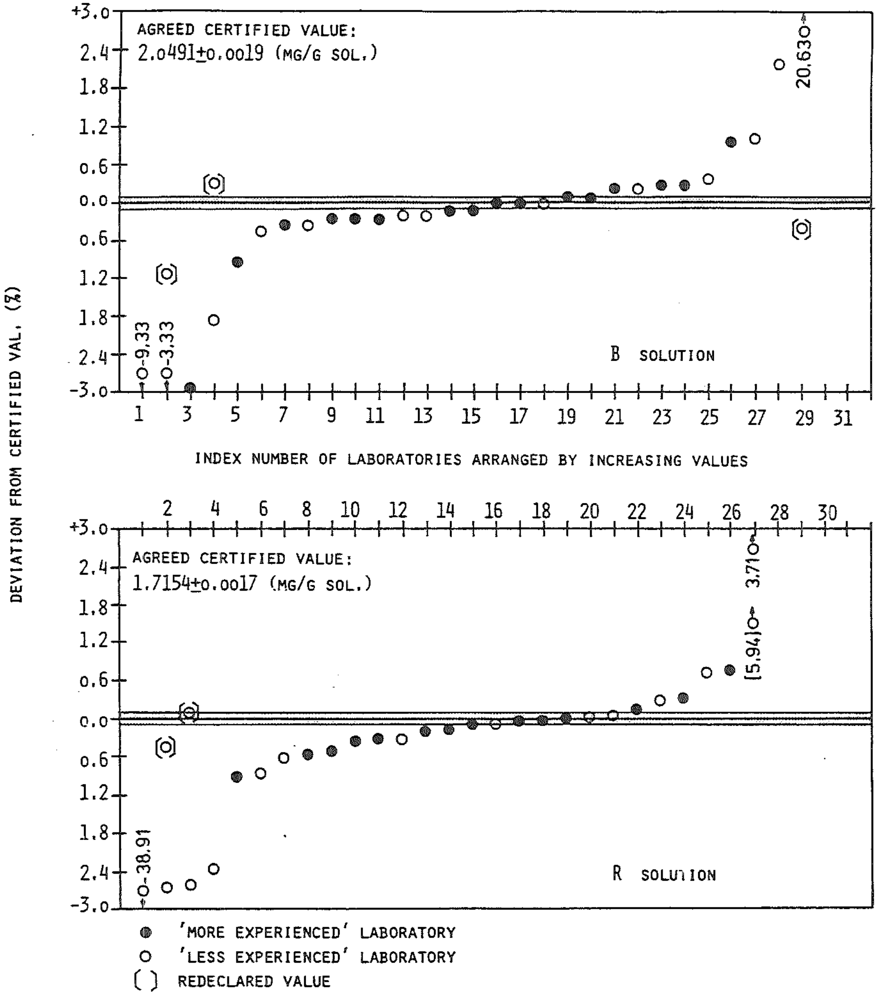
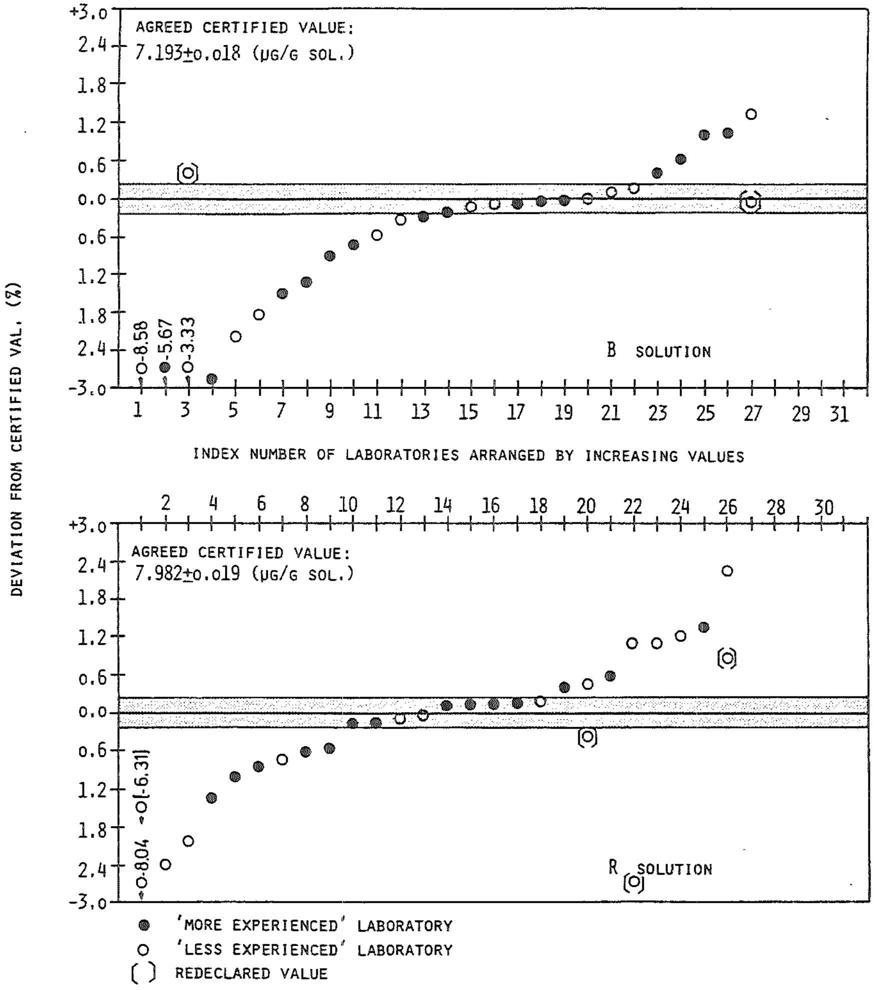
[1] Please note that - as a consequence of this way of presentation - the 'index number' of a laboratory's result differs from figure to figure and that these index numbers have no relation to the code numbers assigned to the participating laboratories in this experiment.

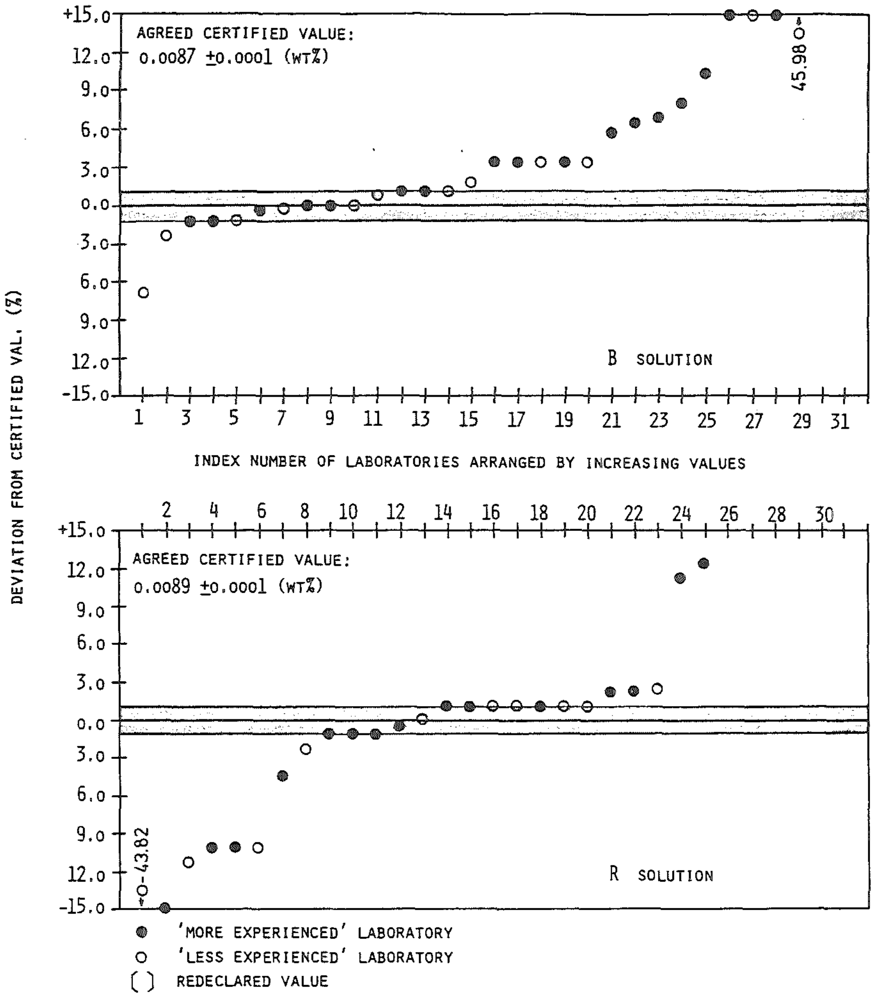
[2] This was the day of sampling at the reprocessing plant.



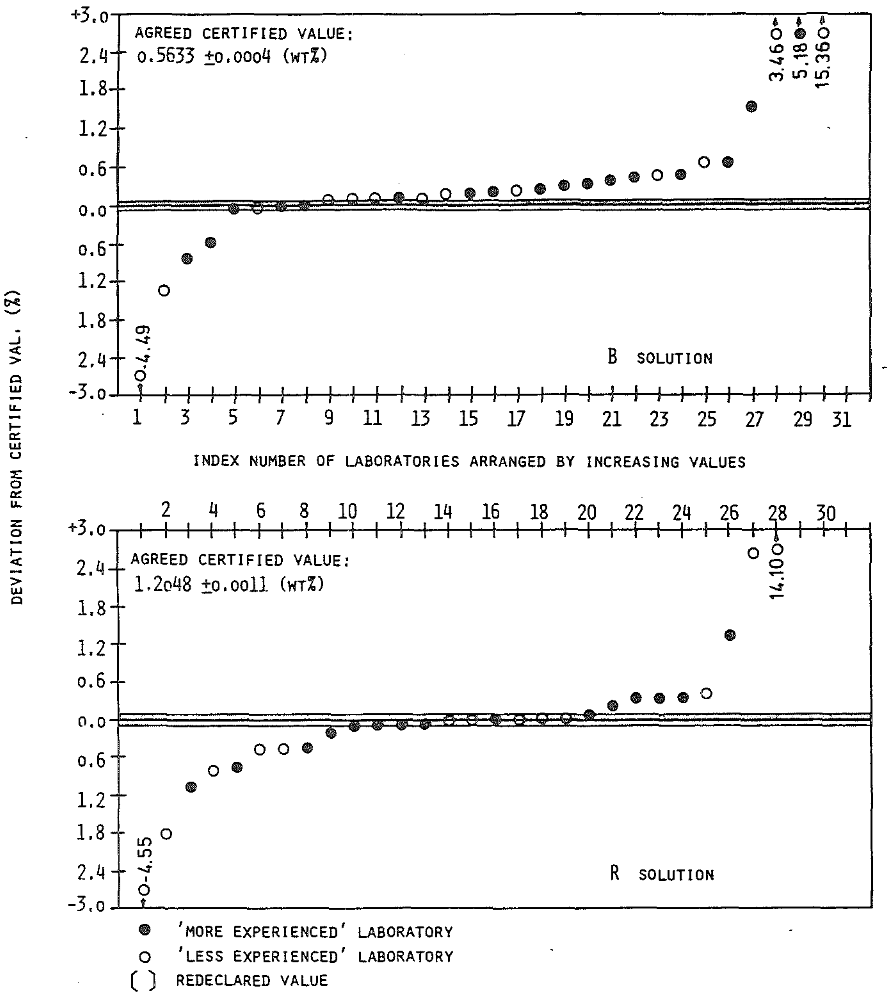
IDA-80/Fig. 9: Reported uranium concentrations



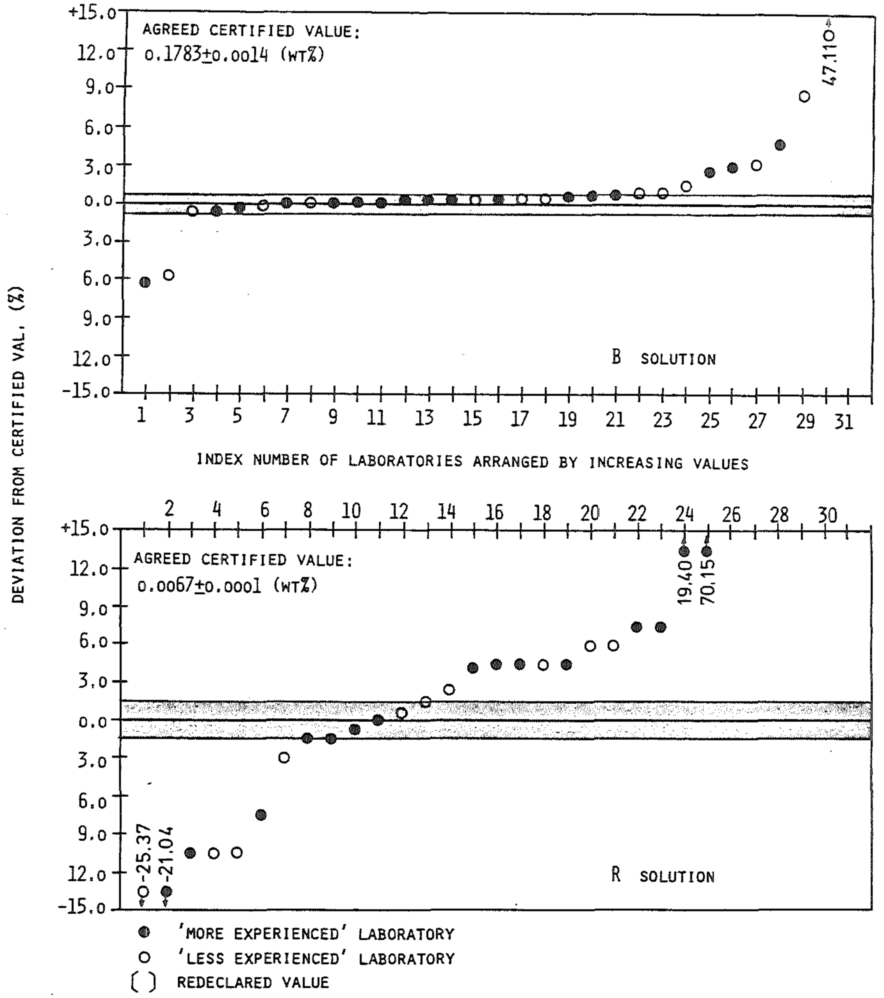
IDA-80/Fig. 10: Reported plutonium concentrations



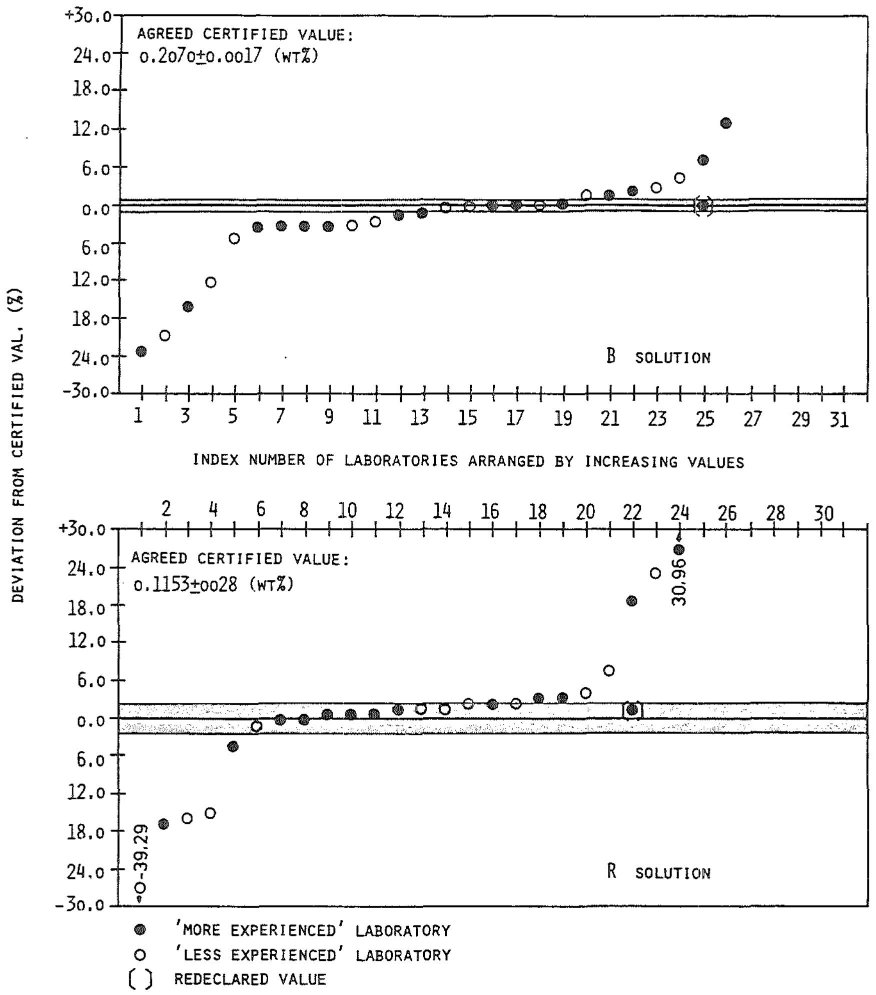
IDA-80/FIG. 11: REPORTED U-234 ABUNDANCES



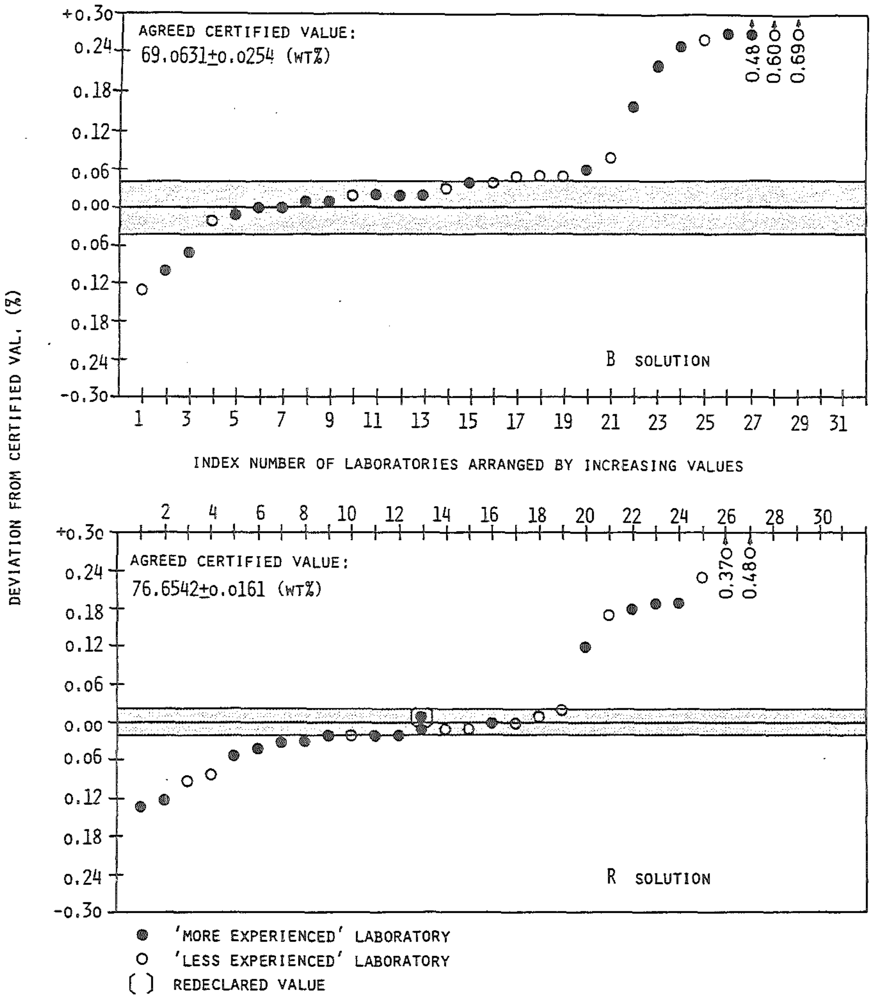
IDA-80/FIG. 12: REPORTED U-235 ABUNDANCES



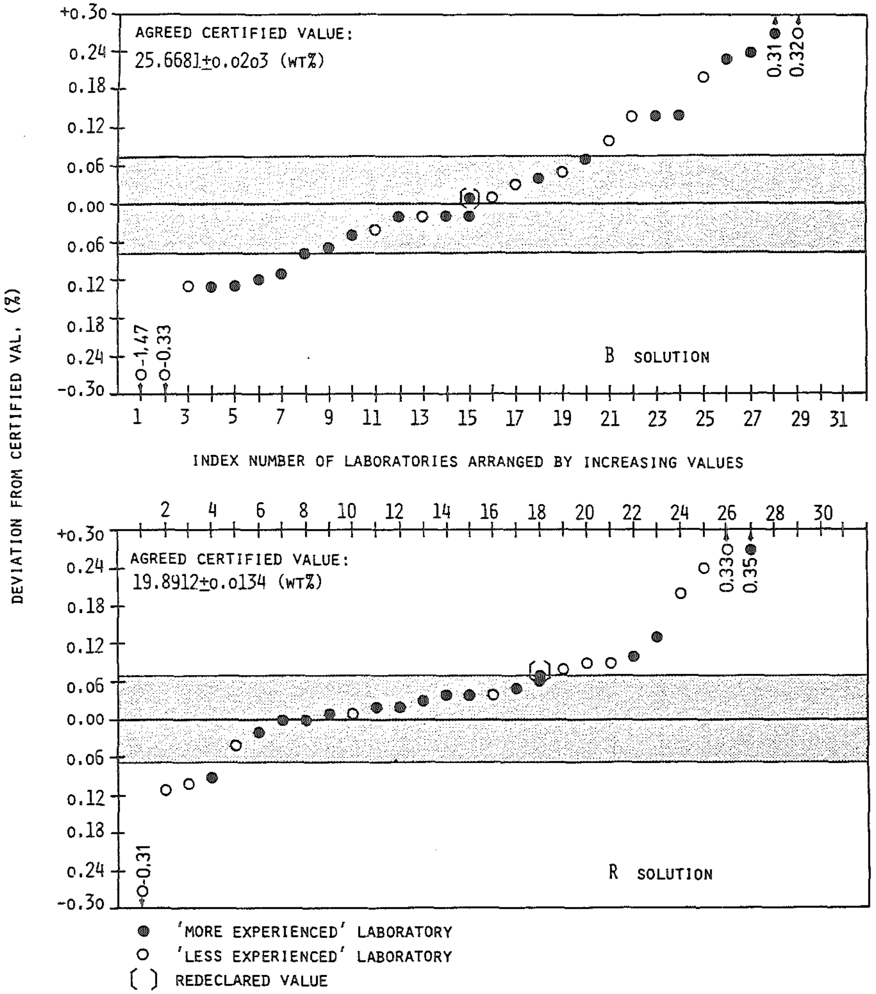
IDA-80/FIG. 13: REPORTED U-236 ABUNDANCES



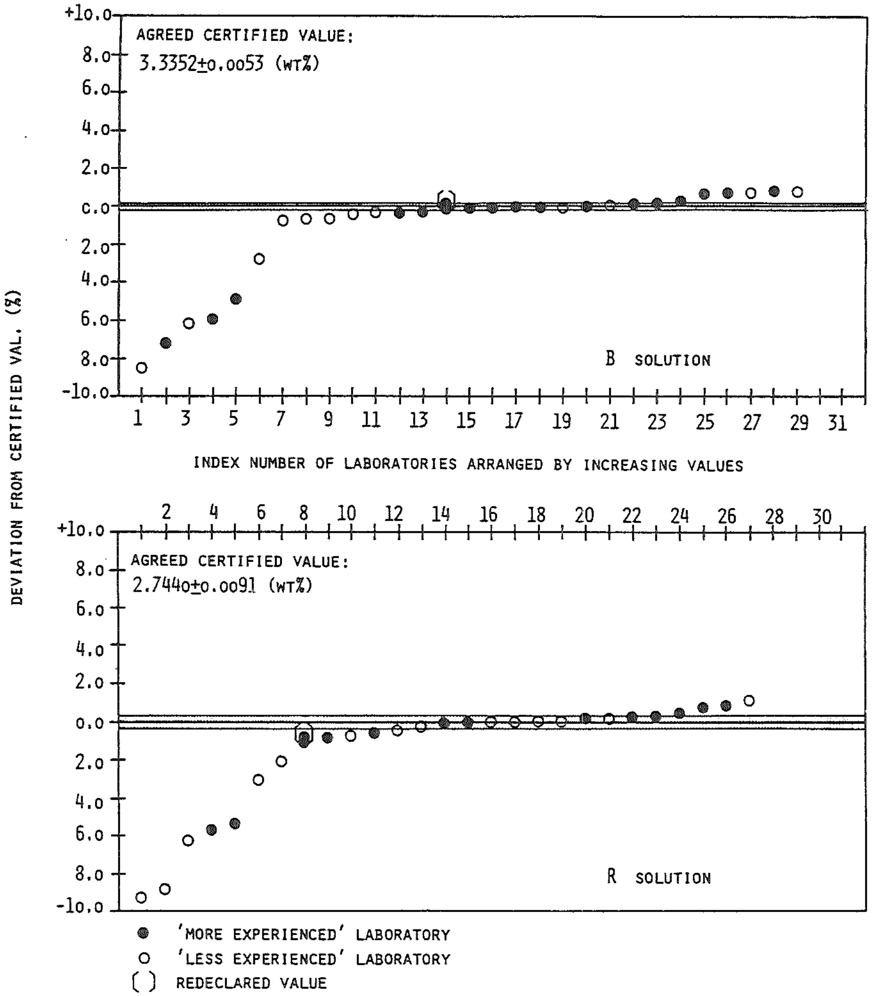
IDA-80/FIG. 14: REPORTED PU-238 ABUNDANCES



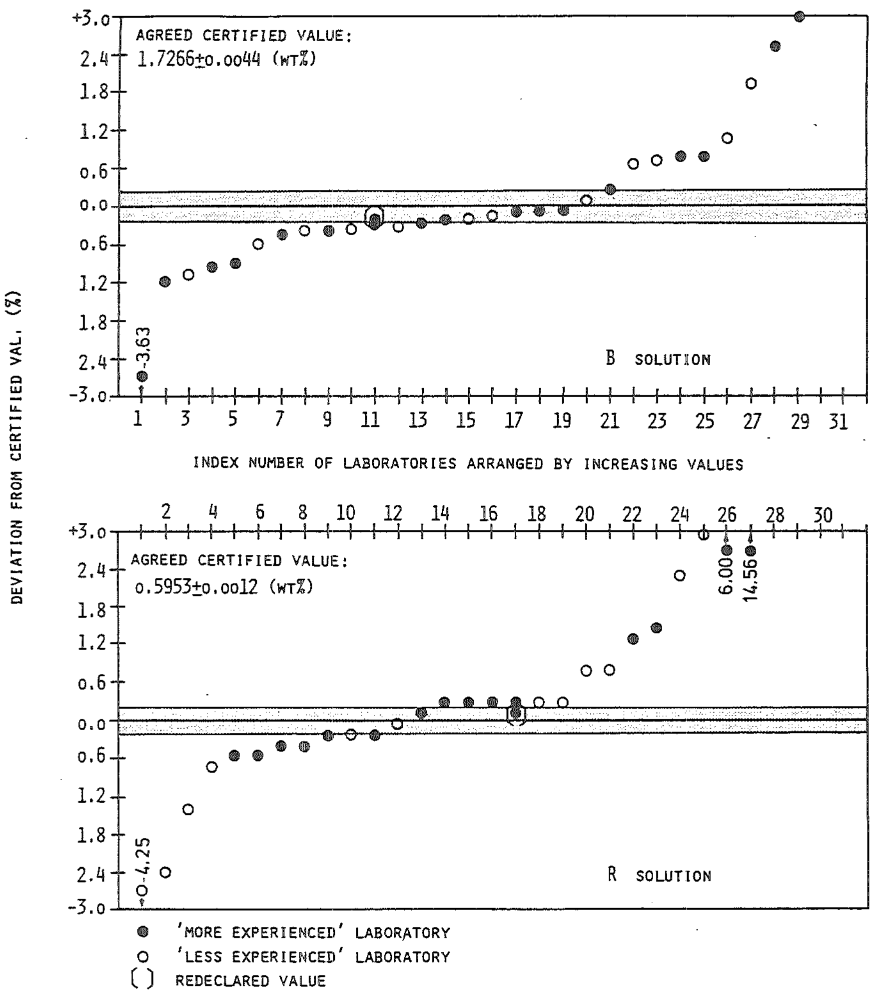
IDA-80/FIG. 15: REPORTED PU-239 ABUNDANCES



IDA-80/FIG. 16: REPORTED PU-240 ABUNDANCES



IDA-80/FIG. 17: REPORTED PU-241 ABUNDANCES



IDA-80/FIG. 18: REPORTED PU-242 ABUNDANCES

IDA-80/TAB. VII: DATA REPORTED BY PARTICIPANTS IN RELATION TO THE UNCERTAINTY RANGES OF THE AGREED CERTIFIED VALUES[a]

	1	2	3	4	5	6	7	8	9	10	11
1		SOLUTION B					SOLUTION R				
2	DESCRIPTION	APPROX. VALUE[b]	UNCERTAINTY RANGE OF CERTIFIED VALUE (%)[c]	TOTAL NUMBER OF DATA	DATA WITHIN UNCERTAINTY RANGE		APPROX. VALUE[b]	UNCERTAINTY RANGE OF CERTIFIED VALUE (%)[c]	TOTAL NUMBER OF DATA	DATA WITHIN UNCERTAINTY RANGE	
					NUMBER	%				NUMBER	%
3	U-ELEMENT CONCENTRATION	$2,0\ \frac{\text{MG U}}{\text{G SOL.}}$	±0,093	29(16)	7(6)	24(38)	$1,7\ \frac{\text{MG U}}{\text{G SOL.}}$	±0,099	27(14)	8(5)	30(36)
4	ABUNDANCE (WT-%) U-234	<0,01	±1,2	29(17)	12(7)	41(41)	<0,01	±1,1	25(15)	12(7)	48(47)
	U-235	0,6	±0,071	30(17)	4(3)	13(18)	1,2	±0,091	28(15)	10(5)	36(33)
	U-236	0,2	±0,79	30(17)	19(13)	63(76)	<0,01	±1,5	25(15)	6(4)	24(27)
5			TOTAL:	118(67)	42(29)	36(43)		TOTAL:	105(59)	36(21)	34(36)
6	PU-ELEMENT CONCENTRATION	$7,2\ \frac{\mu\text{G PU}}{\text{G SOO}}$	±0,25	27(15)	9(4)	33(27)	$8,0\ \frac{\mu\text{G PU}}{\text{G SOL.}}$	±0,24	26(14)	8(5)	31(36)
7	ABUNDANCE (WT-%) PU-238	0,2	±0,82	26(15)	6(4)	23(27)	0,1	±2,4	24(13)	12(8)	50(62)
	PU-239	69,1	±0,037	29(17)	12(9)	41(53)	76,7	±0,021	27(15)	8(4)	30(27)
	PU-240	25,7	±0,079	29(17)	12(7)	41(41)	19,9	±0,067	27(15)	13(10)	48(67)
	PU-241	3,3	±0,16	29(17)	9(7)	31(41)	2,7	±0,33	27(15)	10(5)	37(33)
	PU-242	1,7	±0,25	29(17)	9(6)	31(35)	0,6	±0,20	27(15)	3(2)	11(13)
8			TOTAL:	169(98)	57(37)	34(38)		TOTAL:	158(87)	54(34)	34(39)

a) THE DATA FOR THE GROUP OF 'MORE EXPERIENCED' LABORATORIES ARE GIVEN IN BRACKETS

b) SEE TAB. I

c) SEE TAB. IV

The number of measurement points entered in the figures vary and are in all cases smaller than the total of 31 laboratories which contributed to the IDA-80 programme. This is mainly caused by the fact that five laboratories were unable to complete the whole measurement programme in time, for example because of delayed receipt of samples or budgetary reductions. However, more relevant to the objective of this investigation is the observation that one laboratory could not calculate concentration values because it used volumetric aliquotation and the organizers did not supply the densities of the sample solutions. Another laboratory reported no concentration values for plutonium because of unsatisfactory reproducibility of the measurements.

It should be noted for the Pu-238 determinations (Fig. 14) that three participants reported no data for this particular isotope. It was obviously not determined, neither by mass- nor by alpha spectrometry. Furthermore, uranium isotope abundances below .01% have not been reported by some laboratories[1].

Observations:

a) As shown in Tab. VII, for both uranium and plutonium, about one third of the values reported by the participants on the element concentrations and isotope abundances are within the uncertainty ranges of the agreed certified values (columns 6 and 11). If only the group of 'more experienced' laboratories is taken into consideration, there is only a slight increase of this fraction as shown by the figures given in Tab. VII in brackets: for the total of all data from 34% to 39%.

b) For the Pu-241 abundance determinations, negative deviations of reported values relative to the agreed certified value predominate, indicating unsatisfactory decay corrections (see Fig. 17).

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[1] The reported element concentrations and isotope abundances presented in this Chapter are compared to the values calculated by the evaluation team on the basis of the reported isotope ratio data in Chapt. 7.3 of this Report.

5. Data calculated by the evaluation team

5.1 Introductory remark

The laboratory specific data calculated by the Evaluation Team and their graphical presentation are compiled in Volume III of this Final Report /10/. The considerations of this chapter concern the estimates calculated by analysis of variance for the RSD's of the different uncertainty components based on the data of all participating laboratories (see Chapt. 2.4).

5.2 Isotope ratio determinations

For the reported isotope ratios, the RSD's of the three uncertainty components 'SCAN', 'RUN' and 'BETWEEN LABS' were calculated by analysis of variance. They describe fairly well the average uncertainties involved in the different steps of the mass spectrometric measurement procedure.

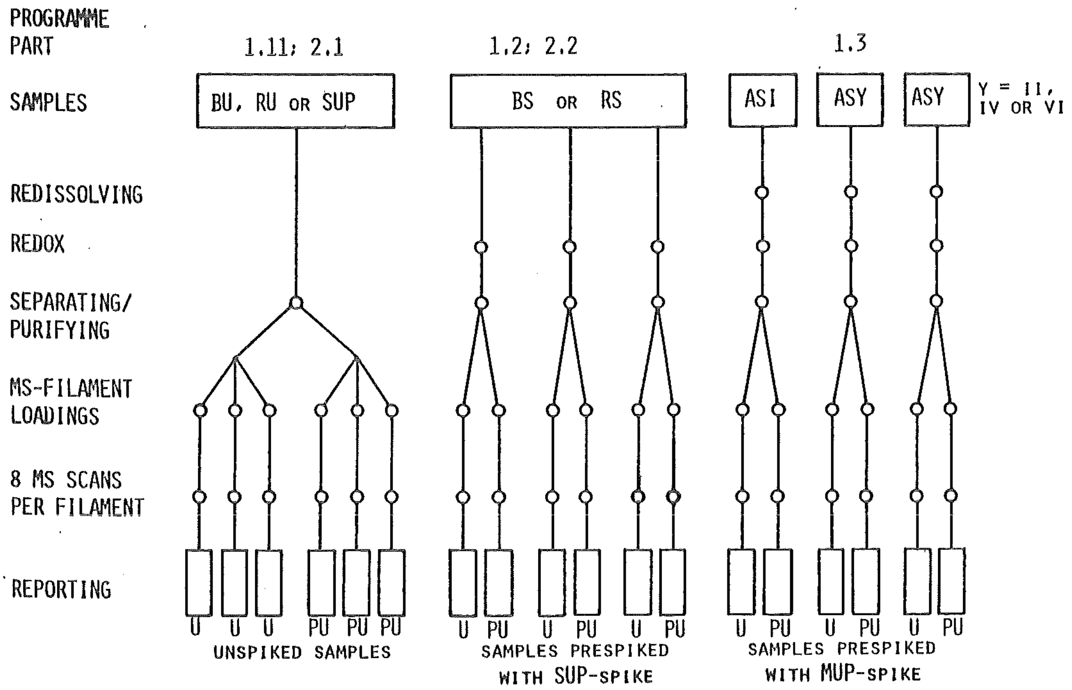
This method of statistical data treatment could be applied to the measurement data obtained from those samples of identical isotopic composition for all participating laboratories. These were:

- the unspiked and prespiked samples of the diluted input solution B and the reference solution R, measured in parts 1.11, 1.2, 2.1 and 2.2

- the SUP spike solution measured in part 2.3

- the AS samples from part 1.3 (with some exceptions explained below) obtained by spiking with the U-235/Pu-242 metal spike.

The schemes of the analytical procedures followed in measuring these samples are given in Fig. 19. Each laboratory scanned three filament loadings ('runs') per sample in the case of the unspiked and prespiked samples of the test solutions B and R as well as of the spike solution SUP. However, in the case of the unspiked samples BU and RU as well as of the spike solution SUP, the sample material for the three filament loadings was taken from one single chemical sample preparation step (redox as well as separation and purification), whereas in the case of the prespiked samples, the sample material



IDA-80/FIG. 19: ANALYTICAL PROCEDURE SCHEME FOR THE EVALUATION OF ISOTOPE RATIO DATA

for each filament loading was prepared separately. Consequently, error contributions originating from the sample preparation, contribute completely to the 'BETWEEN-LABs' component in the case of the samples BU, RU and SUP. For the prespiked samples BS and RS, only systematic parts of the sample-preparation error contribute to the 'BETWEEN-LABs' component, whereas random errors contribute to the 'RUN' component.

Care has to be taken in the comparison of evaluation results of the AS-samples because of the different structure of this programme part (see Fig. 19). Since each laboratory performed only one filament loading from sample AS I, the uncertainty components 'RUN' and 'BETWEEN-LABs' cannot be separated. For the samples AS II, IV and VI, this splitting is possible as two filament loadings were made per laboratory, however each of these samples was measured by different sub-groups of 8 to 10 laboratories (see Chapt. 6.3)[1].

---

[1] From the measurement ratios of the AS-samples, only the 'major' isotope ratios U-235/U-238 and Pu-242/Pu-239 are taken into consideration here. Only incomplete data had been reported by the laboratories for the other isotope ratios. They are given in Vol. III /10/.

The evaluation results obtained are compiled in Tab. VIII for uranium and in Tab. IX for plutonium. In Figs. 20 to 22, the calculated estimates for the error components 'SCAN', 'RUN' and 'BETWEEN-LABs' are presented graphically1). In Tab. X, approximate RSD values of the uncertainty components considered in Figs. 20 to 22 are listed for some typical isotope ratios.

On the average, each data point in the figures is based on the measurement of about 70 filament loadings. The percentage of extreme values rejected before calculation of these data amounts to 11.4% for uranium and 8.3% for plutonium, (see bottom line of columns 10 and 14 in Tabs. VIII and IX).

The Pu-238/Pu-239 ratio determinations involving alpha spectrometric measurements of the Pu-238 isotope were not considered, since in this case the calculated uncertainty components are not directly comparable to those of the mass spectrometric determinations: From each participating laboratory only one value of the alpha activity ratio Pu-238/(Pu-239+Pu-240) had been requested which was used by the evaluation team for calculating the data of all three runs. Therefore, the RSD values of the 'RUN' component for the alpha spectrometric determinations reflect only the uncertainties of the mass spectrometric measurements of the Pu-240/Pu-239 ratios2). All measurement uncertainties of the Pu-238/(Pu-239+Pu-240) alpha activity determinations contribute to the 'BETWEEN-LABs' uncertainty component.

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1) For the abbreviations used refer to Tabs. VIII and IX. - In case the given ratio was greater than 1, the RSD value was displayed at the place of the reciprocal value of that ratio. - Instead of the three values for the isotope ratios U-235/U-238 and Pu-242/Pu-239 of the samples AS II, AS IV and AS VI measured by the sub-groups, the means 'AS' were plotted as approximations for the average values.

2) The formula for calculating the Pu-238/Pu-239 isotope ratio in case of alpha spectrometric Pu-238/(Pu-239+Pu-240) activity ratio measurement is given in Volume III /10/.

IDA-80/TAB. VIII: EVALUATION OF THE RESULTS OF THE MASS SPECTROMETRIC DETERMINATION OF URANIUM ISOTOPE RATIOS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14			15
1	SAMPLE[a]	ISOTOPE RATIO	ABBREVIATION USED	MEDIAN OF LAB. MEANS	GRAND MEAN OF LAB. MEANS	ESTIMATES OF RSD (%)				BASIS OF CALCULATION			NUMBER OF LABS[b]				REFERENCE[d]
						SCAN	RUN	BETWEEN LABS	INTERLAB. SPREAD	NUMBER OF LABS	RUNS	SCANS	NOT PARTICIPATING	EXCLUDED DUE TO EXTR. VALUES[c] +	−	*	
2	ASI	235/238	ASI 58	0.92826	0.92847	-	-	-	0.57	28	28	168	3(2)	-	-	-(-)	2-I
3	ASII	235/238	ASII 58	0.90223	0.90304	0.14	0.06	0.51	0.51	9	18	108	3(2)	-	-	1(0)	2-II
4	ASIV	235/238	ASIV 58	0.91198	0.91289	0.31	0.35	0.62	0.67	10	20	120		-	-	-(-)	2-IV
5	ASVI	235/238	ASVI 58	0.91810	0.91925	0.09	0.05	0.26	0.27	7	14	84		-	-	1(1)	2-VI
6	BU	234/238	BU 48	0.9011 E-4	0.91869E-4	7.91	3.48	2.82	3.93	26	78	468	2(0)	3	-	-(0)	4
7	BU	235/238	BU 58	0.5758 E-2	0.57580E-2	0.59	0.14	0.29	0.33	24	72	432	1(0)	3	2	1(2)	5
8	BU	236/238	BU 68	0.1818 E-2	0.18159E-2	0.92	0.29	2.25	2.26	27	81	486	1(0)	1	-	2(0)	6
9	BS	233/238	BS 38	0.8533	0.85460	0.24	0.16	0.52	0.53	25	75	450	1(0)	2	1	2(2)	7
10	BS	234/238	BS 48	0.21105E-2	0.21213E-2	1.11	0.62	2.52	2.56	26	78	468	4(1)	-	-	1(0)	8
11	BS	235/238	BS 58	0.5861 E-2	0.58714E-2	0.61	0.12	0.96	0.97	25	75	450	2(1)	1	1	2(1)	9
12	BS	236/238	BS 68	0.1813 E-2	0.18177E-2	1.77	0.74	2.83	2.89	27	81	486	2(1)	1	-	1(0)	10
13	RU	234/238	RU 48	0.9178 E-4	0.90508E-4	7.41	3.13	5.53	6.07	24	72	432	5(2)	1	1	-(0)	11
14	RU	235/238	RU 58	0.12351E-1	0.12348E-1	0.34	0.18	0.48	0.50	24	72	432	3(2)	2	1	1(0)	12
15	RU	236/238	RU 68	0.6850 E-4	0.68812E-4	7.54	3.41	6.96	7.44	23	69	414	6(2)	1	-	1(1)	13
16	RS	233/238	RS 38	1.05909	1.05947	0.22	0.16	0.32	0.34	24	72	432	3(2)	2	-	2(0)	14
17	RS	234/238	RS 48	0.25975E-2	0.25970E-2	0.79	0.56	0.89	0.96	21	63	378	5(3)	3	-	2(1)	15
18	RS	235/238	RS 58	1.24883E-2	1.24891E-2	0.34	0.23	0.37	0.40	23	69	414	4(3)	2	-	2(0)	16
19	RS	236/238	RS 68	0.6839 E-4	0.69044E-4	11.89	11.84	4.32	8.56	22	66	396	8(3)	1	-	-(1)	17
20	SUP	234/233	SUP 43	0.2373 E-2	0.23683E-2	1.09	0.72	1.34	1.43	23	69	414	7(3)	1	-	-(1)	18
21	SUP	235/233	SUP 53	0.1267 E-3	0.13063E-3	8.75	2.04	8.31	8.64	23	69	414	6(3)	1	1	-(1)	19
22	SUP	238/233	SUP 83	0.5117 E-3	0.52149E-3	3.11	2.61	5.87	6.10	17	51	306	6(3)	6	1	1(3)	20
23									TOTAL:	458	1292	7752	72(33)	31	8	20(14)	-

a) THE LETTERS 'U' AND 'S' DENOTE UNSPIKED AND SPIKED SAMPLES

b) NUMBER OF 'MORE EXPERIENCED' LABORATORIES IN BRACKETS

c) SIGNS REFER TO DIRECTION OF DEVIATIONS RELATIVE TO MEANS; STAR (*) REFERS TO REJECTION DUE TO HIGH RSD OF LAB MEAN

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

IDA-80/TAB. IX: EVALUATION OF THE RESULTS OF THE MASS SPECTROMETRIC DETERMINATION OF PLUTONIUM ISOTOPE RATIOS

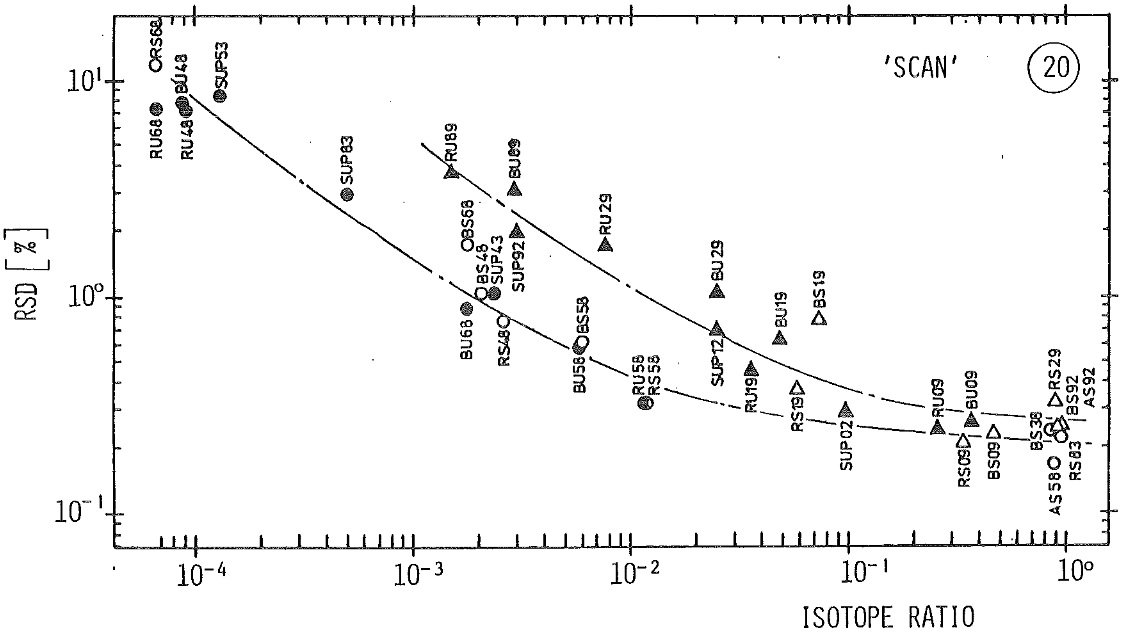
	1	2	3	4	5	6	7	8	9	10	11	12	13	14			15
1	SAMPLE[a]	ISOTOPE RATIO	ABBREVIATION USED	MEDIAN OF LAB. MEANS	GRAND MEAN OF LAB. MEANS	ESTIMATES OF RSD (%) SCAN	RUN	BETWEEN LABS	INTER-LAB. SPREAD	BASIS OF CALCULATION NUMBER OF LABS	RUNS	SCANS	NUMBER OF LABS[b] NOT PARTICIPATING	EXCLUDED DUE TO EXTR. VALUES[c] +	-	*	REFERENCE[d]
2	ASI	242/239	ASI 29	1.09870	1.09822	-	-	-	0.60	27	27	162	4(2)	-	-	-(-)	23-I
3	ASII	242/239	ASII 29	1.0668	1.06550	0.23	0.51	0.65	0.74	10	20	120	4(2)	-	-	-(-)	23-II
4	ASIV	242/239	ASIV 29	1.0766	1.07789	0.35	0.44	0.21	0.39	9	18	108		-	-	-(-)	23-IV
5	ASVI	242/239	ASVI 29	1.08165	1.08228	0.17	0.10	0.07	0.11	7	14	84		-	1	-(1)	23-VI
6	BU	238/239	BU 89	0.2998 E-2	0.30200E-2	3.08	0.42	2.27	2.40	7	21	126	5(2)	-	1	1(1)	26
7	BU	240/239	BU 09	0.36981	0.36984	0.26	0.05	0.21	0.22	27	81	486	2(0)	-	1	1(1)	27
8	BU	241/239	BU 19	0.47905E-1	0.47922E-1	0.64	0.27	0.58	0.62	28	84	504	2(0)	-	-	1(0)	28
9	BU	242/239	BU 29	0.2463 E-1	0.24671E-1	1.10	0.92	1.10	1.25	28	84	504	2(0)	-	-	1(0)	29
10	BS	240/239	BS 09	0.47246	0.47257	0.23	0.26	0.20	0.25	26	78	468	3(1)	1	1	-(0)	30
11	BS	241/239	BS 19	0.7416 E-1	0.74230E-1	0.78	0.33	0.35	0.44	25	75	450	3(1)	2	1	-(1)	31
12	BS	242/239	BS 29	1.0826	1.08247	0.24	0.29	0.23	0.29	23	69	414	2(0)	2	1	3(3)	32
13	RU	238/239	RU 89	0.1545 E-2	0.15351E-2	3.86	0.0	1.23	1.40	7	21	126	7(4)	1	-	1(0)	35
14	RU	240/239	RU 09	0.25851	0.25845	0.24	0.12	0.17	0.19	26	78	468	4(2)	-	-	1(0)	36
15	RU	241/239	RU 19	0.35555E-1	0.35552E-1	0.45	0.37	0.54	0.59	26	78	468	4(2)	-	-	1(0)	37
16	RU	242/239	RU 29	0.7665 E-2	0.76758E-2	1.83	0.32	1.24	1.32	25	75	450	4(2)	2	-	-(2)	38
17	RS	240/239	RS 09	0.34521	0.34515	0.21	0.13	0.14	0.16	23	69	414	5(3)	-	2	1(1)	39
18	RS	241/239	RS 19	0.5780 E-1	0.57842E-1	0.37	0.41	0.26	0.36	23	69	414	5(3)	1	2	-(0)	40
19	RS	242/239	RS 29	0.8974	0.89737	0.32	0.33	0.30	0.37	24	72	432	4(2)	-	2	1(1)	41
20	SUP	239/242	SUP 92	0.29775E-2	0.29900E-2	1.99	0.66	1.87	1.96	22	66	396	5(3)	2	-	2(2)	42
21	SUP	240/242	SUP 02	0.9817 E-1	0.98238E-1	0.29	0.19	0.36	0.38	23	69	414	5(3)	-	1	2(1)	43
22	SUP	241/242	SUP 12	0.2503 E-1	0.25014E-1	0.70	0.49	0.95	1.00	26	78	468	5(3)	-	-	-(-)	44
23									TOTAL:	442	1246	7476	75(35)	11	13	16(14)	

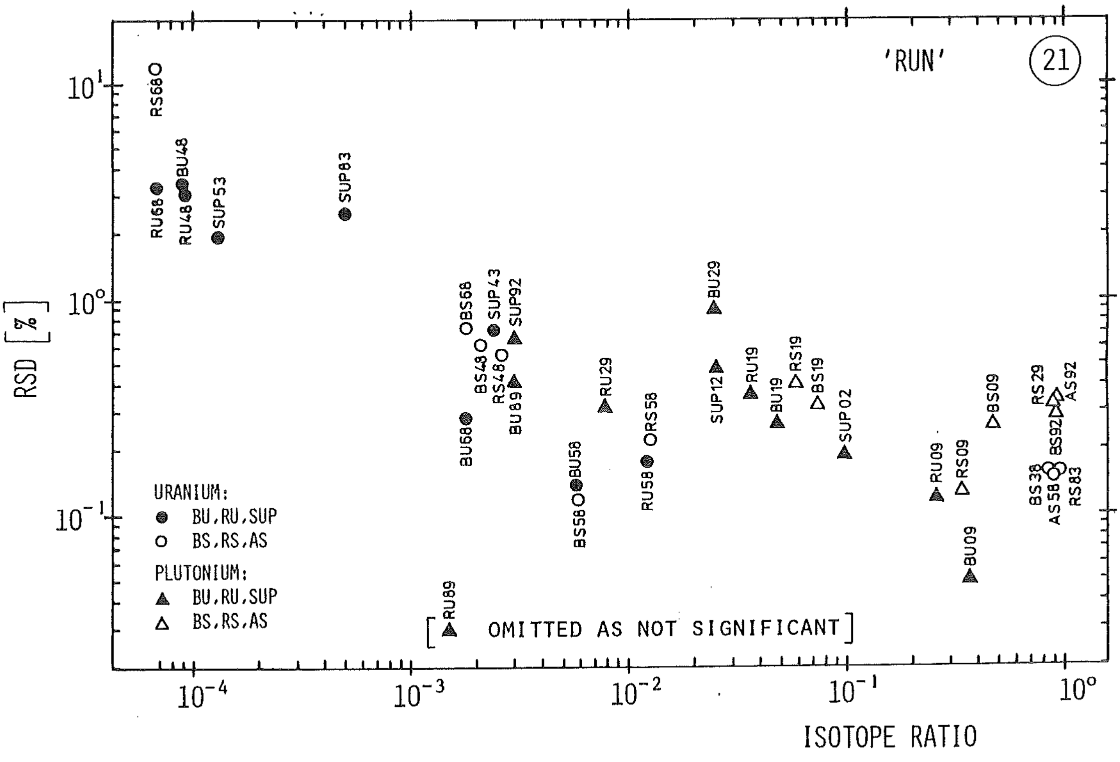
a) THE LETTERS 'U' AND 'S' DENOTE UNSPIKED AND SPIKED SAMPLES

b) NUMBER OF 'MORE EXPERIENCED' LABORATORIES IN BRACKETS

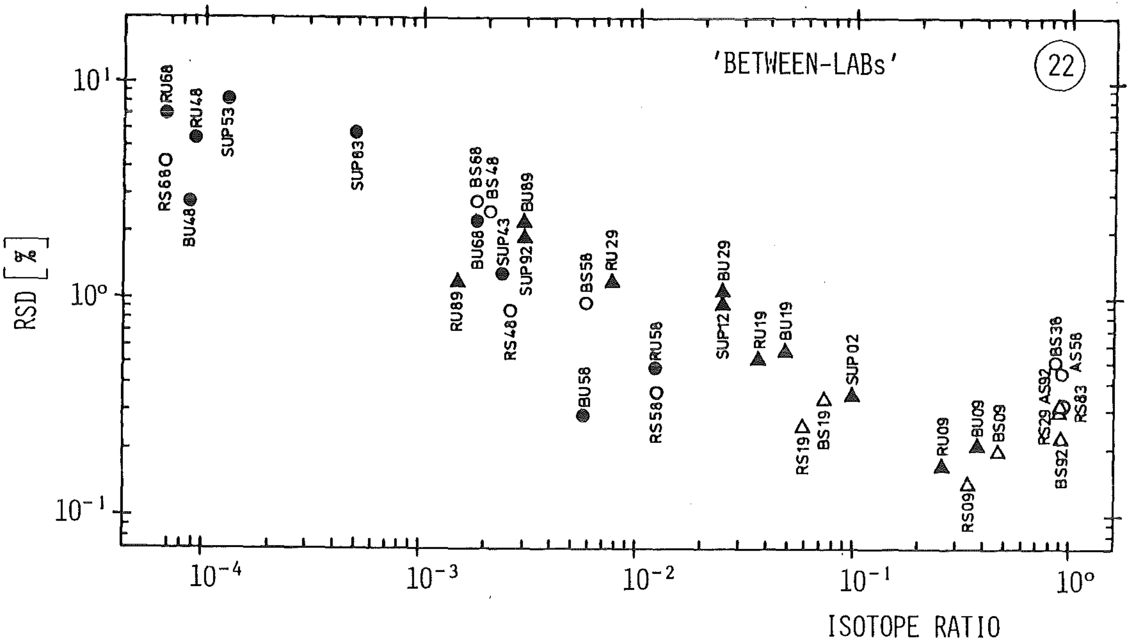
c) SIGNS REFER TO DIRECTION OF DEVIATIONS RELATIVE TO MEANS; STAR (*) REFERS TO REJECTION DUE TO HIGH RSD OF LAB MEAN

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/





IDA-80/FIGS. 20 TO 22: ISOTOPE RATIOS OF URANIUM AND PLUTONIUM; ESTIMATED RSDs OF UNCERTAINTY COMPONENTS



IDA-80/TAB. X: APPROXIMATE RSDS (%) OF UNCERTAINTY COMPONENTS FOR TYPICAL ISOTOPE RATIOS

	1	2	3	4	5
1	UNCERTAINTY COMPONENT	ELEMENT	ISOTOPE RATIO		
			1	10^{-2}	10^{-4}
2	SCAN	U	0,20	0,40	8,0
3		PU	0,25	1,30	-
4	RUN	U	0,15	0,15	3,0
5		PU	0,25	0,30	-
6	BETWEEN-LABS	U	0,40	0,40	5,0
7		PU	0,30	1,00	-

Observations:

a) there is a general tendency for the RSD values of all uncertainty components considered to increase with decreasing isotope ratio and to be smaller for uranium than for plutonium (see Tab. X and Figs. 20 to 22).

b) There is no significant difference indicated between the RSD's of the uncertainty components for samples of the fission product containing solutions A and B and samples of solution R, which was free of fission products (see Figs. 20 to 22).

c) As shown by the averaging curves in Fig. 20, higher RSD 'SCAN' values are observed for plutonium than uranium at least for isotope ratios below 10^{-1}. This is probably caused by smaller ion beam intensities in the plutonium measurements. The values for uranium seem to be about constant for ratios between 10^{-2} and 1[1].

d) The 'RUN' uncertainty components for the Pu-242/Pu-239 ratios measured on the prespiked samples AS, BS and RS are relatively high in comparison to those of the U-235/U-238 ratio of the AS-sample and the U-233/U-238 ratios of the BS and RS samples (see Fig. 21). This may reflect uncertainties in the chemical sample preparation of plutonium, in particular the redox step (see Fig. 19)[2].

e) The Pu-240/Pu-239 ratios show relatively low values for the 'RUN'[3] as well as the 'BETWEEN-LABs' uncertainty components (see Figs. 21 and 22). This may be explained by the fact that isotope fractionation of one mass unit difference influences this isotope ratio less.

---

[1] Unfortunately, no uranium isotope ratio data in the range of 10^{-1} are available to back up this assumption.

[2] For the other isotope ratios of prespiked plutonium samples displayed in Fig. 21, both isotopes of the ratios originate nearly exclusively from plutonium of the sample (i.e. there is very little contribution from plutonium of the spike material) and therefore remain nearly unaffected by uncertainties of chemical sample preparation.

[3] For the unspiked R-sample, no significant 'RUN' component had been found by analysis of variance for the Pu-238/Pu-239 ratio (see Tab. IX, column 7). Therefore, the ordinate value of the RU 89 data point in Fig. 21 is considered to be zero.

f) Ratios involving the Pu-241 isotope show no unusual behaviour, indicating satisfactory decay corrections (see Figs. 21 and 22).

g) The U-238/U-233 ratio determination of the SUP spike solution shows a relatively high number of (positive) extreme values, indicating U-238 contaminations or background (see Tab. VIII, line 22, column 14).

5.3 Isotope abundance determinations

The isotope abundances of the B solution containing fission products and the reference solution R (free of fission products) were calculated starting from the run mean values of the isotope ratios measured in parts 1.11 and 2.1[1)]. From these data, the RSD's of the 'RUN' and 'BETWEEN-LABs' uncertainty components were derived by analysis of variance. Because all three run measurements originate from one redox and separation procedure (see Fig. 19, page 38) the RSD 'RUN' only represents the random uncertainties generated within the laboratory by the mass-spectrometric measurements. All laboratory-specific uncertainty components (redox- and separation procedures as well as all kinds of calibration procedures) contribute to the RSD 'BETWEEN-LABs'[2)].

The evaluation results obtained are compiled in Tab. XI for both, uranium and plutonium. In Figs. 23 and 24, the estimates calculated for the error components 'RUN' and 'BETWEEN-LABs' are presented graphically. In Tab. XII, approximate RSD values of the two uncertainty components considered in Figs. 23 and 24 are listed for some typical isotope abundances. On the average, each data point in the figures is based on the measurement of about 70 filament loadings[3)]. The percentage of extreme values rejected before calculation of these data amounts to 11.1% for uranium and 7.0% for plutonium (derived from data in columns 8 and 10 in Tab. XI).

[1)] The isotopic composition of the undiluted input solution A is identical with that of solution B (experimentally verified).

[2)] This has to be taken in consideration if the calculated data are used to estimate within-laboratory reproducibilities including sample preparation procedures.

[3)] This is not valid for the Pu-238 data points which are mainly based on alpha-spectrometric measurements (see Chapts. 3.5 and 5.2).

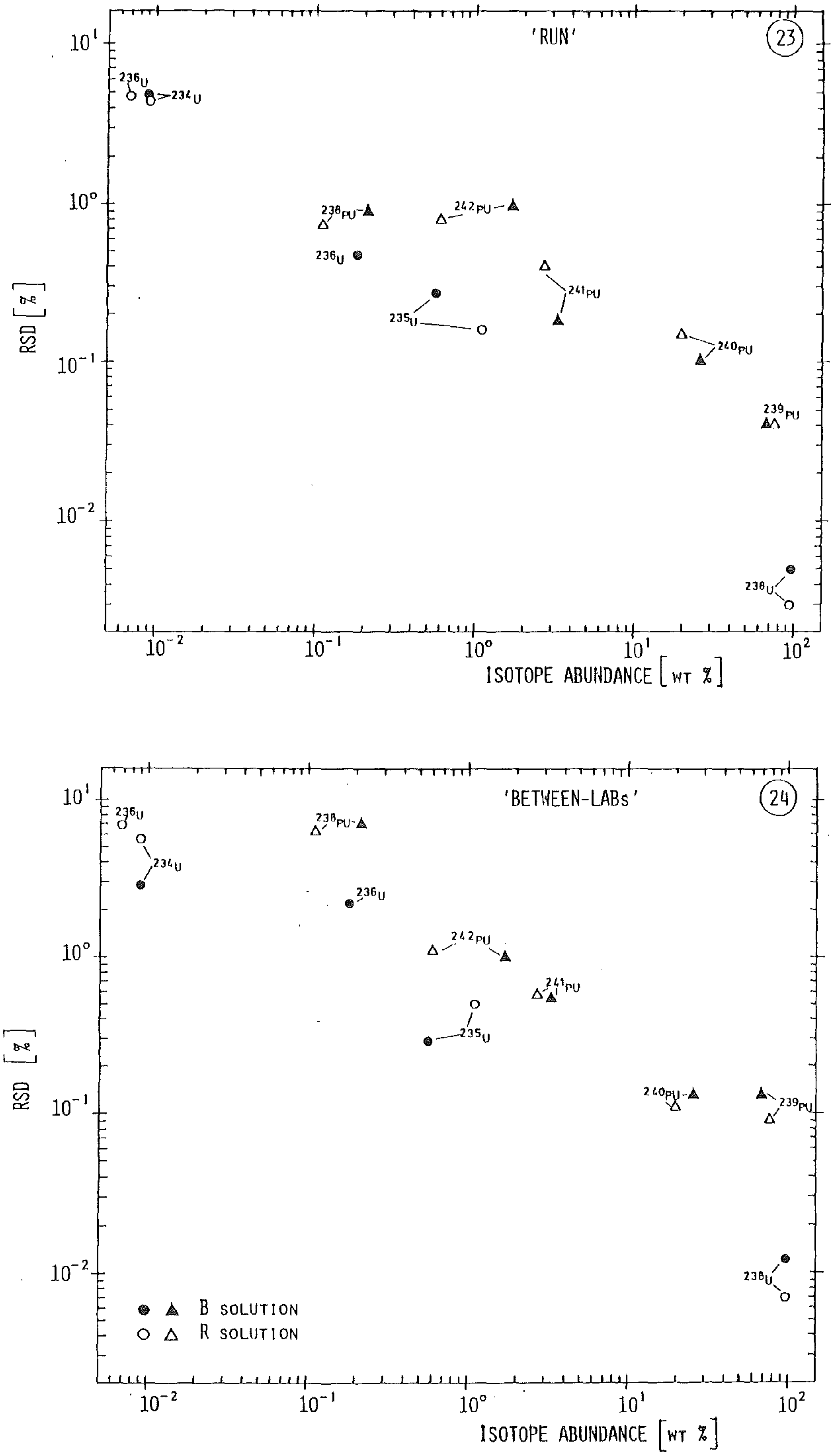
IDA-80/TAB. XI: EVALUATION OF THE RESULTS OF ISOTOPE ABUNDANCE DETERMINATIONS

	1	2	3	4	5	6	7	8	9	10			11
1	SOLUTION	ISOTOPE	ABUNDANCE (WT. %)		ESTIMATES OF RSD (%)			NUMBER OF CONTRIBUT-ING LABS	NUMBER OF LABS[a]				REFER-ENCE[c]
			MEDIAN OF LAB MEANS	GRAND MEAN OF LAB MEANS	RUN	BET-WEEN LABS	INTER-LAB. SPREAD		NOT PARTI-CIPAT-ING	EXCLUDED DUE TO EXTR. VALUES[b]			
										+	-	*	
2	B	U-234	0.0088	0.00896	4.77	2.91	4.01	26	2(0)	3	-	-(0)	45
3		U-235	0.5644	0.56424	0.27	0.29	0.33	24	1(0)	3	2	1(1)	46
4		U-236	0.1789	0.17871	0.47	2.24	2.26	27	1(0)	1	-	2(0)	47
5		U-238	99.24735	99.24536	0.005	0.014	0.015	30	1(0)	-	-	-(-)	48
6	R	U-234	0.0089	0.00878	4.33	5.55	6.08	24	5(2)	1	1	-(0)	49
7		U-235	1.20445	1.20410	0.16	0.50	0.51	22	3(2)	2	1	3(0)	50
8		U-236	0.0067	0.00674	4.67	6.91	7.42	23	6(2)	1	-	1(1)	51
9		U-238	98.7796	98.77920	0.003	0.007	0.007	25	3(2)	1	1	1(0)	52
10	B	PU-238	0.2064	0.20392	0.89	6.99	7.01	24	5(2)	-	1	1(2)	53
11		PU-239	69.0783	69.09682	0.04	0.13	0.13	26	2(0)	1	-	2(1)	56
12		PU-240	25.6598	25.66243	0.10	0.13	0.14	27	2(0)	-	1	1(1)	57
13		PU-241	3.3356	3.33932	0.18	0.55	0.56	25	2(0)	-	-	4(2)	58
14		PU-242	1.7234	1.72634	0.95	1.03	1.17	28	2(0)	-	1	-(0)	59
15	R	PU-238	0.1177	0.11647	0.72	6.20	6.21	20	7(4)	1	1	2(2)	60
16		PU-239	76.6515	76.65849	0.04	0.09	0.09	27	4(2)	-	-	-(-)	63
17		PU-240	19.8923	19.89122	0.15	0.11	0.14	27	4(2)	-	-	-(-)	64
18		PU-241	2.7483	2.74630	0.40	0.57	0.62	27	4(2)	-	-	-(-)	65
19		PU-242	0.5955	0.59586	0.79	1.17	1.26	25	4(2)	2	-	-(2)	66
20							TOTAL:	457	58(22)	16	9	18(12)	

a) NUMBER OF 'MORE EXPERIENCED' LABS IN BRACKETS

b) SIGNS REFER TO DIRECTION OF DEVIATIONS RELATIVE TO MEANS; STAR (*) MEANS REJECTION DUE TO HIGH RSD OF LAB MEAN

c) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/



IDA-80/FIGS. 23 TO 24:

ISOTOPE ABUNDANCES OF URANIUM AND PLUTONIUM IN B AND R TEST SOLUTIONS: ESTIMATED RSDs OF UNCERTAINTY COMPONENTS

IDA-80/TAB. XII: APPROXIMATE RSDs (%) OF UNCERTAINTY COMPONENTS FOR TYPICAL ISOTOPE ABUNDANCES

	1	2	3	4	5
1	UNCERTAINTY COMPONENT	ELEMENT	ISOTOPE ABUNDANCE (WT-%) 0.01	 1	 100
2	RUN	U	5.0	0.15	<0.01
3		PU	-	0.8	0.04
4	BETWEEN-LABS	U	6.0	0.4	0.01
5		PU	-	1.3	0.1

Observations:

a) The RSD values of both uncertainty components considered increase with decreasing isotope abundance and are smaller for uranium than plutonium (see Tab. XII).

b) There is no indication for a significant difference between the uncertainty components of the solution B containing fission products and the reference solution R (without fission products) (see Figs. 23 and 24).

c) The measurement results for the isotope Pu-241 do not show unusual behaviour, indicating satisfactory decay corrections (see Figs. 23 and 24).

5.4 Concentration Determinations

In all parts of the IDA-80 programme, the concentrations of the respective samples have been determined. These results are compiled in Tab. XIII and show the element concentrations in gram of uranium and plutonium.
In addition, in Tab. XIV, the Pu-239 concentrations as number of atoms/g sol, are listed[1]. As they are independent of a precise determination of

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[1] To facilitate intercomparison, the Pu-element data of Tab. XIII are also given.

IDA-80/TAB. XIII: EVALUATION OF THE RESULTS OF ELEMENT CONCENTRATION DETERMINATIONS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16			17
1	SAMPLE	PROGRAMME PART	SAMPLE PREPARATION				ELEMENT	CONCENTRATION[a]		ESTIMATES OF RSD (%)			NUMBER OF CONTRIBUTING LABS	NUMBER OF RUNS PER LABORATORY	NUMBER OF LABS[b]				REFERENCE[d]
			SPIKING PROCEDURE	REDISSOLVING	REDOX	SEPAR./PURIF.		MEDIAN OF LAB. MEANS	GRAND MEAN OF LAB MEANS	RUN	BETWEEN LABS.	INTER-LAB. SPREAD			NOT PARTICIPATING	EXCLUDED DUE TO EXTREME VALUES[c] +	−	*	
2	ASI	1.3	PRESPIKED U-235/PU-242 MUP; CBNM	X	X	X	U PU	1.6945 5.968	1.6943 5.9789	- -	- -	0.61 0.63	28 27	1 1	3(2) 4(2)	- -	- -	- -	67-1 75-1
3	ASII, IV OR VI	1.3		X	X	X	U PU	1.6935 5.986	1.6919 5.9836	0.28 0.43	0.49 0.46	0.53 0.55	28 27	2 2	3(2) 4(2)	- -	- -	- -	67-2 75-2
4	ASI + ASII, IV OR VI	1.3		X	X	X	U PU	1.694 5.982	1.6929 5.9820	0.20 0.39	0.46 0.49	0.47 0.54	27 27	3 3	3(2) 4(2)	- -	- -	1(0) -	67-3 75-3
5	BU	1.11	BY LAB U-233/PU-242 LOS; (SOL.)		X	X	U PU	2.049 7.1875	2.0497 7.1823	0.37 0.38	0.69 0.79	0.72 0.82	28 26	3 3	1(0) 3(1)	- 1	2 1	-(0) -(1)	68 77
6	BU I, II, III	1.12		X	X	X	U PU	2.046 7.180	2.0483 7.1225	0.43 0.50	1.00 2.54	1.03 2.56	25 24	3 3	4(3) 5(3)	- -	2 -	-(0) 2(1)	69 79
7	BS	1.2	PRESPIKED U-233/PU-242 SUP; CBNM		X	X	U PU	2.046 7.201	2.0436 7.2018	0.18 0.31	0.52 0.30	0.53 0.35	25 23	3 3	1(0) 2(0)	1 1	2 2	2(2) 3(3)	70 81
8	RU	2.1	BY LAB U-233/PU-242 LOS; (SOL.)		X	X	U PU	1.7155 7.986	1.7161 7.9924	0.26 0.28	0.46 1.24	0.48 1.25	22 23	3 3	3(2) 5(3)	- -	3 2	3(2) 1(2)	71 83
9	RS	2.2	PRESPIKED U-233/PU-242 SUP; CBNM		X	X	U PU	1.712 7.978	1.7114 7.9778	0.18 0.36	0.32 0.29	0.34 0.35	24 24	3 3	3(2) 4(2)	- 2	2 -	2(0) 1(1)	72 85
10	RU	2.3	BY LAB U-233/PU-242 SUP; CBNM		X	X	U PU	1.712 7.990	1.7122 7.9966	0.37 0.27	0.34 0.47	0.40 0.50	23 23	3 3	3(2) 4(2)	1 1	2 -	2(1) 3(2)	73 87
											TOTAL :		454		59(31)	7	18	20(15)	

a) DIMENSIONS: AS-SAMPLES X 10^{-1}G U/G SOL.; X 10^{-4}G PU/G SOL.; B AND R-SAMPLES: MG U/G SOL.; µG PU/G SOL.

b) NUMER OF 'MORE EXPERIENCED' LABORATORIES ARE IN BRACKETS

c) SIGNS REFER TO DIRECTION OF DEVIATIONS RELATIVE TO MEANS; STAR (*) MEANS REJECTION DUE TO HIGH RSD OF LAB MEAN

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL. III /10/

IDA-80/TAB. XIV: EVALUATION OF THE RESULTS OF PU-239 CONCENTRATION DETERMINATIONS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16			17
1	SAMPLE	PROGRAMME PART	SAMPLE PREPARATION SPIKING PROCEDURE	REDIS-SOLVING	REDOX	SEPAR./PURIF.	ELEMENT	CONCENTRATION[a] MEDIAN OF LAB. MEANS	GRAND MEAN OF LAB. MEANS	ESTIMATES OF RSD (%) RUN	BETWEEN LABS.	INTER-LAB. SPREAD	NUMBER OF CONTRIBUTING LABS	NUMBER OF RUNS PER LABORATORY	NUMBER OF LABS[b] NOT PARTICIPATING	EXCLUDED DUE TO EXTREME VALUES[c] +	-	*	REFERENCE[d]
2	ASI	1.3	PRESPIKED U-235/PU-242 MUP; CBNM	X	X	X	PU-239 PU	1.039 5.968	1.0412 5.9789	- -	- -	0.62 0.63	27 27	1 1	4(2) 4(2)	- -	- -	- -	74-1 75-1
3	ASII, IV OR VI	1.3		X	X	X	PU-239 PU	1.043 5.986	1.0419 5.9836	0.43 0.43	0.45 0.46	0.54 0.55	27 27	2 2	4(2) 4(2)	- -	- -	- -	74-2 75-2
4	ASI + ASII, IV OR VI	1.3		X	X	X	PU-239 PU	1.041 5.982	1.0417 5.9820	0.40 0.39	0.48 0.49	0.53 0.54	27 27	3 3	4(2) 4(2)	- -	- -	- -	74-3 75-3
5	BU	1.11	BY LAB U-233/PU-242 LOS; (SOL.)		X	X	PU-239 PU	1.251 7.1875	1.2502 7.1823	0.38 0.38	0.75 0.79	0.79 0.82	26 26	3 3	3(1) 3(1)	1 1	1 1	-(1) -(1)	76 77
6	BU I, II, III	1.12		X	X	X	PU-239 PU	1.249 7.180	1.2398 7.1225	0.50 0.50	2.48 2.54	2.50 2.56	24 24	3 3	5(3) 5(3)	- -	- -	2(1) 2(1)	78 79
7	BS	1.2	PRESPIKED U-233/PU-242 SUP; CBNM		X	X	PU-239 PU	1.253 7.201	1.2538 7.2018	0.31 0.31	0.24 0.30	0.30 0.35	23 23	3 3	2(0) 2(0)	1 1	2 2	3(3) 3(3)	80 81
8	RU	2.1	BY LAB U-233/PU-242 LOS; (SOL.)		X	X	PU-239 PU	1.541 7.986	1.5432 7.9924	0.28 0.28	1.27 1.24	1.28 1.25	23 23	3 3	5(3) 5(3)	- -	2 2	1(2) 1(2)	82 83
9	RS	2.2	PRESPIKED U-233/Pu-242 SUP; CBNM		X	X	PU-239 PU	1.5405 7.978	1.5404 7.9778	0.36 0.36	0.31 0.29	0.37 0.35	24 24	3 3	4(2) 4(2)	2 2	- -	1(1) 1(1)	84 85
10	RU	2.3	BY LAB U-233/PU-242 SUP; CBNM		X	X	PU-239 PU	1.543 7.990	1.5442 7.9966	0.27 0.27	0.49 0.47	0.51 0.50	23 23	3 3	4(2) 4(2)	1 1	- -	3(2) 3(2)	86 87
												TOTAL:	448		70(34)	10	10	20(20)	

a) DIMENSIONS: AS-SAMPLES: $x10^{18}$AT.PU-239/G SOL.; $x10^{-4}$G PU/G SOL.; B AND R-SAMPLES: $x10^{16}$AT.PU-239/G SOL.; µG PU/G SOL.

b) NUMBER OF 'MORE EXPERIENCED' LABORATORIES ARE IN BRACKETS

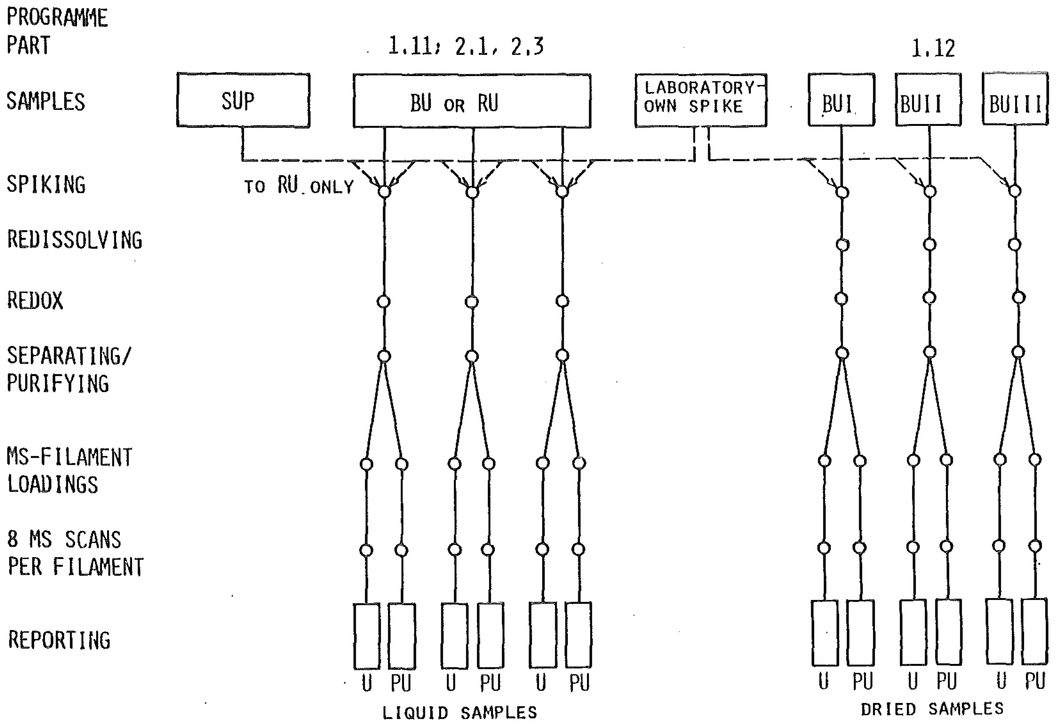
c) SIGNS REFER TO DIRECTION OF DEVIATIONS RELATIVE TO MEANS; STAR (*) MEANS REJECTION DUE TO HIGH RSD OF LAB MEAN

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

the complete isotopic composition of the sample materials, these data are more suitable for comparison of results obtained in different parts of the programme.

In total 174 concentration determinations of uranium and 170 of plutonium were performed in the programme, each one being the mean of three 'RUN' values 14.4% of the uranium data and 11.8% of the plutonium data had to be excluded from the evaluation as extreme values.

Fig. 25 shows schematically the layout of the analytical procedure for the analyses of the unspiked diluted input solution B and the reference solution R: From solution B, liquid and dried samples were measured by the laboratories using their own spike solution (parts 1.11 and 1.12). From solution R, only liquid sample material was used, but spiked by the laboratories with their own spike as well as with the SUP spike solution prepared by CBNM (parts 2.1 and 2.3). For the schemes of the analytical procedures followed in the analyses of the prespiked samples of the three test solutions A, B and R, reference is made to Fig. 19, page 38.



IDA-80/FIG. 25: ANALYTICAL PROCEDURE SCHEME FOR THE EVALUATION OF CONCENTRATIONS OF UNSPIKED SAMPLES

Due to the different ways of sample treatment, the uncertainty sources contributing to the RSD's of the error components 'RUN' and 'BETWEEN-LABs' calculated by variance analyses (columns 10 and 11 in Tabs. XIII and XIV) are different. They are identified with the relevant sample preparation steps (columns 3 to 6) and will be discussed together with the specific subjects under investigation in the following chapters.

In calculating the concentration values of the prespiked BS samples (Part 1.2), for the U-238/U-233 and Pu-239/Pu-242 ratios of the SUP-spike solution the values determined by CBNM were used for all laboratories (part 1.2). The laboratory own measurement values were used for the RS samples (part 2.2).$^{1)}$.

Observations:

a) In most cases, the estimates of uncertainty components calculated for uranium are smaller than the corresponding ones for plutonium$^{2)}$ (see Tab. XIII, columns 10 to 12).

b) The differences between the RSD's of uncertainty components calculated for the Pu-239 isotope concentrations and the plutonium element concentrations are in no case significant (see Tab. XIV, columns 10 to 12).

c) It is the 'BETWEEN-LABs' RSD which gives the main contribution to the total uncertainty of results$^{3)}$.

d) Extreme values of negative sign predominate for uranium, for plutonium both signs were observed equally frequently (data in column 16 of Tab. XIII).

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1) Because this correction term was small, this simplification does not influence the results of evaluation.

2) For the use of externally calibrated spike materials, see Chapter 7.6.

3) The RSD of the total measurement uncertainty is given by $\sqrt{\mathrm{RSD}^2_{\mathrm{BETW}} + \mathrm{RSD}^2_{\mathrm{RUN}}/r}$ with r being the number of runs.

6. Investigations of analytical methods

6.1 Use of dried samples

For practical safeguards, the use of samples which are evaporated to dryness has advantages: Sample representativity seems to be guaranteed because no evaporation losses can occur, nor (radiolytic or other) 'ageing' effects and sample transportation is facilitated. However, analyses are rendered more difficult since unspiked sample materials have to be redissolved quantitatively from the surface of the vials[1].

To examine the operational performance capability of this method, the U and Pu element concentrations had to be determined by the participants in the diluted input solution B which was distributed both as liquid in sealed glass ampoules (part 1.11) and as dried sample aliquots in glass vials (part 1.12). The latter had been prepared at CBNM and the masses of the sample aliquots were not known to the laboratories at the time of analysis[2]. The laboratories used their own spike solutions and no specific procedure for redissolution of the sample material was recommended.

CBNM corrected the weighings of the sample aliquots of the dried samples for air buoyancy but nearly none of the participants corrected the weighings of the spike aliquots for this effect. Therefore, the participants' concentration values for the dried samples are about 0.1 % too low.

The analytical steps to be followed by the laboratories are shown in Fig. 25 (page 51): Three aliquots had to be taken from the glass ampoule with the liquid sample BU and spiked separately analogous to the spiking of the three dried samples BUI to BUIII which each laboratory received.

According to these layouts, the calculated estimates of the 'RUN' uncertainty component include all random uncertainties of aliquotation, chemical sample

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[1] An alternative is the use of thin Alu-capsules which are completely dissolved together with the sample material /17/.

[2] For details of sample preparation see Vol. II of the Final Report /9/.

preparation and mass-spectrometric measurement. For the dried samples, the random component of measurement uncertainties due to insufficient redissolution contributes additionally to this uncertainty component. Systematic losses of sample material, however, contribute to the 'BETWEEN-LABs' component together with all other laboratory specific biases.

The evaluation results (extracted from Tabs. XIII and XIV) are compiled in Tab. XV. Since the laboratory groups for which these calculations were performed differ, the calculations were repeated for the group of those laboratories, which contributed to all four concentration determinations considered and did not produce extreme values in any case. These results are given in Tab. XV in brackets: Although the agreement of the individual RSD values calculated for the different groups of laboratories is unsatisfactory in most cases, the general tendency is evident.

Observations:

a) The calculated RSDs of error components are always higher for the dried samples than for the liquid ones - more pronounced for plutonium than for uranium (lines 5 and 9, columns 4 to 6). It is difficult not to assign this effect to incomplete redissolution of the samples since this is the only difference in the analytical procedure.

b) Taking into consideration the air buoyancy correction, the median values of concentrations obtained with the dry sample technique are within the uncertainty ranges of the agreed certified values for both elements (lines 4 and 8, columns 7 and 8) and on average, only about 0.1 % smaller than for liquid sample analysis (lines 5 and 9, column 8). This confirms that quantitative redissolution has been achieved by the majority of the participating laboratories.

c) In contrast to the median, the grand mean of dried sample analyses for plutonium is clearly smaller than for liquid samples (line 9, column 9). This is understandable if less than 50 % of the laboratories produce concentration values, which are too small since the median remains unchanged in this case, whereas the grand mean is influenced. Indeed

IDA-80/TAB. XV: RESULTS OF MEASUREMENTS ON DRIED SAMPLES

	1	2	3	4	5	6	7	8	9	10	11	12
1	SAMPLE	PRO-GRAMME PART	STATE OF SAMPLE	ESTIMATES OF RSD (%)			CONCENTRATION[a]			DEV.(%) OF MEDIAN FROM CERT.VAL.	NUMBER OF CONTRIBUT-ING/MORE EXPER'D LABS	REFER-ENCE[c]
				RUN	BETWEEN LABS	INTERLAB. SPREAD	CERTI-FIED[b]	MEDIAN	GRAND MEAN			
2	URANIUM[d]											
3	BU	1.11	LIQUID	0.37 (0.23)	0.69 (0.38)	0.72 (0.40)	2.0491 ±0.0019	2.049 (2.0520)	2.0497 (2.0515)	±0.0 (+0.14)	28/17 20/12	68 -
4	BU I, II,III	1.12	DRIED	0.43 (0.36)	1.00 (0.39)	1.03 (0.44)	2.0491 ±0.0019	2.046 (2.0460)	2.0483 (2.0467)	-0.15 (-0.16)	25/14 (20/12)	69 -
5	DEVIATION (%) OF DRIED FROM LIQUID SAMPLE METHOD			+16 (+57)	+45 (+ 3)	+43 (+10)	-	-0.15 (-0.29)	-0.07 (-0.23)	- -	- -	- -
6	PU-239[d]											
7	BU	1.11	LIQUID	0.38 (0.25)	0.75 (0.77)	0.79 (0.78)	1.2504 ±0.0031	1.251 (1.251)	1.2502 (1.2497)	+0.05 (+0.06)	26/15 (20/12)	76 -
8	BU I, II,III	1.12	DRIED	0.50 (0.48)	2.48 (1.49)	2.50 (1.51)	1.2504 ±0.0031	1.249 (1.248)	1.2398 (1.2399)	-0.11 (-0.15)	24/13 (20/12)	78 -
9	DEVIATION (%) OF DRIED FROM LIQUID SAMPLE METHOD			+32 (+92)	+231 (+ 94)	+216 (+ 94)	-	-0.16 (-0.24)	-0.83 (-0.78)	- -	- -	- -

a) DIMENSION: MG U/G SOL.; x10^{16} ATOMS PU-239/G SOL

b) SEE TAB. IV

c) INDICATES THE EVALUATION SHEET NUMBER IN VOL. III /10/

d) VALUES IN BRACKETS ARE BASED ON THE FOLLOWING 20 LABORATORIES ('MORE EXPERIENCED' ONES UNDERLINED): 1,2,3,4,6,7,9,10,12,13,14,15,16,19,20,21,23,25,29,30

four laboratories of the group produced small values[1] and it is interesting to note that three of them reported no heating during redissolution of the samples while the fourth reported only gently warming[2].

d) The observation of smaller RSD's for the uncertainty components in the measurements of liquid as opposed to dried sample material (see Par. a) indicates that no aging effects occurred in the diluted input solution B containing fission products (see also Chapt. 6.2), although the time of analysis in the different laboratories differed in some cases more than one year.

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[1] See Evaluation Sheet 78 in Vol. III of the Final Report /10/; the codes of the four laboratories are 17, 20, 21 and 23.

[2] No relationship could be found between the performance of the laboratories and the acidity of the nitric acid which was used for redissolution of samples.

6.2 Conventional spiking method

One of the main objectives of the IDA-80 programme was to study the different uncertainty error sources involved in the spiking procedure if solutions of dissolved spike materials are used. Because of the small size of the effects expected, reference solution R (fission product free) was used for this purpose, on the assumption that more accurate measurements could be performed on such material than in case it would contain fission products. As shown in Fig. 1 (page 7) three different spiking procedures were used for this purpose:

- In part 2.1, spiking of the R-solution with the participants' own spike solution. This procedure involves all possible uncertainty sources.

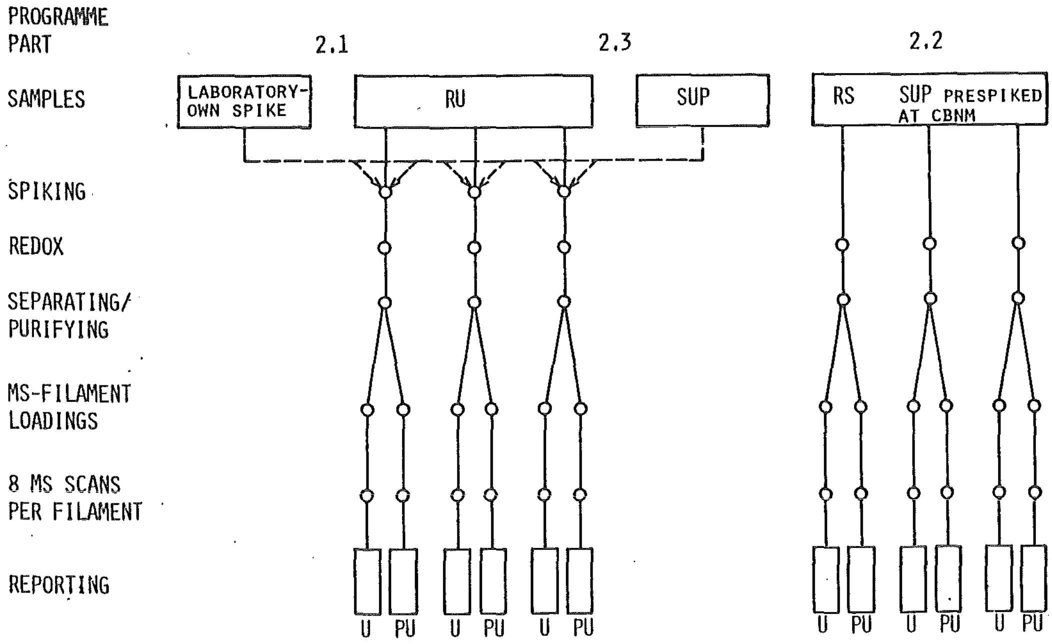
- In part 2.3, all participants spiked with the same U-233/Pu-242 spike-solution 'SUP' supplied as a liquid in sealed glass ampoules by CBNM. Therefore, in this case the procedure involved all possible uncertainty sources except the calibration of the spike solution.

- In part 2.2, samples of the R-solution, prespiked by CBNM with the SUP spike solution, had to be measured. The uncertainty contributions are limited in this case to chemical sample praparation (redox, element separation, purification) and mass spectrometric measurement.

Schemes of the analytical procedures followed are shown in Fig. 26.

In Table XVI, the evaluation results of those measurements are summarized. The corresponding results for the maximum common laboratory group are given in brackets. Agreement is fairly satisfactory and gives some idea of the confidence of the calculated estimates.

In column 1, the main uncertainty sources are mentioned according to the layout of the programme parts: The total measurement uncertainty S_T is directly determined in part 2.1 of the programme (use of laboratory-own



IDA-80/FIG. 26: ANALYTICAL PROCEDURE SCHEME FOR THE DETERMINATION OF SPIKING UNCERTAINTIES; CONVENTIONAL SPIKING METHOD (R-SOLUTION, PART 2)

IDA-80/TAB. XVI: ESTIMATES OF THE UNCERTAINTY CONTRIBUTIONS TO THE URANIUM ELEMENT AND PU-239 CONCENTRATION DETERMINATIONS OF REFERENCE SOLUTION R[a]

	1	2	3	4	5	6	7	8	9	10
1	DESCRIPTION AND SYMBOL OF UNCERTAINTY SOURCE	PROGRAMME PART	ELEMENT/ ISOTOPE	ESTIMATES OF RSD (%) [b] RUN	 BETWEEN LABS	 INTERLAB. SPREAD	CONCENTRATION (MG U/G SOL.; x10^{16} AT PU-239/G SOL.) CERTIFIED[c]	 MEDIAN	NUMBER OF CONTRIBUTING/MORE EXPER'D LABS	REFERENCE[d]
2	TOTAL UNCERTAINTY S_T	2.1	U	0.26 (0.28)	0.46 (0.37)	0.48 (0.40)	1.7154 ± .0017	1.7155 (1.716)	22/13 18/11	71 -
3			PU-239	0.28 (0.24)	1.27 (1.06)	1.28 (1.07)	1.5414 ± .0037	1.541 (1.5425)	23/12 18/11	82 -
4	ALIQUOTATION, CHEM. SAMPLE PREP. AND MS-MEASUREMENT $S_{A,P,M}$	2.3	U	0.37 (0.32)	0.34 (0.35)	0.40 (0.39)	1.7154 ± .0017	1.712 (1.712)	23/14 18/11	73 -
5			PU-239	0.27 (0.20)	0.49 (0.41)	0.51 (0.43)	1.5414 ± .0037	1.543 (1.544)	23/13 18/11	86 -
6	CHEM. SAMPLE PREP. AND MS-MEASUREMENT $S_{P,M}$	2.2	U	0.18 (0.13)	0.32 (0.35)	0.34 (0.35)	1.7154 ± .0017	1.712 (1.713)	24/15 18/11	72 -
7			PU-239	0.36 (0.15)	0.31 (0.33)	0.37 (0.34)	1.5414 ± .0037	1.5405 (1.541)	24/14 18/11	84 -

a) VALUES IN BRACKETS ARE BASED ON THE FOLLOWING 18 LABORATORIES ('MORE EXPERIENCED' ONES UNDERLINED): 1,2,3,4,6,7,8,10,12,14,15,16,20,22,25,26,30,31

b) DATA TAKEN FROM TABS.XIII AND XIV

c) SEE TAB. IV

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL. III /10/

spike solution, see Fig. 26). In part 2.3, in which the laboratories used the SUP-spike solution supplied by CBNM, all uncertainty contributions $S_{A,P,M}$ are considered except the uncertainty in spike solution calibration. Finally, part 2.2, in which prespiked samples are analyzed, yields $S_{P,M}$, i.e. all uncertainty contributions except those from the complete spiking procedure[1].

From the data given in Tab. XVI (lines 2,3,6 and 7) estimates S_S can be derived for the uncertainty associated with the spiking procedure of the R-solution. Since in part 2.3 the participants also performed measurements using the same spike solution (SUP), this uncertainty component of spiking can further be split into the subcomponents 'aliquotation' (S_A) and 'spike solution calibration' (S_C). In Tab. XVII, the formulae for the calculation of the estimates of these uncertainty components and the results are compiled.

Observations:

a) The different uncertainty contributions to the uranium measurements are more or less equal (see Tab. XVI, columns 4 to 6).

b) The calibration of the spike solution is obviously the main uncertainty source for plutonium and determines to a large extent the total uncertainty of the concentration determination (see Tab. XVII, column 5). As could be expected, this error source contributes as a laboratory bias to the 'BETWEEN-LABs' component but not to the 'RUN' RSDs for both uranium and plutonium (Tab. XVII, lines 4 and 5).

c) The median of the uranium concentration values as determined by the participants is in excellent agreement with the certified value if the laboratories applied their own spike solutions (Tab. XVI, line 2), but is found outside the uncertainty range of ± 0.1% when the SUP spike

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[1] The indices A, P and M stand for aliquotation, chemical sample preparation and mass spectrometric measurement.

IDA-80/TAB. XVII: ESTIMATES OF THE UNCERTAINTY CONTRIBUTIONS TO THE SPIKING PROCEDURE (R-SOLUTION PART 2)[a]

	1	2	3	4	5
1	DESCRIPTION AND SYMBOL OF UNCERTAINTY SOURCE	ELEMENT OR ISOTOPE	ESTIMATES OF RSD (%)		
			RUN	BETWEEN LABS	INTERLAB. SPREAD
2	SPIKING	U	0.19 (0.25)	0.33 (0.12)	0.34 (0.19)
3	$S_S = \sqrt{S_T^2 - S_{P,M}^2}$	PU-239	N.S.[b] (0.19)	1.23 (1.01)	1.23 (1.01)
4	SPIKE-CALIBRATION	U	N.S.[b] (N.S.)[b]	0.31 (0.12)	0.27 (0.09)
5	$S_C = \sqrt{S_T^2 - S_{A,P,M}^2}$	PU-239	0.07 (0.13)	1.17 (0.98)	1.17 (0.98)
6	ALIQUOTATION	U	0.32 (0.29)	0.11 (0.0)	0.21 (0.17)
7	$S_A = \sqrt{S_{A,P,M}^2 - S_{P,M}^2}$	PU-239	N.S.[b] (0.13)	0.38 (0.24)	0.35 (0.26)

a) VALUES IN BRACKETS ARE BASED ON THE FOLLOWING 18 LABORATORIES ('MORE EXPERIENCED' ONES UNDERLINED): 1,2,3,4,6,7,8,10,12,14, 15,16,20,22,25,26,30,31

b) IN THESE CASES NEGATIVE VALUES ARE OBTAINED BY VARIANCE ANALYSIS INDICATING THAT THE UNCERTAINTY COMPONENTS ARE NOT SIGNIFICANT

solution was used (Tab. XVI, lines 4 and 6)[1]. The medians of the laboratory mean values for plutonium are within the uncertainty range of ± 0.24% of the certified value in all parts of the programme (Tab. XVI, lines 3, 5 and 7).

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[1] This effect is studied in Chapt. 7.6.

Since in practice this spiking technique is applied to diluted reprocessing input solutions, the possible influence of fission products on the measurement uncertainties has to be investigated. For this purpose, the evaluation results obtained on the R-solution (free of fission products) in parts 2.1 and 2.2 of the programme have been compared with those derived from the measurements of diluted input solution B (containing fission products) in the corresponding parts 1.11 and 1.2. The values are compiled in Tab. XVIII for uranium element and in Tab. XIX for Pu-239 concentration determinations[1]. From these data, an estimate S_S for the spiking uncertainty could be derived (lines 6 and 7) also for the measurements of the B-solution.

Again, those values are given in brackets which were calculated on the basis of the maximum groups of laboratories contributing without exception to the four parts of the IDA-80 programme considered here.

In addition to the considerations above, the following observations can be made:

d) There is little evidence for a significant influence of the fission product content of samples on the measurement uncertainties: Only the RSD's of uncertainty components calculated for uranium on the basis of all data are higher for the fission-product-containing solution B than the reference solution R (Tab. XVIII, lines 2, 3 and 4, 5) For plutonium most of the corresponding results are reversed (Tab. XIX, lines 2, 3 and 4, 5) and for both elements approximately equivalent data are obtained if the comparison is made on the same group of laboratories (data in brackets).

e) The contributions to the total measurement uncertainty S_T for uranium for fission-product-containing material (B-solution) are approximately balanced between chemical sample preparation and mass spectrometric measurement $S_{P,M}$ on one side and the spiking uncertainty S_S on the other (Tab. XVIII, columns 4 to 6).

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[1] The data are taken from Tabs. XIII and XIV and are partly identical with those in Tab. XVI. The analytical procedures followed in parts 1.11 and 1.2 are identical to those in parts 2.1 and 2.2, shown schematically in Fig. 26.

IDA-80/TAB. XVIII: COMPARISON OF URANIUM CONCENTRATION DETERMINATIONS; ESTIMATION OF SPIKING UNCERTAINTY[a]

	1	2	3	4	5	6	7	8	9	10
1	DESCRIPTION AND SYMBOL OF UNCERTAINTY SOURCE	SAMPLE	PROGRAMME PART	ESTIMATES OF RSD (%)[b]			CONCENTRATION (MG U/G SOL.)		NUMBER OF CONTRIBUTING/ MORE EXPER'D LABS	REFERENCE[d]
				RUN	BETWEEN LABS	INTERLAB. SPREAD	CERTIFIED[c]	MEDIAN		
2	TOTAL UNCERTAINTY S_T	BU	1.11	0.37 (0.19)	0.69 (0.38)	0.72 (0.40)	2.0491 ± .0019	2.049 (2.051)	28/17 19/13	68 -
3		RU	2.1	0.26 (0.24)	0.46 (0.43)	0.48 (0.45)	1.7154 ± .0017	1.7155 (1.715)	22/13 19/13	71 -
4	CHEM. SAMPLE PREP. AND MS-MEASUREMENT $S_{P,M}$	BS	1.2	0.18 (0.14)	0.52 (0.33)	0.53 (0.34)	2.0491 ± .0019	2.046 (2.047)	25/15 19/13	70 -
5		RS	2.2	0.18 (0.12)	0.32 (0.34)	0.34 (0.34)	1.7154 ± .0017	1.712 (1.714)	24/15 19/13	72 -
6	SPIKING	B		0.32 (0.13)	0.45 (0.19)	0.49 (0.21)				
7	$S_S = \sqrt{S_T^2 - S_{P,M}^2}$	R		0.19 (0.21)	0.33 (0.26)	0.34 (0.29)				

a) VALUES IN BRACKETS BASED ON THE FOLLOWING 19 LABORATORIES ('MORE EXPERIENCED' ONES UNDERLINED):
1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 15, 16, 19, 20, 21, 22, 25, 26, 30

b) VALUES IN LINES 2 TO 5 TAKEN FROM TAB. XIII

c) SEE TAB. IV

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL. III /10/

IDA-80/TAB. XIX: COMPARISON OF PU-239 CONCENTRATION DETERMINATIONS; ESTIMATION OF SPIKING UNCERTAINTY[a]

	1	2	3	4	5	6	7	8	9	10
1	DESCRIPTION AND SYMBOL OF UNCERTAINTY SOURCE	SAMPLE	PROGRAMME PART	ESTIMATES OF RSD (%)[b]			CONCENTRATION ($\times 10^{16}$ AT.PU-239/G SOL.)		NUMBER OF CONTRIBUTING/ MORE EXPER'D LABS	REFERENCE[d]
				RUN	BETWEEN LABS	INTERLAB. SPREAD	CERTIFIED[c]	MEDIAN		
2	TOTAL UNCERTAINTY S_T	BU	1.11	0.38 (0.17)	0.75 (0.87)	0.79 (0.87)	1.2504 ± .0030	1.251 (1.252)	26/15 15/9	76 -
3		RU	2.1	0.28 (0.24)	1.27 (0.99)	1.28 (1.00)	1.5414 ± .0037	1.541 (1.541)	23/12 15/9	82 -
4	CHEM. SAMPLE PREP. AND MS-MEASUREMENT $S_{P,M}$	BS	1.2	0.31 (0.14)	0.24 (0.24)	0.30 (0.25)	1.2504 ± .0030	1.253 (1.252)	23/14 15/9	80 -
5		RS	2.2	0.36 (0.14)	0.31 (0.26)	0.37 (0.28)	1.5414 ± .0037	1.5405 (1.542)	24/14 15/9	84 -
6	SPIKING	B		0.22 (0.10)	0.71 (0.84)	0.73 (0.83)				
7	$S_S = \sqrt{S_T^2 - S_{P,M}^2}$	R		N.S.[e] (0.19)	1.23 (0.96)	1.23 (0.96)				

a) VALUES IN BRACKETS ARE BASED ON THE FOLLOWING 15 LABORABORIES ('MORE EXPERIENCED' ONES UNDERLINED):
1, 2, 3, 4, 6, 7, 10, 12, 14, 15, 16, 19, 20, 23, 30

b) VALUES IN LINES 2 TO 5 TAKEN FROM TAB. XIV

c) SEE TAB. IV

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL. III /10/

e) MEANS 'NOT SIGNIFICANT'

For plutonium analysis, the total measurement uncertainty is again determined by the 'BETWEEN-LABs' component of the spiking uncertainty (Tab. XIX, column 5).

f) As already observed for the analyses of the R-solution (Par. c, page 58) the medians of the results obtained on solution B also lie in all cases within the uncertainty ranges of the agreed certified values (Tab. XVIII and XIX, columns 7 and 8) - except for the uranium determinations of the prespiked samples (Tab. XVIII, lines 4 and 5).

g) For the total spiking procedure, higher values are calculated for plutonium determinations in the R-solution than in the B-solution (Table XIX, lines 6 and 7). It remains open whether this unexpected effect occurs randomly (due to the uncertainties of the calculated estimates) or reflects a specific reason.1)

As to be expected, the calculated concentration values of the prespiked samples BS and RS (programme parts 1.2 and 2.2) are almost exclusively governed by the measured ratio of spike isotope to main isotope of the test sample concerned. This can be verified by comparison of the distributions of these two quantities which are almost exactly mirror symmetrical. As an example they are given in Fig. 27 for the measurements on the B-solution2).

Further considerations regarding the use of dissolved spike material are made in Chapters 7.6, 7.8 and 7.9.

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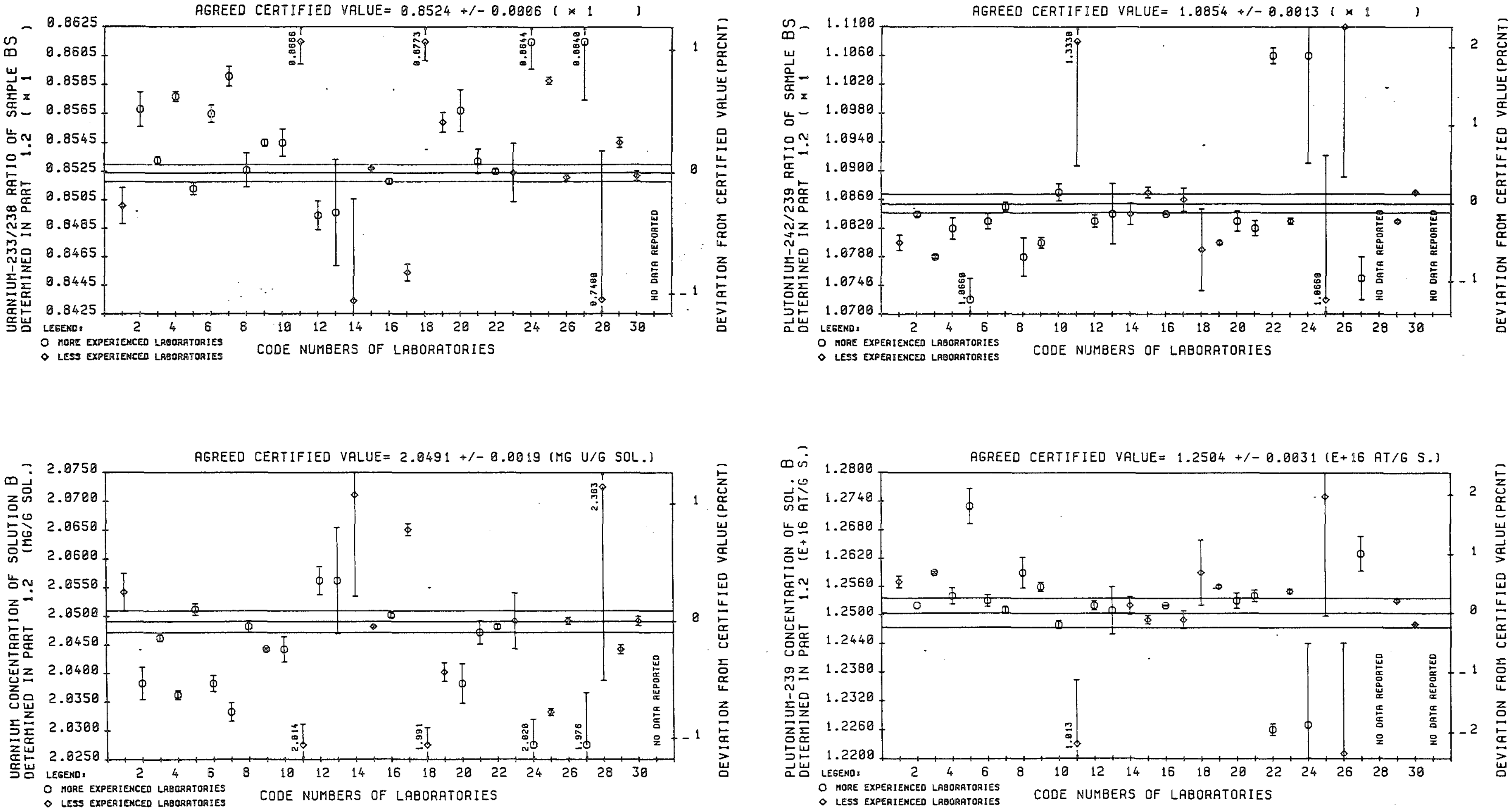
1) See App. A, p. A-14, Pars. 1 and 2.

2) Taken from the Evaluation Sheets 7, 32, 70 and 80 in Vol. III /10/. For the measurements of the R-solution, the corresponding Evaluation Sheets are 14, 41, 72 and 84.



IDA-80/FIG. 27: SPREAD OF MAIN ISOTOPE RATIOS AND CONCENTRATION VALUES FOR PRESPIKED SAMPLE ANALYSES

(SAMPLE BS, PART 1.2)

6.3 Metal spike technique

From the safeguards point of view, spiking of the undiluted input solution with U/Pu-metal alloy spikes is of special interest, since this 'in-situ' method allows the nuclear material content at the place and time of sampling to be fixed and avoids the uncertainty associated with the dilution step /11, 12/. In order to study the applicability and capability of this method on a broad basis, aliquots of the undiluted input solution A were spiked in a hot cell with U-235/Pu-242 metal spikes, prepared at CBNM /9/. This was done in part 1.3 of the programme. After dilution with 6M nitric acid, samples 'AS' of the spiked A-solution were transferred into glass vials and evaporated to dryness[1].

As shown in Fig. 28, each laboratory obtained one sample ASI of 'spiking I' and two samples out of one of three other spiking procedures called II, IV and VI. Thereby, three groups of laboratories were generated as shown in Tab. XX[2]. The mass spectrometric measurements of the filament loading with the sample ASI was called 'run 1', the measurements of the two other filament loadings with material of one of the other spikings 'run 2' and 'run 3'.

According to that layout, the uncertainty components of the following data sets were evaluated:

i) All measurements of the participating laboratories.

Because in this case the three samples analyzed per laboratory originate from two different spikings, possible uncertainties introduced

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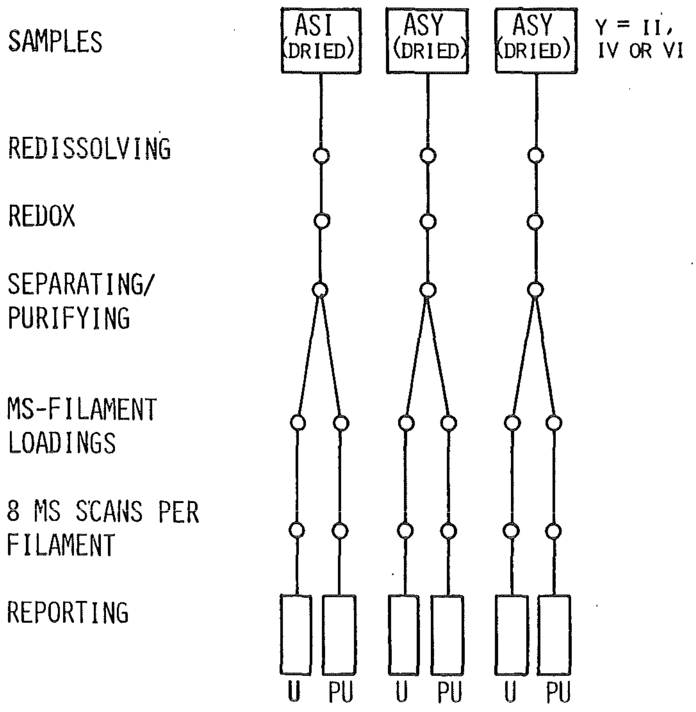
[1] Please note that incomplete redissolution of the dried AS-samples from the glass vials has no effect on the analytical results as the A-solution is already spiked. This is a basic difference to the conditions of re-dissolving the B-solution aliquots studied in part 1.12 of the programme (Chapt. 6.1).

[2] It was the intention of the organizers to create as closely as possible laboratory groups of equal size and composition with respect to the degree of experience stated by the laboratories. However, this aim could be reached only incompletely, as some laboratories cancelled their participation later when the samples had already been packed.



IDA-80/FIG. 28:
METAL SPIKE TECHNIQUE; ANALYTICAL PROCEDURE SCHEME (PART 1.3)

IDA-80/TAB. XX: STUDY OF METAL SPIKE TECHNIQUE; LABORATORY SUBGROUPS

	1	2	3	4	5
1	SUBGROUP (SPIKING)	NUMBER OF LABORATORIES/ 'MORE EXPERIENCED' ONES		CODES OF CONTRIBUTING LABORATORIES[a]	PERCENTAGE OF 'MORE EXPERIENCED' LABORATORIES
		URANIUM	PLUTONIUM		
2	II	10/4	10/4	1, $\underline{4}$, $\underline{5}$, $\underline{6}$, $\underline{8}$, 14 18, 19, 25, 29	40
3	IV	10/6	9/6	$\underline{2}$, $\underline{9}$, $\underline{10}$, 11, $\underline{12}$, $\underline{13}$, $\underline{16}$, 17, 28[b], 30	67[c]
4	VI	8/5	8/5	$\underline{3}$, $\underline{7}$, 15, $\underline{20}$, $\underline{21}$, $\underline{22}$, 23, 26	63
5	TOTAL	28/15	27/15		

a) 'MORE EXPERIENCED' LABORATORIES UNDERLINED;
LABORATORIES $\underline{24}$, $\underline{27}$ AND 31 DID NOT PARTICIPATE IN THIS PART OF THE PROGRAMME

b) LABORATORY 28 PERFORMED URANIUM MEASUREMENTS ONLY

c) CALCULATED WITHOUT LABORATORY 28

by these procedures contribute not only to the calculated estimates of the 'BETWEEN-LABs' RSDs, but also to the 'RUN' RSDs, together with those from sample preparation (redox, purification etc.) and mass-spectrometric measurement.

ii) The double determinations of all participating laboratories, i.e. all measurements except those performed on samples ASI.

In this case, the estimates of the 'RUN' RSD's (based only on two measurements per laboratory) only include the uncertainties of sample preparation (redox, purification etc.) and mass-spectrometric measurement. Uncertainties of the spiking procedure contribute to the 'BETWEEN-LABs' component only.

iii) The determinations performed on sample ASI by all participating laboratories.

As there exists only one value per laboratory, no splitting in RSDs 'RUN' and 'BETWEEN-LABs' by analysis of variance can be made but only an 'INTERLABORATORY-SPREAD' estimate can be calculated in which all uncertainty contributions are contained - except those of the spiking procedure (which exist as a bias in all measurements).

These three kinds of evaluation were also performed separately for each of the three laboratory subgroups mentioned before (see Tab. XX). The results obtained are given in Tabs. XXI and XXII for the data sets of all laboratories and the subgroups.1)

Furthermore, the calculated estimates of uncertainty components based on all measurements of the AS samples are compared in Tab. XXIII to the corresponding values observed in the analysis of the prespiked samples BS and RS (parts 1.2 and 2.2 of the programme; the data were taken from Tabs. XIII and XIV,

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1) In order to base the evaluation of uranium and plutonium measurements on the same groups of laboratories, laboratory 28, which performed uranium measurements only, was excluded from these evaluations.

IDA-80/TAB. XXI: STUDY OF METAL SPIKE TECHNIQUE; ESTIMATED UNCERTAINTY COMPONENTS AND MEDIANS OF CONCENTRATION DETERMINATIONS BASED ON ALL LABORATORIES[a]

	1	2	3	4	5	6	7	8	9	10
1	SAMPLES (RUN NUMBERS)	ELEMENT OR ISOTOPE	ESTIMATES OF RSD (%) RUN	 BETWEEN LABS	 INTER-LAB. SPREAD	CONCENTRATION (x10^{-1} gU/g SOL.; x10^{18}AT.PU-239/g SOL.) CERTIFIED[b]	 MEDIAN	DEV. (%) OF MEDIAN FROM CERTIFIED VALUE (%)	NUMBER OF RUNS ON WHICH EVALUATION IS BASED	REFERENCE[c]
2	ASI AND ASII, IV OR VI (1, 2, 3)	U	0.20	0.46	0.47	1.6966 ± .0012	1.694	-0.15	81	67-3
3		PU-239	0.40	0.48	0.53	1.0391 ± .0031	1.041	+0.18	81	74-3
4	ASII, ASIV, OR ASVI (2, 3)	U	0.28	0.49	0.53	1.6966 ± .0012	1.6935	-0.18	54	67-2
5		PU-239	0.43	0.45	0.54	1.0391 ± .0031	1.043	+0.38	54	74-2
6	ASI (1)	U	-	-	0.61	1.6966 ± .0012	1.6945	-0.12	28	67-1
7		PU-239	-	-	0.62	1.0391 ± .0031	1.039	-0.01	27	74-1

[a] ALL DATA ARE BASED ON THE SAME GROUP OF 27 LABORATORIES (ALL 31 PARTICIPANTS EXCEPT LABORATORIES 24, 27, 28 AND 31) [b] SEE TAB. IV [c] INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

IDA-80/TAB. XXII: STUDY OF METAL SPIKE TECHNIQUE; ESTIMATED UNCERTAINTY COMPONENTS AND MEDIANS OF CONCENTRATION DETERMINATIONS FOR LABORATORY SUBGROUPS

	1	2	3	4	5	6	7	8	9	10	11
1	SAMPLES (RUN NUMBERS)	ELEMENT OR ISOTOPE	SUB-GROUP OF LABS.[a]	ESTIMATES OF RSD (%) RUN	 BETWEEN LABS	 INTER-LAB. SPREAD	CONCENTRATION (x10^{-1} gU/g SOL.; x10^{18}AT.PU-239/g SOL.) CERTIFIED[b]	 MEDIAN	DEV. (%) OF MEDIAN FROM CERTIFIED VALUE (%)	NUMBER OF RUNS ON WHICH EVALUATION IS BASED	REFERENCE[c]
2	ASI AND ASII, IV OR VI (1, 2, 3)	U	II	0.18	0.54	0.55	1.6966 ± .0012	1.693	-0.21	30	67-3
3			IV[d]	0.26	0.53	0.55		1.694	-0.15	27	
4			VI	0.15	0.27	0.28		1.6945	-0.12	24	
5		PU-239	II	0.48	0.70	0.75	1.0391 ± .0031	1.0395	+0.04	30	74-3
6			IV	0.40	0.30	0.38		1.041	+0.18	27	
7			VI	0.26	0.17	0.23		1.0425	+0.33	24	
8	ASII, ASIV OR ASVI (2, 3)	U	II	0.20	0.51	0.53	1.6966 ± .0012	1.6935	-0.18	20	67-2
9			IV[d]	0.33	0.53	0.58		1.694	-0.15	18	
10			VI	0.16	0.24	0.26		1.6935	-0.18	16	
11		PU-239	II	0.53	0.67	0.77	1.0391 ± .0031	1.0415	+0.23	20	74-2
12			IV	0.49	0.23	0.41		1.042	+0.28	18	
13			VI	0.11	0.20	0.22		1.044	+0.47	16	
14	AS I (1)	U	II	-	-	0.59	1.6966 ± .0012	1.6925	-0.24	10	67-1
15			IV[d]	-	-	0.50		1.696	-0.04	9	
16			VI	-	-	0.34		1.694	-0.15	8	
17		PU-239	II	-	-	0.79	1.0391 ± .0031	1.041	+0.18	10	74-1
18			IV	-	-	0.38		1.038	-0.11	9	
19			VI	-	-	0.28		1.0395	+0.04	8	

[a] SEE TAB. XX

[b] SEE TAB. IV

[c] INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10

[d] CALCULATED OMITTING LAB 28

IDA-80/TAB. XXIII: METAL SPIKE TECHNIQUE COMPARED TO CONVENTIONAL SPIKING; EXTREME VALUES AND ESTIMATES OF UNCERTAINTY COMPONENTS OF CONCENTRATION DETERMINATIONS[a]

	1	2	3	4	5	6	7	8
1	ELEMENT OR ISOTOPE	SAMPLE/ PROGRAMME PART	NUMBER OF PARTICIPATING LABS	PERCENTAGE OF EXTREME VALUES EXCLUDED	ESTIMATES OF RSD (%)			REFERENCE[b]
					RUN	BETWEEN LABS	INTER-LAB. SPREAD	
2	URANIUM	AS / 1.3	28 (16)	4 -	0.20 (0.13)	0.46 (0.26)	0.47 (0.27)	67-3 -
3		BS / 1.2	30 (16)	17 -	0.18 (0.18)	0.52 (0.31)	0.53 (0.33)	70 -
4		RS / 2.2	28 (16)	14 -	0.18 (0.14)	0.32 (0.33)	0.34 (0.34)	72 -
5	PU-239	AS / 1.3	27 (16)	0 -	0.40 (0.36)	0.48 (0.34)	0.53 (0.40)	74-3 -
6		BS / 1.2	29 (16)	21 -	0.31 (0.17)	0.24 (0.25)	0.30 (0.27)	80 -
7		RS / 2.2	27 (16)	11 -	0.36 (0.17)	0.31 (0.28)	0.37 (0.30)	84 -

[a] VALUES IN BRACKETS ARE BASED ON THE FOLLOWING 16 LABORATORIES ('MORE EXPERIENCED' ONES UNDERLINED): 1,2,3,4,6,7,8,10,12,15,16,19,20,21,23,30

[b] INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

pages 49 and 50). The estimates calculated for the maximum common laboratory group, which performed measurements in all programme parts concerned without producing extreme values are given in brackets.

Observations:

a) The values calculated for the estimates of the uncertainty component 'RUN' is somewhat higher for plutonium than for uranium (Tabs. XXI and XXII). Only subgroup II shows this effect also for the uncertainty component 'BETWEEN-LABs' (Tab. XXII, column 5).

b) According to the considerations made above (Par. i and ii), smaller 'RUN' and higher 'BETWEEN-LAB' RSD values might be expected for the double determinations (Tab. XXI, lines 4 and 5) than for those of all three samples (lines 2 and 3). This is not confirmed[1], indicating that the spiking procedure does not contribute significantly to the uncertainties of analyses.

c) Considerable discrepancies are observed in the values calculated for the estimates of uncertainty components for the three subgroups. There is no clear relationship to the percentage of 'more experienced' laboratories in the subgroups (Tab. XXII and Tab. XX, column 5).

d) The median values of the concentration determinations of uranium do show in all cases a negative deviation relative to the agreed certified value (Tab. XXI, column 8 and Tab. XXII column 9) exceeding its uncertainty range of ± 0.07 % by approximately 0.1 %[2] (only exception: Tab. XXII, line 15).

e) The median values for plutonium show positive deviations from the agreed certified value (exceptions: Tab. XXI, line 7 and Tab. XXII, line 18), exceeding in a few cases its uncertainty range of ± 0.3 %, by maximum 0.17 % (Tab. XXII, line 13).

f) Although systematic components of the deviations of the median values from the agreed certified values cannot be excluded (according to the observations made before) it should be noted that the differences of the medians obtained by the three subgroups with the same sample material ASI (Tab. XXII, lines 14 to 19) show variations of the same size as if samples of different spiking procedures are analyzed (Tab. XXII, lines 8 to 13).

g) The percentage of data excluded as extreme values is considerably smaller for the U-235/Pu-242 metal-spiked samples AS than for the U-233/Pu-242

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[1] The reverse effect of slightly increasing values with decreasing number of run values (see in particular the interlab spread columns 5 and 9 of Tab. XXI) can be explained by statistics only.

[2] Please refer in this context to Chapt. 7.5.

solution spiked samples BS and RS (Tab. XXIII, column 4). The estimates of uncertainty components for uranium are of the same size - for the same laboratory group even smaller. For plutonium they are somewhat higher (see Tab. XXIII, columns 5 to 7).

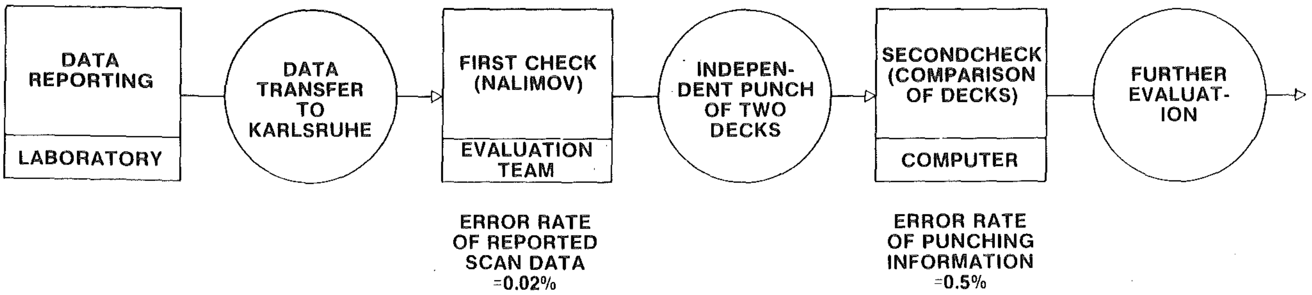
7. Special subjects

7.1 Errors of data transfer

Fig. 29 displays the procedure of data transfer from the participating laboratory to the storage media of the KfK Central Computer System. The laboratories were asked to complete forms (Fig. 3, page 17) giving especially the measured scan data (8 scan data per isotope ratio, each consisting on the average of 7 digits). The evaluation team transfered the data (written on these forms) onto punched cards; then in addition this punched data was stored on disc.

Out of 60,000 pieces of information received, 86% were isotope ratios and 14% 'general' data such as sample numbers and dates. The first category of information was checked applying the Nalimov outlier test /13/ to each group of the 8 scan data. In this way, gross errors during data transfer could be detected. This test revealed an error rate of 0.02 %. The second class of 'general' data was tested visually and revealed a much higher error rate, namely 0.9% or 0.13% of the total amount of data. This implies a total error rate of 0.15% induced by the participants during generation and transfer of the data from the laboratories to the evaluation site.

As shown in Fig. 29 a further possible error source stemming from the data punching was eliminated by punching the same data twofold by different persons. A comparison of these two 'identical' data sets revealed an error rate of 0.5% per piece of information or 0.07% of punched digits assuming on average 7 digits per information.



IDA-80/Fig. 29: Data transcription

7.2 Pu-241 reference date

In order to avoid the interference of the Pu-241 measurements by Am-241 ions, the time interval between chemical Pu/Am separation of the sample and its mass spectrometric measurement should not exceed a few days. According to the information reported by the participants (see Tab. XXIV), it is obviously difficult for many laboratories to meet this requirement in practice. In addition the question arises whether the date of chemical sample preparation or the date of mass spectrometric measurement is the more suitable one as reference for the analytical result.

The data given in this report are based on the dates of mass spectrometric measurements. The basis of this approach is the observation that during the first minutes of (pre-)heating a sample on a filament, traces of more volatile elements (such as americium) are preferentially eliminated. Hence, they do not interfere with the actual measurement. To test the validity of taking the date of measurement rather than the date of Pu/Am separation, the laboratory means of the Pu-241/Pu-239 ratios were calculated in both cases for the unspiked and prespiked samples of solutions B and R and corrected to the reference date of this programme1). The comparative results are compiled in Tab. XXV.

Observation:

The desirability of using the date of the mass spectrometric measurement is confirmed: Using the date of the Pu/Am separation increases the deviation of the laboratory mean value from the agreed certified value ('impairment') more frequently than that it is decreased ('improvement').

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1) February 9, 1980

IDA-80/TAB. XXIV: REPORTED TIME INTERVALS BETWEEN AMERICIUM SEPARATION AND MS-MEASUREMENT OF PLUTONIUM (DAYS)

1	2	3	4	5	6	7	8	9	10	11	12	13
SAMPLE	BU			BS			RU			RS		
LAB CODE	RUN			RUN			RUN			RUN		
	1	2	3	1	2	3	1	2	3	1	2	3
1	2	2	5	4	6	5	5	5	6	4	5	5
2	11	12	13	5	6	8	6	7	8	7	8	11
3	6	11	11	8	8	41	12	13	13	3	3	4
4	17	17	17	4	4	4	7	9	9	2	2	2
5	4	4	4	6	41	6	13	13	14	9	10	10
6	7	7	23	18	21	18	11	11	11	9	9	9
7	70	70	106	112	112	118	99	105	105	118	119	119
8	0	0	1	1	1	2	5	5	5	2	2	2
9	6	7	7	4	4	7	-	-	-	-	-	-
10	5	5	6	6	5	5	13	14	14	12	12	12
11	29	52	58	70	36	37	123	123	150	196	197	184
12	7	7	7	5	5	5	10	10	10	6	6	6
13	26	26	26	28	28	28	26	27	27	29	29	29
14	10	12	12	14	14	18	11	13	13	78	73	73
15	20	39	39	26	26	26	14	32	33	20	17	14
16	7	7	7	7	7	7	3	3	3	8	8	8
17	10	10	7	2	3	3	3	7	8	4	5	5
18	30	30	33	12	14	15	85	86	86	114	120	120
19	114	114	115	33	34	33	106	107	107	109	109	110
20	7	8	9	29	30	30	70	71	71	82	83	83
21	7	7	7	3	3	3	1	1	1	1	1	1
22	21	21	21	5	14	5	21	21	21	28	28	28
23	17	18	19	17	17	10	4	5	5	6	7	7
24	15	15	17	49	48	79	31	29	28	27	22	35
25	7	8	8	4	8	6	14	15	15	6	7	5
26	4	4	22	36	36	40	14	14	14	40	29	42
27	49	49	49	77	77	77	-	-	-	-	-	-
28	-	-	-	-	-	-	-	-	-	-	-	-
29	3	3	3	1	3	2	-	-	-	-	-	-
30	5	5	5	1	1	1	0	0	1	0	1	1
31	-	-	-	-	-	-	5	6	6	5	3	2

IDA-80/TAB. XXV: Pu-241/Pu-239 ISOTOPE RATIOS: DECAY CORRECTIONS BASED ON THE DATE OF AM-SEPARATION COMPARED TO THOSE BASED ON THE DATE OF MASS SPECTROMETRIC MEASUREMENTS[a]

	1	2	3	4	5
1	SAMPLE	IMPAIRMENTS		IMPROVEMENTS	
		WITH RESPECT TO THE AGREED CERTIFIED VALUES			
		NUMBER OF LABS	CODE NUMBERS	NUMBER OF LABS	CODE NUMBERS
2	BU	8 (3)	2, 4, 11, 13, 14, 15, 22, 27 (11, 15, 27)	3 (2)	7, 18, 19 (7, 19)
3	BS	8 (3)	5, 7, 13, 18, 19, 20, 24, 27 (7, 24, 27)	4 (1)	6, 11, 15, 26 (11)
4	RU	9 (5)	11, 14, 15, 18 19,20,21,24,26 (11,18,19,20,21)	4 (1)	1, 5, 6, 7 (7)
5	RS	6 (4)	7, 11, 15, 18, 19, 24 (7, 11, 18, 19)	3 (1)	13, 14, 26 (26)

a) VALUES IN BRACKETS RELATE TO CHANGES EXCEEDING 0.5 % OF THE VALUE

7.3 Discrepancies between reported values and those calculated by the evaluation team ('Δ-Values').

The participants had been asked to report not only the measured scan values of isotope ratios, but also the isotope abundances and the element concentrations of uranium and plutonium in the BU and RU samples in parts 1.11 and 2.1.
A comparison with the results of the evaluation team derived from the reported scan values of the isotope ratios was intended to check to which degree in practical safeguards discrepancies of results may be caused by the use of different values for atomic masses, half-lives etc.

The relative deviations of the evaluation team data from those reported[1] were called 'Δ-values'. According to this definition, a positive deviation indicates that the evaluation team obtained a higher value than the laboratory.

The data are compiled in Tab. XXVI for uranium and in Tab. XXVII for plutonium[2]. Some statistical evaluation with respect to their signs and sizes is given in Tab. XXVIII for both elements, uranium and plutonium. Furthermore, in Tabs. XXIX and XXX, the estimates of the interlaboratory spreads and the median values of the reported data and those of the results calculated by the evaluation team are compared.

Observations:

a) From the total of 284 cases considered for uranium (Tab. XXVI), 25% of the discrepancies are zero (within the precision of data treatment), 42% have a positive and 33% a negative sign. The great number of zero-values for the U-238 abundances are due to the nearly mono-isotopic composition of the uranium materials. However, there seems to be no evident reasoning for the preponderance of positive values for the other isotope abundances as well as the element concentrations (see Tab. XXVIII, lines 2 and 3). In this context it is interesting to note that in most cases the interlaboratory spreads estimated from the data calculated by the evaluation team are equal or smaller than those derived from the reported data (Tab. XXIX, columns 3, 4, 6 and 7). Also the medians of the evaluation team data are equal or closer to the agreed certified values than those of the reported values in nearly all cases (see Tab. XXX, lines 4 and 5). For the grand means, this is not the case (see Tab. XXX, lines 6 and 7).

b) From the total of 328 cases considered for plutonium (Tab. XXVII), 12% of the discrepancies are zero (within the precision of data treatment), 47% have a positive and 41% a negative sign. As to be expected, zero-values are mostly observed for abundant isotopes, but it is interesting to note that for these abundant isotopes negative deviations are observed much

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[1] For this consideration, the 'redeclared' reported values were used (see Chapt. 4).

[2] The 'Δ-values' are displayed graphically on the corresponding evaluation sheets in Vol. III /10/.

IDA-80/TAB. XXVI: RELATIVE DEVIATIONS Δ (%) BETWEEN URANIUM VALUES CALCULATED BY THE EVALUATION TEAM AND THOSE REPORTED BY LABORATORIES

1	2	3	4	5	6	7	8	9	10	11
	ISOTOPE ABUNDANCE								CONCENTRATION ∼2MGU/G SOL.	
SAMPLE	BU				RU				BU	RU
LAB. CODE	<0.01% U-234	0.6% U-235	0.2% U-236	99.2% U-238	<0.01% U-234	1.2% U-235	<0.01% U-236	98.8% U-238	U - ELEMENT	
1	0.58	-0.09	0.05	0.0	-0.31	-0.06	-0.05	0.0	0.0	0.02
2	-0.45	-0.01	-0.20	0.0	-0.46	0.09	-0.43	0.0	-0.03	0.04
3	0.32	-0.02	0.0	0.0	-0.19	0.0	-0.32	0.0	0.02	0.02
4	-0.80	0.07	-0.05	0.0	2.13	0.0	0.31	0.0	0.06	0.0
5	-0.12	0.02	0.05	0.0	0.57	0.02	0.30	0.0	0.01	0.01
6	4.82	0.09	0.23	0.0	0.13	0.04	3.40	0.0	0.03	0.03
7	0.04	0.18	-0.12	0.0	0.56	-0.03	0.80	0.0	-0.08	-0.04
8	-3.52	0.02	0.34	0.0	-3.44	-0.05	-5.47	0.0	-0.06	0.25
9	1.36	0.06	-0.05	0.0	-	-	-	-	0.0	-
10	2.80	0.04	0.15	0.0	-2.82	-0.01	-5.78	0.0	0.01	0.02
11	-2.45	-0.21	-0.70	0.0	1.20	0.01	3.54	0.0	-0.14	-0.15
12	-0.56	-0.06	0.05	0.0	6.96	-0.02	2.77	0.0	0.05	0.59
13	1.35	0.26	-0.21	0.0	2.39	0.18	4.29	0.0	-0.09	10.25
14	-0.67	-0.01	0.04	0.0	-0.06	0.11	-0.45	0.0	0.48	0.04
15	-2.42	0.07	-0.20	0.0	-0.43	0.0	7.29	0.0	0.03	0.05
16	-1.39	0.01	-0.03	0.0	0.98	0.0	-1.66	0.0	0.0	0.0
17	20.99	-0.52	-0.03	0.01	0.0	0.05	-	-0.12	0.07	-6.01
18	0.0	0.04	-0.19	0.01	-	-0.10	-	0.0	-2.06	-2.31
19	0.19	0.03	0.30	0.0	-0.66	0.08	4.55	0.0	-0.02	0.07
20	0.60	0.04	-0.03	0.0	-0.02	0.09	-0.58	0.0	-0.08	0.05
21	-0.66	-0.10	-0.23	0.0	0.67	-0.01	1.24	0.0	0.0	0.0
22	-3.62	0.02	-0.10	0.0	-4.98	0.04	-7.96	0.0	-0.08	0.11
23	-2.05	-0.12	0.40	0.0	-2.29	0.04	-1.90	0.0	0.02	0.38
24	1.01	0.0	0.11	0.0	0.29	-0.25	-0.30	0.0	0.27	-0.23
25	13.29	-0.27	0.46	0.0	10.08	0.06	9.93	0.0	0.01	-0.04
26	0.19	-0.01	-0.07	0.0	-0.71	-0.01	0.29	0.0	0.03	-0.04
27	-0.20	-0.04	0.29	0.0	-	-	-	-	0.74	-
28	-	-12.56	-13.25	0.12	-	0.31	-	0.0	1.41	49.62
29	0.55	0.02	-0.05	0.0	-	-	-	-	-0.01	-
30	0.73	-0.01	0.05	0.0	0.11	0.01	0.94	0.0	0.02	0.02
31	-	-	-	-	0.45	-0.02	-0.61	0.0	-	0.0
REFERENCE[a]	45	46	47	48	49	50	51	52	68	71

a) INDICATES EVALUATION SHEET NUMBER IN VOL.III /10/

IDA-80/TAB. XXVII: RELATIVE DEVIATIONS Δ (%) BETWEEN PLUTONIUM VALUES CALCULATED BY THE EVALUATION TEAM AND THOSE REPORTED BY LABORATORIES

1	2	3	4	5	6	7	8	9	10	11	12	13
	ISOTOPE ABUNDANCE										CONCENTRATION ~8μGPU/G SOL.	
SAMPLE	BU					RU					BU	RU
LAB. CODE	0,2% PU-238	69,1% PU-239	25,7% PU-240	3,3% PU-241	1,7% PU-242	0,1% PU-238	76,7% PU-239	19,9% PU-240	2,7% PU-241	0,6% PU-242	PU - ELEMENT	
1	0,60	-0,10	-0,13	3,23	-0,08	0,96	-0,09	-0,13	3,43	-0,01	0,13	0,10
2	-0,13	0,01	-0,04	0,06	0,0	0,13	0,0	0,0	0,07	0,0	0,11	0,18
3	0,68	0,0	-0,01	0,14	0,0	0,09	0,0	-0,01	0,0	0,10	0,11	0,24
4	3.17	0,0	-0,02	-0,06	0,08	2.91	0,0	-0,01	0,12	-0,10	3,65	0,0
5	0,32	0,0	-0,04	0,15	0,14	0.85	0,01	-0,07	-0,01	0,31	0,0	0,03
6	2,98	-0,01	-0,02	0,15	-0,17	4,73	0,0	-0,01	0,08	-0,02	0,19	0,21
7	1.48	-0,01	0,01	-0,02	0,05	-0,57	-0,01	0,02	0,22	0,10	0,17	-0,01
8	-	0,0	-0,01	0,10	-0,01	-	-0,01	0,01	0,15	-0,04	9,69	3,57
9	-0,21	-0,01	0,01	0,12	-0,03	-	-	-	-	-	0,04	-
10	0,39	0,01	0,01	-0,12	-0,24	13,04	-0,02	-0,02	0,10	0,03	0,32	-0,17
11	2,87	0,01	-0,11	0,38	0,21	68,47	-0,07	-0,05	0,38	2,07	-0,64	-0,05
12	-0,24	0,02	-0,04	-0,08	-0,15	0,01	0,0	0,0	-0,03	0,0	0,01	0,03
13	7,64	-0,22	-0,24	6,36	0,57	-0,34	-0,17	-0,13	6,25	-0,21	0,35	-10,03
14	1,27	-0,02	0,03	-0,02	0,16	-0,23	0,0	0,01	-0,13	-0,05	0,13	0,03
15	1,40	-0,22	-0,21	6,73	-0,25	1,62	-0,18	-0,19	6,78	-0,25	0,24	0.22
16	2,88	0,0	-0,01	-0,01	0,07	2,87	0,0	-0,01	-0,03	0,01	0,0	-0,01
17	-	-0,25	-0,28	8,28	-0,44	-	-0,22	-0,30	8,94	0,08	0,21	-4,20
18	0,08	0,02	-0,06	0,15	-0,21	0,87	-0,24	-0,19	8,88	-0,44	1,02	1,07
19	-0,02	-0,01	0,01	0,06	-0,04	0,21	0,0	0,0	0,11	-0,08	0,12	0,11
20	-1,55	-0,01	0,0	0,23	-0,10	-0,64	0,0	0,0	-0,05	0,02	0,06	0,28
21	-	0,0	0,0	0,04	-0,05	-	-0,01	0,0	0,14	0,17	0,0	-
22	-58,48	-0,07	-0,09	6,09	0,16	-52,14	-0,12	-0,10	6,05	0,52	0,22	0,26
23	0,94	0,0	-0,01	0,08	0,02	1,49	0,0	-0,03	0,03	0,08	0,02	-0,02
24	5,06	-0,07	0,14	0,44	-0,20	3,27	-0,02	0,0	0,61	-0,05	0,18	0,07
25	-0,80	-0,06	-0,07	1.82	-0,09	-0,49	0,01	-0,01	-0,06	0,02	-0,01	-1,57
26	0,71	0,06	0,05	0,63	-4,61	0,39	-0,02	-0,01	0,61	0.16	-0,21	0,02
27	0,94	-0,16	-0,20	5,20	-0,28	-	-	-	-	-	-	-
28	-	-	-	-	-	-	-	-	-	-	-	-
29	-0,05	-0,01	0,0	0,17	-0,06	-	-	-	-	-	0,0	-
30	0,0	0,01	-0,01	-0,06	-0,02	0,0	0,01	-0,02	-0,06	0,03	-0,18	-0,56
31	-	-	-	-	-	1,70	-0,01	-0,01	0,23	0,04	-	0,02
REFERENCE[a]	53	56	57	58	59	60	63	64	65	66	77	83

[a] INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

IDA-80/TAB. XXVIII: STATISTICAL EVALUATION OF DISCREPANCIES (%) BETWEEN VALUES CALCULATED BY THE EVALUATION TEAM AND THOSE REPORTED BY PARTICIPANTS ('Δ-VALUES')

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	ELE-MENT	SIGN OR RANGE (%) OF Δ	ISOTOPE ABUNDANCE SAMPLE BU					ISOTOPE ABUNDANCE SAMPLE RU					CONCENTRATION ∿2MG U/G SOL.	
			<0.01% 234	0.6% 235	0.2% 236	99.2% 238		<0.01% 234	1.2% 235	<0.01% 236	98.8% 238		BU	RU
2	URANIUM	PLUS	52	50	54	10		50	50	52	0		54	61
3		MINUS	45	47	43	0		46	36	48	4		33	25
4		ZERO	3	3	3	90		4	14	0	96		13	14
5		$\lvert\Delta\rvert \le 0.1$	7	74	43	97		11	86	4	96		84	65
6		$0.1<\lvert\Delta\rvert\le 1.0$	48	23	54	3		54	14	44	4		13	21
7		$\lvert\Delta\rvert > 1.0$	45	3	3	0		35	0	52	0		3	14
8	PLUTONIUM		0.2% 238	69.1% 239	25.7% 240	3.3% 241	1.7% 242	0.1% 238	76.7% 239	19.9% 240	2.7% 241	0.6% 242	∿8µG PU/G SOL.	
9		PLUS	65	24	24	76	31	71	11	11	70	56	72	61
10		MINUS	31	52	66	24	62	25	52	67	26	37	14	35
11		ZERO	4	24	10	0	7	4	37	22	4	7	14	4
12		$\lvert\Delta\rvert \le 0.1$	15	86	76	38	52	12	81	81	41	70	32	46
13		$0.1<\lvert\Delta\rvert\le 1.0$	43	14	24	38	45	46	19	19	37	26	57	35
14		$\lvert\Delta\rvert > 1.0$	42	0	0	24	3	42	0	0	22	4	11	19

[a]) STATISTICAL DATA ARE GIVEN IN PERCENT

more frequently than positive ones (see Tab. XXVIII, lines 9 and 10). As for uranium, the interlaboratory spreads estimated from the data calculated by the evaluation team are equal or smaller than those derived from the reported data (see Tab. XXIX, columns 3, 4, 6 and 7). The medians as well as the grand means of the evaluation team data deviate from the agreed certified values less than those of the reported data in about two thirds of the cases (Tab. XXX, lines 11 to 14).

c) The high percentages of positive Δ-values (Tab. XXVIII, line 9) for Pu-238 and Pu-241 as well as their high absolute values (lines 13 and 14) signalize insufficient decay corrections of reported data. For an indication of Pu-238, uncertainties in deriving Pu-238/Pu-239 isotope ratios from Pu-238/(Pu-239+Pu-240) alpha-activity ratios may be another explanation.

d) Discrepancies Δ below ±0.1 % (Tab. XXVIII, lines 5 and 12) may be explained mainly by differences in data treatment such as rounding off etc. Because of the interdependence of abundance values (due to their normalization to 100%), that explanation might also be valid for higher discrepancies where isotope abundances lie below 0.1%.

IDA-80/TAB. XXIX: ESTIMATES OF INTERLABORATORY SPREAD OF RESULTS AS REPORTED BY PARTICIPANTS AND AS CALCULATED BY THE EVALUATION TEAM

	1	2	3	4	5	6	7	8
1			SOLUTION B			SOLUTION R		
2			INTERLAB. SPREAD (%) BASED ON VALUES		REFERENCE^{a}	INTERLAB. SPREAD (%) BASED ON VALUES		REFERENCE^{a}
			REPORTED BY LABS	CALCULATED BY EV.TEAM		REPORTED BY LABS	CALCULATED BY EV.TEAM	
3	U-ELEMENT CONCENTR.		0.82	0.74	68	0.39	0.46	71
4	ABUNDANCE (WT.%)	U-234	4.50	4.01	45	6.49	6.08	49
5		U-235	0.33	0.33	46	0.50	0.51	50
6		U-236	2.14	2.26	47	8.25	7.42	51
7		U-238	0.032	0.015	48	0.007	0.007	52
8	PU-ELEMENT CONCENTR.		0.96	0.84	77	0.93	1.25	83
9	ABUNDANCE (WT.%)	PU-238	6.87	7.01	53	10.61	6.21	60
10		PU-239	0.18	0.13	56	0.15	0.09	63
11		PU-240	0.14	0.14	57	0.13	0.14	64
12		PU-241	2.75	0.56	58	2.98	0.62	65
13		PU-242	1.23	1.17	59	1.40	1.26	66

a) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

e) Discrepancies greater than 1 % (Tab. XXVIII, lines 7 and 14) in the determination of uranium isotope abundances above 0.1 % and concentration determinations of both uranium and plutonium could be identified in many cases as errors of data reporting, writing errors or interchange of information.

f) The fraction of Δ-values between 0.1 % and 1 % (Tab. XXVIII, lines 6 and 13) seems to be rather high and effects nearly all laboratories[1]. Possible explanations are e. g. the use of different basic data sets (e.g. more than 6 scan values) by the participants, too much rounding off in atomic mass values (for concentrations), application of different half-live values for plutonium isotopes and data transmission errors which are too small to be detected in the data checking by the evaluation team (see Chapt. 7.1).

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[1] 19 % for uranium and 30 % for plutonium if isotopes with abundances below 0.1 % as well as Pu-238 and Pu-241 are not taken into consideration. 26 out of the 31 laboratories (84 %) are concerned by at least one such Δ-value.

IDA-80/TAB. XXX: RELATIVE DEVIATIONS (%) OF MEDIANS AND GRAND MEANS FROM AGREED CERTIFIED VALUES FOR REPORTED DATA AND AS CALCULATED BY THE EVALUATION TEAM[a]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1			ISOTOPE ABUNDANCE - SAMPLE BU					ISOTOPE ABUNDANCE - SAMPLE RU					CONCENTRATION ≈2MG U/G SOL.	
2	URANIUM		<0.01% U-234	0.6% U-235	0.2% U-236	99.2% U-238		<0.01% U-234	1.2% U-235	<0.01% U-236	98.8% U-238		BU	RU
3	UNCERTAINTY RANGE[b] OF CERTIFIED VALUE		±1.1	±0.071	±0.79	±0.0015		±1.1	±0.091	±1.5	±0.0011		±0.093	±0.099
4	DEVIATION FROM CERTIF. VALUE[b] MEDIAN	EVAL.TEAM	+1.15	+0.20	+0.34	-0.0024		±0.00	-0.03	±0.00	±0.0000		-0.005	+0.006
5		REPORTED	+1.72	+0.20	+0.39	-0.0024		+0.56	-0.02	+1.49	±0.0000		-0.05	-0.02
6	GRAND MEAN	EVAL.TEAM	+2.99	+0.17	+0.23	-0.0044		-1.35	-0.06	+0.60	-0.0004		+0.02	+0.006
7		REPORTED	+3.33	+0.16	+0.21	-0.0087		-1.12	-0.06	+0.30	-0.0001		-0.02	-0.05
8		REFERENCE[c]	45	46	47	48		49	50	51	52		68	71
9	PLUTONIUM		0.2% PU-238	69.1% PU-239	25.7% PU-240	3.3% PU-241	1.7% PU-242	0.1% PU-238	76.7% PU-239	19.9% PU-240	2.7% PU-241	0.6% PU-242	≈8μG PU/G SOL.	
10	UNCERTAINTY RANGE[b] OF CERTIFIED VALUE		±0.82	±0.037	±0.079	±0.16	±0.25	±2.4	±0.021	±0.067	±0.33	±0.20	±0.25	±0.24
11	DEVIATION FROM CERTIF. VALUE[b] MEDIAN	EVAL.TEAM	-0.29	+0.02	-0.03	+0.01	-0.19	+2.08	±0.00	+0.01	+0.16	+0.03	-0.08	+0.05
12		REPORTED	-0.39	+0.03	+0.01	-0.07	-0.16	+0.95	-0.01	+0.04	+0.07	+0.12	-0.10	+0.13
13	GRAND MEAN	EVAL.TEAM	-1.49	+0.05	-0.02	+0.12	-0.02	+1.01	+0.01	±0.00	+0.08	+0.09	-0.15	+0.13
14		REPORTED	-2.33	+0.09	+0.02	-1.18	0.02	-2.40	+0.05	+0.05	-1.40	-0.01	-0.38	-0.04
15		REFERENCE[c]	53	56	57	58	59	60	63	64	65	66	77	83

a) ALL DATE ARE GIVEN IN PERCENT

b) SEE TAB IV AND VOL.II /9/

c) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

7.4 Statistics on extreme values

The calculated laboratory means of isotope ratios, abundances and element concentrations as well as their standard deviations were checked for extreme values applying statistical criteria (see Chapt. 2.4).

Statistical data are compiled in Tab. XXXI in order to study the frequency of such outlier observations as a function of the experience of the measurement laboratories. The group of 17 'more experienced' laboratories which claimed to have performed this kind of analysis frequently or even continuously for more than five years and the second group of the remaining 14 'less experienced' laboratories were considered separately. The statistics apply to all laboratory mean values of determinations of isotope ratios, abundances and element concentrations evaluated in this programme except the isotope ratio data of the AS-samples[1].

Observations:

a) For uranium, 4.6 % and 21.5 % extreme values were observed in this programme with the measurements of 47.1 % of the 'more experienced' and 78.6 % of the 'less experienced' laboratories (Tab. XXXI, columns 5 and 8, lines 12 and 13). This means a total of about 12 % outlier values for uranium observed in the results of about 60 % of the participating laboratories (Tab. XXXI, columns 5 and 8, line 14).

b) For plutonium 6.9 % and 10.6 % extreme values were observed in this programme with the measurements of 52.9 % of the 'more experienced' and 69.2 % of the less experienced laboratories (Tab. XXXI, columns 5 and 8, lines 25 and 26). This means a total of about 9 % outlier values

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[1] Because of the different structure of that programme part (see Chapt. 5.2).

IDA-80/TAB. XXXI: NUMBERS OF EXTREME VALUES REPORTED RELATIVE TO LABORATORY EXPERIENCE

	1	2	3	4	5	6	7	8
1	DETERMINATION	EXPERIENCE OF LABS	NUMBER OF CONTRIBUTING LABS	EXTREME VALUES REPORTING LABS		NUMBER OF CONTRIBUTED LAB MEANS	EXTREME VALUES EXCLUDED	
				NUMBER	(%)		NUMBER	(%)
2			URANIUM					
3	ISOTOPE RATIO[a]	'MORE'	17	7	41.2	260	13	5.0
4		'LESS'	14	8	57.1	201	44	21.9
5		Σ	31	15	48.4	461	57	12.4
6	ISOTOPE ABUNDANCE	'MORE'	17	5	29.4	128	5	3.9
7		'LESS'	14	5	35.7	98	20	20.4
8		Σ	31	10	32.3	226	25	11.1
9	ELEMENT CONCENTRATION	'MORE'	17	3	17.6	108	5	4.6
10		'LESS'	14	8	57.1	91	20	22.0
11		Σ	31	11	35.5	199	25	12.6
12	TOTAL	'MORE'	17	8	47.1	496	23	4.6
13		'LESS'	14	11	78.6	390	84	21.5
14		Σ	31	19	61.3	886	107	12.1
15	PLUTONIUM							
16	ISOTOPE RATIO[a]	'MORE'	17	8	47.1	258	16	6.2
17		'LESS'	13	8	61.5	202	25	12.4
18		Σ	30	16	50.0	460	41	8.9
19	ISOTOPE ABUNDANCE	'MORE'	17	7	41.2	156	10	6.4
20		'LESS'	13	3	23.1	118	8	6.8
21		Σ	30	10	33.3	274	18	6.6
22	ELEMENT CONCENTRATION	'MORE'	17	4	23.5	106	10	9.4
23		'LESS'	13	6	46.2	84	10	11.9
24		Σ	30	10	33.3	190	20	10.5
25	TOTAL	'MORE'	17	9	52.9	520	36	6.9
26		'LESS	13	9	69.2	404	43	10.6
27		Σ	30	18	60.0	924	79	8.6

a) AS-SAMPLES ARE NOT TAKEN INTO CONSIDERATION for plutonium observed in the results of about 60 % of the participating laboratories (Tab. XXXI, columns 5 and 8, line 27).

c) If no distinction is made between uranium and plutonium determinations, the percentage of extreme values observed in the programme (according to the applied criteria) amounts to 10.3 %, produced by 71 % of the participants. (About 32 % of the extreme values were produced by 11 of the 17 'more experienced' laboratories, about 68 % by 11 of the 14 'less experienced' ones).

7.5 Comparison of medians with agreed certified values

A summarizing survey on the deviations of the median values of laboratory means (calculated by the evaluation team) for isotope ratios, abundances and element concentrations from the agreed certified values is presented in Tab. XXXII for uranium and Tab. XXXIII for plutonium. In addition to the relative deviations of the data, the excess of the deviations of the medians over the stated uncertainty ranges of the agreed certified values is given.

Observations:

a) In about 56 % of the uranium cases considered, the medians are within the uncertainty ranges of the agreed certified values (Tab. XXXII, column 8).

b) Almost without exception, the medians of isotope ratio and abundance determinations of uranium are greater and the medians of concentration determinations smaller than the certified values. This indicates, for some reason, a tendency to determine the U-238 isotope too low (Tab. XXXII, column 7).

IDA-80/TAB. XXXII: MEDIANS COMPARED TO AGREED CERTIFIED VALUES FOR URANIUM

1	2	3	4	5	6	7	8
DETERMI-NATION	DESCRIP-TION	CERTIFIED VALUE[a]	$3\bar{s}$-UNCERTAINTY RANGE[a]	$3\bar{s}$-UNCERTAIN-TY RANGE[a] (%)	MEDIAN[b]	DEV. (%) FROM CERTIFIED VALUE[c]	EXCESS OF $3\bar{s}$ UNCER-TAINTY RANGE (%)[c,d]
ISOTOPE RATIO	ASI 58	0.92759	±0.00024	±0.026	0.92826	+0.07	+0.04
	ASII 58	0.90039	±0.00044	±0.049	0.90223	+0.20	+0.15
	ASIV 58	0.91032	±0.00043	±0.047	0.91198	+0.18	+0.13
	ASVI 58	0.91626	±0.00034	±0.037	0.91810	+0.20	+0.16
	BU 48	0.000089	±0.000001	±1.1	0.000090	+1.12	0.02
	BU 58	0.005748	±0.000005	±0.087	0.005758	+0.17	+0.08
	BU 68	0.001812	±0.000013	±0.72	0.001818	+0.33	0.00
	BS 38	0.85242	±0.00057	±0.067	0.8533	+0.10	+0.03
	BS 48	0.002107	±0.000022	±1.0	0.0021105	+0.17	0.00
	BS 58	0.005854	±0.000007	±0.12	0.005861	+0.12	0.00
	BS 68	0.001811	±0.000014	±0.77	0.001813	+0.11	0.00
	RU 48	0.000092	±0.000001	±1.1	0.000092	0.00	0.00
	RU 58	0.012353	±0.000011	±0.089	0.012351	-0.02	0.00
	RU 68	0.000068	±0.000001	±1.5	0.0000685	+0.74	0.00
	RS 38	1.05590	±0.00089	±0.084	1.05909	+0.30	+0.22
	RS 48	0.002594	±0.000027	±1.0	0.0025975	+0.13	0.00
	RS 58	0.012481	±0.000013	±0.10	0.012488	+0.06	0.00
	RS 68	0.000068	±0.000001	±1.5	0.000068	0.00	0.00
	SUP 43	0.002368	±0.000024	±1.0	0.002373	+0.21	0.00
	SUP 53	0.000127	±0.000007	±5.5	0.000127	0.00	0.00
	SUP 83	0.000496	±0.000012	±2.4	0.000512	+3.23	+0.83
	DIMENSION	WEIGHT-%			WEIGHT-%		
ISOTOPE ABUNDANCE	BU						
	U-234	0.0087	±0.0001	±1.1	0.0088	+1.15	+0.05
	U-235	0.5633	±0.0004	±0.071	0.5644	+0.20	+0.13
	U-236	0.1783	±0.0014	±0.79	0.1789	+0.34	0.00
	U-238	99.2497	±0.0015	±0.0015	99.24735	0.00	0.00
	RU						
	U-234	0.0089	±0.0001	±1.1	0.0089	0.00	0.00
	U-235	1.2048	±0.0011	±0.091	1.20445	-0.03	0.00
	U-236	0.0067	±0.0001	±1.5	0.0067	0.00	0.00
	U-238	98.7796	±0.0011	±0.0011	98.7796	0.00	0.00
	DIMENSION	G ELEM./G SOL.			G ELEM./ G SOL.		
CONCENTRATION	AS-1.3	1.6966×10^{-1}	$\pm 0.0012 \times 10^{-1}$	+0.071	1.694×10^{-1}	-0.15	-0.08
	BU-1.11	2.0491×10^{-3}	$\pm 0.0019 \times 10^{-3}$	±0.093	2.049×10^{-3}	0.0	0.00
	BU-1.12				2.046×10^{-3}	-0.15	-0.06
	BS-1.2				2.046×10^{-3}	-0.15	-0.06
	RU-2.1	1.7154×10^{-3}	$\pm 0.0017 \times 10^{-3}$	+0.099	1.7155×10^{-3}	+0.01	0.00
	RS-2.2				1.712×10^{-3}	-0.20	-0.10
	RU-2.3				1.712×10^{-3}	-0.20	-0.10

a) SEE TABS. IV,V AND VOL.II /9/

b) SEE TABS. VIII (RATIOS); XI (ABUNDANCES); XIII AND XIV (CONCENTRATIONS)

c) PRESENTED WITH TWO DECIMALS REGARDLESS OF SIGNIFICANCE

d) VALUES DIFFERENT FROM ZERO REPRESENT THE DEVIATION OF THE DATA GIVEN IN COLUMN 7 FROM THOSE OF COLUMN 5

IDA-80/TAB, XXXIII: MEDIANS COMPARED TO AGREED CERTIFIED VALUES FOR PLUTONIUM

1	2	3	4	5	6	7	8
DETERMI-NATION	DESCRIP-TION	CERTIFIED VALUE[a]	$3\bar{s}$ UNCERTAINTY RANGE[a]	$3\bar{s}$-UNCERTAIN-TY RANGE[a] (%)	MEDIAN[b]	DEV, (%) FROM CERTIFIED VALUE[c]	EXCESS OF $3\bar{s}$ UNCER-TAINTY RANGE (%)[c,d]
ISOTOPE RATIO	ASI 29	1,1022	±0,0010	±0,091	1,09870	-0,32	-0,23
	ASII29	1,0701	±0,0022	±0,21	1,0668	-0,31	-0,10
	ASIV29	1,0771	±0,0014	+0,13	1,0766	-0,05	0,00
	ASVI29	1,0839	±0,0014	±0,13	1,08165	-0,21	-0,08
	BU 89	0,00301	±0,00003	±1,0	0,002998	-0,39	0,00
	BU 09	0,37011	±0,00039	±0,11	0,36981	-0,08	0,00
	BU 19	0,04789	±0,00008	±0,17	0,047905	+0,03	0,00
	BU 29	0,02469	±0,00007	±0,28	0,02463	-0,24	0,00
	BS 09	0,4728	±0,0006	±0,13	0,47246	-0,07	0,00
	BS 19	0,07420	±0,00014	±0,19	0,07416	-0,05	0,00
	BS 29	1,0854	±0,0013	±0,12	1,0826	-0,26	-0,14
	RU 89	0,00151	±0,00004	±2,6	0,001545	+2,32	0,00
	RU 09	0,25841	±0,00022	±0,085	0,25851	+0,04	0,00
	RU 19	0,03550	±0,00012	±0,34	0,035555	+0,15	0,00
	RU 29	0,00767	±0,00002	±0,26	0,007665	-0,07	0,00
	RS 09	0,34484	±0,00041	±0,12	0,34521	+0,11	0,00
	RS 19	0,05761	±0,00016	±0,28	0,05780	+0,33	+0,05
	RS 29	0,8979	±0,0010	+0,11	0,8974	-0,06	0,00
	SUP 92	0,00298	±0,00003	±1,0	0,29775	-0,08	0,00
	SUP 02	0,09798	±0,00012	±0,12	0,9817	+0,19	+0,07
	SUP 12	0,02497	±0,00003	±0,12	0,02503	+0,24	+0,12
	DIMENSION	WEIGHT-%			WEIGHT-%		
ISOTOPE ABUNDANCE	BU						
	PU-238	0,2070	±0,0017	±0,82	0,2064	-0,29	0,00
	PU-239	69,0631	±0,0254	±0,037	69,0783	+0,02	0,00
	PU-240	25,6681	±0,0203	±0,079	25,6598	-0,03	0,00
	PU-241	3,3352	±0,0053	±0,16	3,3356	+0,01	0,00
	PU-242	1,7266	±0,0044	±0,25	1,7234	-0,19	0,00
	RU						
	PU-238	0,1153	±0,0028	±2,4	0,1177	+2,08	0,00
	PU-239	76,6542	±0,0161	±0,021	76,6515	0,0	0,00
	PU-240	19,8912	±0,0134	±0,067	19,8923	+0,01	0,00
	PU-241	2,7440	±0,0091	±0,33	2,7483	+0,16	0,00
	PU-242	0,5953	±0,0012	±0,20	0,5955	+0,03	0,00
	DIMENSION	G ELEM./G SOL.			G ELEM./ G SOL./		
ELEM.CONC.	AS-1,3	$5,973\mathrm{x}10^{-4}$	$\pm0,018\mathrm{x}10^{-4}$	±0,30	$5,982\mathrm{x}10^{-4}$	+0,15	0,00
	BU-1,11	$7,193\mathrm{x}10^{-6}$	$\pm0,018\mathrm{x}10^{-6}$	±0,25	$7,1875\mathrm{x}10^{-6}$	-0,08	0,00
	BU-1,12				$7,180\mathrm{x}10^{-6}$	-0,18	0,00
	BS-1,2				$7,201\mathrm{x}10^{-6}$	+0,11	0,00
	RU-2,1	$7,982\mathrm{x}10^{-6}$	$\pm0,019\mathrm{x}10^{-6}$	±0,24	$7,986\mathrm{x}10^{-6}$	+0,05	0,00
	RS-2,2				$7,978\mathrm{x}10^{-6}$	-0,05	0,00
	RU-2,3				$7,990\mathrm{x}10^{-6}$	+0,10	0,00
	DIMENSION	ATOMS PU-239/G SOL.			ATOMS PU-239/ G SOL.		
PU-239 CONCENTRATION	AS-1,3	$1,0391\mathrm{x}10^{18}$	$\pm0,0031\mathrm{x}10^{18}$	±0,30	$1,041\mathrm{x}10^{18}$	+0,18	0,00
	BU-1,11	$1,2504\mathrm{x}10^{16}$	$\pm0,0031\mathrm{x}10^{16}$	±0,25	$1,251\mathrm{x}10^{16}$	+0,05	0,00
	BU-1,12				$1,249\mathrm{x}10^{16}$	-0,11	0,00
	BS-1,2				$1,253\mathrm{x}10^{16}$	+0,21	0,00
	RU-2,1	$1,5414\mathrm{x}10^{16}$	$\pm0,0037\mathrm{x}10^{16}$	±0,24	$1,541\mathrm{x}10^{16}$	-0,03	0,00
	RS-2,2				$1,5405\mathrm{x}10^{16}$	-0,06	0,00
	RU-2,3				$1,543\mathrm{x}10^{16}$	+0,10	0,00

FOR FOOTNOTES SEE TAB, XXXII

c) The medians of the uranium concentration determinations are in excellent agreement with the certified values if the laboratories used their own spikes and liquid samples (programme parts 1.11 and 2.1)[1]. In all the other cases, however, a bias of about -0.2 % is observed[2] (Tab. XXXII, column 7).

d) For plutonium, the medians are within the stated uncertainty ranges in about 82 % of the cases considered[3] (Tab. XXXIII, column 8). This percentage is higher than in the case of uranium (Par. a) mainly due to the broader uncertainty ranges given.

e) In contrast to uranium, negative deviations of the medians from the agreed certified values are about as frequent as positive ones for the isotope ratio and abundance determinations of plutonium. The positive deviation of the Pu-238 determination of the RU-sample could be understood assuming U-238 memory effect in the mass spectrometer. However, this assumption is not confirmed by the Pu-238 measurements on the BU-sample (Tab. XXXIII, column 7).

f) The varying deviations of the medians from the agreed certified values for the different concentration determinations of plutonium are difficult to understand (Tab. XXXIII, column 7).

g) Summarizing the uranium and plutonium determinations, it can be stated that in 69 % of the cases considered, the medians are within the uncertainty range of the agreed certified values. They exceed them by more than 0.1 % in about 12 % of the cases.

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[1] As already discussed (Chapt. 6.1) in the case of dried B-samples (programme part. 1.12), there is a bias of about -0.1 % due to lack of air buoyancy corrections apart from possible influence of incomplete redissolution.

[2] One possible reason is discussed in Chapt. 7.6.

[3] Plutonium element and Pu-239 concentration determinations were considered as the same case.

7.6 Use of spike material not calibrated by the user - mass dependent effects

Comparing the medians of uranium concentration determinations with the agreed certified values, a bias of about -0.2 % was observed for the analysis of prespiked samples, whereas excellent agreement was obtained if the laboratories used their own spike solutions (see Chapt. 7.5). This raised the question[1] if there could be a self-compensating error source when the spike is calibrated by the same equipment which is used for sample analysis. Because this effect became more evident for uranium than for plutonium, a mass-dependence effect such as isotope fractionation was considered to be a possible explanation: it would affect the U-233/U-238 isotope ratio of five mass units difference more than the Pu-239/Pu-242 isotope ratio of only three mass units difference[2]. Although isotope fractionation varies in principle from the measurement of one filament to another (i.e. 'from run to run'), it seems justified to assume that it includes a systematic component from the instrument and the routinely applied measurement procedure, i.e. a 'laboratory bias'.

In order to check whether calibration of the SUP-spike solution by the individual participating laboratories would lead to an improvement compared to the application of the calibration data certified by CBNM, the following procedure was used: the analysis of the reference solution R with SUP-spike solution in part 2.3 of the IDA-80 programme (see Chapt. 2.1) was considered as a participant's calibration of the SUP-spike solution using the R-solution with its certified concentration values as common reference material. Using these laboratory specific calibration data of the SUP-spike solution, the concentrations of the prespiked BS and RS samples (programme parts 1.2 and 2.2) were recalculated. If C_{BS}' and C_{RS}' denote these 'corrected' concentration values of the prespiked samples BS and RS and C_{BS} and C_{RS} are

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[1] See Minutes of the Final Meeting, Appendix A

[2] Besides this, the generally greater measurement uncertainties in the case of plutonium will complicate to recognize such an effect.

the values calculated by the evaluation team using the data certified by CBNM for the SUP spike solution, then

$$C'_{BS} = K_S \cdot C_{BS} \text{ and}$$
$$C'_{RS} = K_S \cdot C_{RS}$$

with the 'correction factor' K_S[1] being the ratio of the certified concentration C* of the reference solution R to the value C(2.3) determined by the individual laboratory in part 2.3 of the programme.

These data are compiled in Tabs. XXXIV and XXXV for uranium and the Pu-239 isotope. The deviations Δ of those 'uncorrected' and 'corrected' concentration values of the prespiked samples from the agreed certified values are also listed (columns 6, 7, 11 and 12) as well as the differences of the absolute values of these deviations (columns 8 and 13). Those concentration values which lie within the uncertainty ranges of the certified values are marked by '+'. In Tab. XXXVI, the interlaboratory spreads of the sets of 'corrected' and 'uncorrected' data are presented. They were calculated after the exclusion of extreme values according to the Bartsch criterion /14/. These calculations were additionally made for each pair of 'corrected' and 'uncorrected' data sets for the maximum common laboratory groups[2].

Observations:

a) Application of the K_S-factor changes the concentration values by more than ±0.5 % for 9 laboratories (35 %) in the case of uranium and for 6 laboratories (23 %) in the case of plutonium[3]. For uranium, 74 % of

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[1] The index 'S' refers to the SUP spike solution.

[2] Data rejection because of extreme standard deviations of the laboratory means was not made. For this reason and the somewhat different laboratory groups, the estimates calculated for the laboratory spreads differ from those obtained in the main part of the evaluation which are given on the evaluation sheets in Vol. III /10/.

[3] Laboratory 19 was not taken into consideration. The outlier value in the concentration determination of sample RU in part 2.3 is due to a 'human error' (see Evaluation Sheets 73 and 86, Vol. III /10/) and therefore meaningless for this study.

IDA-80/TAB. XXXIV: INFLUENCE OF LABORATORY OWN CALIBRATION OF SUP-SPIKE SOLUTION ON URANIUM CONCENTRATION DETERMINATIONS

1	2	3	4	5	6	7	8	9	10	11	12	13
LAB. CODE	CONC. (RU/2.3) (MG U / G SOL.) C	'CORR.' FACTOR[a] K_S= C*/C	CONCENTRATION (MGU/G SOL.)[b] C_{BS}	C'_{BS}= $K_S \times C_{BS}$	REL.DEV.(%) FROM CERTIFIED VALUE[c] ΔC_{BS}	$\Delta C'_{BS}$	$\|\Delta C_{BS}\|$ - $\|\Delta C'_{BS}\|$	CONCENTRATION (MGU/G SOL.)[b] C_{RS}	C'_{RS}= $K_S \times C_{RS}$	REL.DEV.(%) FROM CERTIFIED VALUE[a] ΔC_{RS}	$\Delta C'_{RS}$	$\|\Delta C_{RS}\|$ - $\|\Delta C'_{RS}\|$
1.	1,712	1,0020	2,054	2,058	0,24	0,44	-0,20	1,716$^+$	1,719	0,04	0,21	-0,17
2	1,709	1,0037	2,038	2,046	-0,54	-0,17	0,37	1,707	1,713	-0,49	-0,14	0,35
3	1,712	1,0020	2,046	2,050$^+$	-0,15	0,05	0,10	1,714$^+$	1,717$^+$	-0,08	0,12	-0,04
4	1,705	1,0061	2,036	2,048$^+$	-0,64	-0,03	0,61	1,708	1,718	-0,43	0,18	0,25
5	1,716	0,9997	2,051$^+$	2,050$^+$	0,09	0,06	0,03	1,715$^+$	1,714$^+$	-0,02	-0,06	-0,04
6	1,703	1,0073	2,038	2,053	-0,54	0,18	0,36	1,702	1,714$^+$	-0,78	-0,06	0,72
7	1,702	1,0079	2,033	2,049$^+$	-0,79	±0,00	0,79	1,703	1,716$^+$	-0,72	0,06	0,66
8	1,715	1,0002	2,048	2,049$^+$	-0,05	±0,00	0,05	1,719	1,719	0,23	0,23	±0,00
9	-	-	(2,044)	-	(-0,25)	-	-	-	-	-	-	-
10	1,712	1,0020	2,044	2,048$^+$	-0,25	-0,05	0,20	1,711	1,714$^+$	-0,26	-0,06	0,20
11	1,689	1,0156	2,014	2,046	-1,71	-0,18	1,53	1,692	1,718	-1,36	0,18	1,38
12	1,727	0,9933	2,056	2,042	0,34	-0,34	±0,00	1,722	1,710	0,38	-0,29	0,09
13	1,723	0,9956	2,056	2,047$^+$	0,34	-0,11	0,23	1,711	1,704	-0,66	-0,70	-0,04
14	1,719	0,9979	2,071	2,067	1,07	0,86	0,21	1,717$^+$	1,713	0,09	-0,12	-0,03
15	1,711	1,0026	2,048	2,053	±0,00	0,20	-0,20	1,715$^+$	1,719	-0,02	0,23	-0,21
16	1,714	1,0008	2,050$^+$	2,052	0,04	0,13	-0,09	1,715$^+$	1,716$^+$	-0,02	0,06	-0,04
17	1,701	1,0085	2,065	2,083	0,78	1,63	-0,85	1,723	1,738	0,44	1,29	-0,85
18	1,664	1,0309	1,991	2,053	16,07	0,17	15,90	1,663	1,714$^+$	-3,05	-0,06	2,99
19	24,820	0,0691	2,040	0,141	-0,44	-93,12	-92,68	1,709	0,118	-0,37	-93,11	-92,74
20	1,710	1,0032	2,038	2,044	-0,54	-0,23	0,31	1,705	1,710	-0,60	-0,29	0,31
21	1,713	1,0014	2,047$^+$	2,050$^+$	-0,10	0,04	0,06	1,708	1,710	-0,43	-0,29	0,14
22	1,719	0,9979	2,048$^+$	2,044	-0,05	-0,26	-0,21	1,715$^+$	1,711	-0,02	-0,23	-0,21
23	1,711	1,0026	2,049$^+$	2,054	±0,00	-0,25	-0,25	1,710	1,714$^+$	-0,31	-0,06	0,25
24	1,720	0,9973	2,020	2,015	-1,42	-1,68	-0,26	1,701	1,697	-0,84	-1,10	-0,26
25	1,700	1,0091	2,033	2,051$^+$	-0,79	-0,11	0,68	1,704	1,719	-0,66	0,23	0,43
26	1,714	1,0008	2,049$^+$	2,051$^+$	±0,00	0,11	-0,11	1,717$^+$	1,718	0,09	0,18	-0,09
27	-	-	(1,976)	-	(-3,57)	-	-	-	-	-	-	-
28	1,656	1,0359	2,363	2,448	15,32	19,46	-4,14	1,666	1,726	-2,88	0,60	2,28
29	-	-	(2,044)	-	(-0,25)	-	-	-	-	-	-	-
30	1,718	0,9985	2,049$^+$	2,046	±0,00	-0,16	-0,16	1,718	1,715$^+$	0,15	±0,00	0,15
31	1,714	1,0008	-	-	-	-	-	1,713	1,714	-0,14	-0,08	0,06
REFERENCE[d]	73		70					72				

[a] AGREED CERTIFIED VALUE R-SOLUTION C*=1,7154 ±0,0017 MG U/G SOL.

[b] VALUES WITHIN THE UNCERTAINTY RANGE OF THE CERTIFIED VALUE ARE MARKED BY '+'

[c] AGREED CERTIFIED VALUE B-SOLUTION 2,049 ±0,0019 MG U/G SOL.

[d] INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

IDA-80/TAB. XXXV: INFLUENCE OF LABORATORY OWN CALIBRATION OF SUP-SPIKE SOLUTION ON PU-239 CONCENTRATION DETERMINATIONS

1	2	3	4	5	6	7	8	9	10	11	12	13
LAB. CODE	CONC. (RU/2.3) ($\frac{\text{AT.PU-239}}{\text{G SOL.}}$)	'CORR.' FACTOR[a]	CONCENTRATION[b] x10^{16} ($\frac{\text{AT.PU-239}}{\text{G SOL.}}$)		REL.DEV.(%) FROM CERTIFIED VALUE[c]			CONCENTRATION[b] x10^{16} ($\frac{\text{AT.PU-239}}{\text{G SOL.}}$)		REL.DEV.(%) FROM CERTIFIED VALUE[a]		
	$C \times 10^{-16}$	$K_S = C^*/C$	C_{BS}	$C'_{BS} = K_S \times C_{BS}$	ΔC_{BS}	$\Delta C'_{BS}$	$\lvert\Delta C_{BS}\rvert - \lvert\Delta C'_{BS}\rvert$	C_{RS}	$C'_{RS} = K_S \times C_{RS}$	ΔC_{RS}	$\Delta C'_{RS}$	$\lvert\Delta C_{RS}\rvert - \lvert\Delta C'_{RS}\rvert$
1	1,547	0,9964	1,257	1,252$^+$	0,52	0,16	0,36	1,549	1,543$^+$	0,49	0,13	0,36
2	1,542	0,9996	1,252$^+$	1,252$^+$	0,16	0,16	±0,0	1,539$^+$	1,538$^+$	-0,16	-0,19	-0,03
3	1,548	0,9957	1,259	1,254$^+$	0,69	0,26	0,43	1,549	1,542$^+$	0,49	0,06	0,43
4	1,542	0,9996	1,254$^+$	1,254$^+$	0,29	0,29	±0,0	1,540$^+$	1,539$^+$	-0,09	-0,13	-0,04
5	1,541	1,0003	1,273	1,273	1,81	1,81	±0,0	1,526	1,526	-1,00	-1,00	±0,0
6	1,546	0,9970	1,253$^+$	1,249$^+$	0,21	-0,09	0,12	1,545$^+$	1,540$^+$	0,23	-0,06	0,17
7	1,549	0,9951	1,251$^+$	1,245	0,05	-0,44	-0,39	1,542$^+$	1,537	0,04	-0,26	-0,22
8	1.552	0,9932	1,259	1,250$^+$	0,69	0,00	0,69	1.550	1,539$^+$	0,56	-0,13	0,43
9	-	-	(1,256)	-	(0,45)	-	-	-	-	-	-	-
10	1,538	1,0022	1,248$^+$	1,251$^+$	-0,19	0,03	0,16	1,532	1,553	0,56	0,78	-0,22
11	1,557	0,9900	1,013	1,003	-18,99	-19,80	-0,81	1,540$^+$	1,525	-0,09	-1,09	-1,00
12	1,546	0,9970	1,252$^+$	1,248$^+$	0,13	-0,17	-0,04	1,543$^+$	1,538$^+$	0,10	-0,19	-0,09
13	1,543	0,9990	1,251$^+$	1,250$^+$	0,05	-0,05	±0,0	1,535	1,534	-0,42	-0,51	-0,09
14	1,557	0,9900	1,252$^+$	1,240	0,13	-0,88	-0,75	1,540$^+$	1,525	-0,09	-1,09	-1,00
15	1.536	1,0035	1,249$^+$	1,253$^+$	-0,11	0,24	-0,13	1,540$^+$	1,545$^+$	-0,09	0,26	-0,17
16	1,538	1,0022	1,252$^+$	1,255	0,13	0,35	-0,22	1,542$^+$	1,545$^+$	0,04	0,26	-0,22
17	1,535	1,0042	1,249$^+$	1,254$^+$	-0,11	0,30	-0,19	1,584	1,591	2,76	3,19	-0,43
18	1,568	0,9830	1,259	1,238	0,69	-1,02	-0,33	1,566	1,539$^+$	1,60	-0,13	1,47
19	22,050	0,0699	1,256	0,088	0,45	-92,98	-92,53	1,541$^+$	0,108	-0,03	-93,01	-92,98
20	1,546	0,9970	1,253$^+$	1,249$^+$	0,21	-0,09	0,12	1,543$^+$	1,538$^+$	0,10	-0,19	-0,09
21	1,543	0,9990	1,254$^+$	1,253$^+$	0,29	0,18	0,11	1,541$^+$	1,539$^+$	-0,03	-0,13	-0,10
22	1,542	0,9996	1,226	1,226	-1,95	-1,95	±0,0	1,540$^+$	1,539$^+$	-0,04	-0,13	-0,04
23	1,548	0,9957	1,255	1,250$^+$	0,37	-0,06	0,31	1,546	1,539$^+$	0,30	-0,13	0,17
24	1,528	1,0088	1,227	1,238	-1,87	-1,01	0,86	1,534	1,548	-0,48	0,39	0,09
25	1,537	1,0029	1,275	1,279	1,97	2,26	-0,29	1,540$^+$	1,544$^+$	-0,09	0,20	-0,11
26	1.542	0,9996	1,221	1,221	-2,35	-2,35	±0,0	1,542$^+$	1,541$^+$	0,04	±0,00	0,04
27	-	-	(1,263)	-	(1,01)	-	-	-	-	-	-	-
28	-	-	-	-	-	-	-	-	-	-	-	-
29	-	-	(1,253)	-	(0,21)	-	-	-	-	-	-	-
30	1.547	0,9964	1,248$^+$	1,244	-0,19	-0,55	-0,36	1,538$^+$	1,532	-0,22	-0,58	-0,36
31	1,528	1,0088	-	-	-	-	-	1,529	1,542$^+$	-0,80	·0,07	0,73
REF.[d]	86		80					84				

a) AGREED CERTIFIED VALUE R-SOLUTION $C^* = 1,5414 \pm 0,0037 \times 10^{16}$ AT.PU-239/G SOL.

b) VALUES WITHIN THE UNCERTAINTY RANGE OF THE CERTIFIED VALUE ARE MARKED BY '+'

c) AGREED CERTIFIED VALUE B-SOLUTION $1,2504 \pm 0,0030 \times 10^{16}$ AT.PU-239/G SOL.

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

IDA-80/TAB. XXXVI: INFLUENCE OF LABORATORY OWN CALIBRATION OF SUP-SPIKE SOLUTION ON INTERLABORATORY SPREADS OF CONCENTRATION VALUES

	1	2	3	4	5	6	7
1	ELEMENT	DATA BASIS	REFERENCE TABLE/ COLUMN	LABORATORY EXCLUDED BECAUSE OF INCOMPLETE DATA	EXTREME VALUE	NUMBER OF CONTRIBUTING LABS^a	INTERLAB SPREAD^a (%)
2	URANIUM	C_{BS}	XXXIV/4	9, 27, 29, 31	18, 28	25 (21)	0.60 (0.48)
3		C'_{BS}	XXXIV/5		14, 17, 19 24, 28	22 (21)	0.19 (0.19)
4		C_{RS}	XXXIV/9	9, 27, 29	18, 28	26 (23)	0.42 (0.40)
5		C'_{RS}	XXXIV/10		17, 19, 24	25 (23)	0.25 (0.22)
6	PLUTONIUM	C_{BS}	XXXV/4	9, 27, 28, 29, 31	11	25 (24)	0.96 (0.98)
7		C'_{BS}	XXXV/5		11, 19	24 (24)	0.93 (0.93)
8		C_{RS}	XXXV/9	9, 27, 28, 29	17, 18	25 (24)	0.38 (0.38)
9		C'_{RS}	XXXV/10		17, 19	25 (24)	0.43 (0.44)

a) THE VALUES FOR THE MAXIMUM COMMON LABORATORY GROUP OF 'CORRECTED' AND 'UNCORRECTED' DATA ARE GIVEN IN BRACKETS

K_S-values are greater than one, indicating a tendency to determine uranium concentrations somewhat too low as already observed in other studies (see e.g. Chapt. 7.3). In contrast to this, for plutonium nearly the same fraction of K_S-values is less than one. This opposite sign of the effect may indeed indicate that it depends on the ratio of the main sample isotope mass to the spike isotope mass as expected with isotope fractionation (see Tabs. XXXIV and XXXV, columns 2).

b) Multiplication with the K_S factor brings the results of 13 laboratories into the uncertainty ranges of the agreed certified values for uranium but pushes 9 of them out (see marked data in columns 4, 5, 9 and 10 of Tab. XXXIV). For plutonium, this ratio is 10:9 (Tab. XXXV). This shows that this kind of 'correction' is not meaningful in each case but may indicate the existence of an error source such as isotope fractionation at least for those laboratories whose values improved for both samples.

c) Application of the K_S-factor improves clearly the calculated estimates for uranium as judged by the interlaboratory spreads. For plutonium, no effect is found (see Tab. XXXVI, column 7).

7.7 Isotope fractionation

In the previous chapter isotope fractionation in the ion source of the mass spectrometer was considered as a source of measurement uncertainty. The size of this effect varies from one filament load to the next (i.e. 'from run to run'), and only its systematic component can be considered as a 'laboratory bias'. This systematic component will become more and more apparent when the laboratories' filament heating procedures become more reproducible. Since the evaporation rates of light isotopes are slightly higher than those of heavier ones, the value measured for the ratio of a light to a heavy isotope (e.g. U-233/U-238) is too high at the beginning of the measurement procedure. However, because of faster depletion of the light isotope, the measured ratio reaches its true value after some time and, later becomes too low. The time delay until the 'true value' is observed depends not only on the size of the sample but also on the mass difference of the isotopes of the ratio in question, e.g. is different for the U-233/U-238 and the U-235/U-238 ratios.

In order to gain information about this effect and its magnitude, the relative deviations of the measured isotope ratios from the certified values have been compiled in Tab. XXXVII for the isotope ratios U-233/U-238, U-235/U-238, and Pu-242/Pu-239 of the prespiked test solutions AS, BS and RS.

Observations

a) 75.9 % of the U-233/U-238 ratios and 71.4 % of the U-235/U-238 ratios are larger whereas 74.5 % of the Pu-242/Pu-239 ratios are smaller than the agreed certified values (Tab. XXXVII). Assuming that the majority of the laboratories performs their measurements during the 'initial' phase of the filament heating process - an assumption which seems to be justified - this observation is in agreement with expectations for isotope fractionation. This observation subsists if only deviations of participants' values from the border lines of the certified uncertainty ranges are taken into account (see bottom line of Tab. XXXVII): the percentages are then 65.5 %, 66,1 % and 53.6 % for the three isotope ratios considered. Hence the conclusion about isotope fractionation effects holds even when the agreed certified values move within their uncertainty range.

b) The magnitude of the assumed isotope fractionation effect is apparently in the range of a few per mille up to one percent or even higher.

Increased measurement uncertainty by mass dependent effects should also become visible when comparing the interlaboratory spreads of the U-233/U-238 isotope ratio measurements of the BS and RS samples with those of the U-235/U-238 determinations of the AS-samples in part 1.3. The values for both

IDA-80/TAB. XXXVII: RELATIVE DEVIATIONS (%) OF MEASURED ISOTOPE RATIOS FROM AGREED CERTIFIED VALUES

1	2	3	4	5	6	7	8	9
	U-233/U-238		U-235/U-238		PU-242/PU-239			
LAB. CODE	BS	RS	ASI	ASII, IV, VI	BS	RS	ASI	ASII, IV, VI
1	- 0,27	0,10	± 0,00	- 0,21	- 0,50	- 0,58	- 0,65	- 0,76
2	0,51	0,58	0,29	0,32	- 0,13	0,02	0,07	- 0,20
3	0,10	0,20	0,03	0,12	- 0,68	- 0,61	- 0,74	- 0,73
4	0,62	0,58	0,40	0,38	- 0,32	- 0,01	- 0,65	0,08
5	- 0,13	0,10	- 0,11	- 0,28	- 1,79	0,89	- 1,92	- 1,69
6	0,48	0,86	- 0,13	- 0,12	- 0,22	- 0,34	- 0,47	- 0,38
7	0,78	0,86	0,55	0,75	- 0,04	- 0,18	- 0,29	- 0,18
8	0,02	- 0,09	0,31	0,50	- 0,68	- 0,68	- 1,11	- 0,85
9	0,24	-	- 0,03	0,07	- 0,50	-	- 0,38	- 0,38
10	0,24	0,39	- 0,09	0,12	0,15	0,44	0,53	0,83
11	1,66	1,43	0,62	1,09	22,81	- 0,07	- 0,74	- 0,29
12	- 0,35	- 0,27	0,15	0,21	- 0,22	- 0,21	- 0,02	0,27
13	- 0,33	0,29	- 0,14	0,01	- 0,13	0,26	0,25	0,55
14	- 1,06	0,01	- 0,28	- 0,20	- 0,13	- 0,02	- 0,02	0,08
15	0,03	0,10	0,09	0,12	0,15	- 0,03	- 0,02	- 0,08
16	- 0,07	0,10	0,06	0,16	- 0,13	- 0,05	- 0,02	- 0,10
17	- 0,82	- 0,37	- 1,11	- 0,97	0,05	- 2,67	0,07	- 0,01
18	2,92	3,32	1,75	1,39	- 0,59	- 1,73	- 2,10	- 1,41
19	0,41	0,48	0,60	0,60	- 0,50	- 0,09	- 0,29	0,64
20	0,50	0,67	0,76	0,68	- 0,22	- 0,25	- 0,38	- 0,27
21	0,09	0,58	- 0,03	0,19	- 0,32	- 0,08	- 0,56	- 0,18
22	0,01	0,10	0,11	0,15	1,90	- 0,03	- 0,02	- 0,08
23	± 0,00	0,39	- 0,21	0,20	- 0,22	- 0,39	- 0,02	0,01
24	1,41	0,96	-	-	1,90	0,44	-	-
25	0,75	0,77	0,13	0,20	- 1,79	- 0,05	0,16	0,18
26	- 0,04	0,01	0,22	0,27	2,26	- 0,13	- 0,29	- 0,27
27	3,70	-	-	-	- 0,96	-	-	-
28	-13,19	3,23	- 1,56	1,58	-	-	-	-
29	0,24	-	0,27	0,18	- 0,22	-	- 0,02	- 0,20
30	- 0,03	0,01	0,01	0,25	0,15	0,08	- 0,11	- 0,01
31	-	0,29	-	-	-	0,69	-	-
REFERENCE[a]	7	14	2	2	32	41	23	23
UNCERTAINTY-RANGE[b]	± 0,07%	± 0,08%	± 0,03%	II,IV: ± 0,05%, VI: ±0,04%	± 0,12%	± 0,11%	± 0,09%	II: ±0,21% IV,VI: ± 0,13%

[a] INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/.

[b] VALUES ROUNDED TO TWO DECIMAL PLACES; SEE VOL.II /9/.

IDA-80/TAB. XXXVIII: COMPARISON OF ESTIMATED INTERLABORATORY SPREADS OF U-235/U-238 AND U-233/U-238 ISOTOPE RATIO MEASUREMENTS

	1	2	3	4
1	SAMPLE	ISOTOPE RATIO	RUN	INTER-LABORATORY SPREAD[a] (%)
2	AS I	235/238	1	0.26
3	BS	233/238	1	0.33
			2	0.39
			3	0.37
4	RS	233/238	1	0.36
			2	0.36
			3	0.36

a) ALL DATA ARE BASED ON THE SAME GROUP OF THE FOLLOWING 20 LABORATORIES ('MORE EXPERIENCED' ONES UNDERLINED): 1,2,3,4,5,6,7,8,10,12,15,16,19,20,21,22,23,25,26 AND 30

ratios are approximately one. This comparison is made in Tab. XXXVIII. To evaluate U-235/U-238 ratio data, only the measurements of the AS-I sample were used, because it is the only AS-sample measured by all laboratories (see Chapt. 5.2). Since only one filament loading ('run') of this sample material was measured per laboratory, the interlaboratory spreads were calculated separately for the three runs performed on the BS and RS samples[1]. All calculations are based on the group of twenty laboratories[2] which participated in all these measurements and did not produce any extreme values.

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[1] See Evaluation Sheets 2, 7 and 14 in Vol. III /10/.

[2] These are the laboratories 1,2,3,4,5,6,7,8,10,12,15,16,19,20,21,22,23,25, 26 and 30 ('more experienced' ones underlined).

The value calculated for the U-235/U-238 ratio is indeed somewhat smaller than the others, what may confirm again the isotope fractionation effect.

In the framework of IDA-80, more detailed studies of isotope fractionation are difficult to perform due to its complicated dependences on isotope masses, sample sizes, filament loading and heating procedures, acidity of the sample solutions etc.

7.8 Calibration of spike solution with common reference material

The majority of the laboratories reported the use of NBS-reference materials for calibrating the spike solutions: 71 % for uranium, 57 % for plutonium. The remaining laboratories used reference materials of different origin.

The design of the experiment allows the effect of the use of common reference materials to be checked: the analysis of the reference solution R with the laboratory own spike solution (LOS) in part 2.1 (see Chapt. 2.1) is considered as calibration of the laboratory own spike solution with the certified R-solution. Then, using these data of the laboratory own spike solution, the concentrations of the BU samples of programme part 1.11 were recalculated. If C_B' denotes these 'corrected' concentration values of the BU sample and C_B the values calculated by the evaluation team using the laboratory's own values, then

$$C_B' = K_L \cdot C_B$$

with the 'correction factor' K_L [1] being the ratio of the certified concentration C* of the reference solution R to the values C(2.1) determined by the individual laboratory in part 2.1 of the programme.

These data are compiled in Tabs. XXXIX for uranium and in Tab. XL for the Pu-239 isotope. The deviations Δ of these 'uncorrected' and 'corrected'

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[1] The index 'L' refers to the LOS spike solution.

IDA-80/TAB. XXXIX: USE OF COMMON REFERENCE MATERIAL FOR CALIBRATION OF LABORATORY OWN SPIKE SOLUTIONS (LOS) FOR URANIUM

1	2	3	4	5	6	7	8
LAB. CODE	CONC. (RU/2.1) $(\frac{\text{MG U}}{\text{G SOL.}})$	'CORR.' FACTOR[a] $K_L = C^*/C$	CONCENTRATION (MGU/G SOL.)[b] C_{BU}	$C'_{BU} = K_L x C_{BU}$	REL.DEV.(%) FROM CERTIFIED VALUE[c] ΔC_{BU}	$\Delta C'_{BU}$	$\lvert \Delta C_{BU} \rvert - \lvert \Delta C'_{BU} \rvert$
1	1,718	0,9985	2,056	2,053	0,34	0,19	0,15
2	1,729	0,9921	2,069	2,053	0,97	0,18	0,79
3	1,710	1,0032	2,047+	2,054	-0,10	0,21	-0,11
4	1.707	1,0049	2,045	2,055	-0.20	0,29	-0,09
5	1.715	1,0002	2,055	2,055	0,29	0,31	-0,02
6	1.713	1,0014	1.052	2,055	0,14	0,28	-0,14
7	1.712	1,0020	2,053	2,057	0,19	0,39	-0,20
8	1,719	0,9979	2,043	2,039	-0,30	-0,51	-0,21
9	-	-	-	-	-	-	-
10	1,714	1,0008	2,049+	2,051+	-0,01	0,08	-0,07
11	1.698	1,0102	2,038	2,059	-0,54	0,48	0,06
12	1.731	0,9910	2.048+	2,030	-0,05	-0,95	-0,90
13	1.531	1.1204	2,040	2.286	-0,44	11,55	-11,11
14	1.721	0,9967	2,055	2,048+	0,29	-0,04	0,25
15	1.717	0,9991	2,058	2,056	0,43	0,34	0,09
16	1,716	0,9997	2,052	2,051+	0,14	0,11	0,03
17	1,708	1,0043	2,095	2.104	2,24	2,68	-0,44
18	1.669	1.0284	1.984	2,040	-3.18	-0,43	2,75
19	1,706	1,0055	2,039	2,050+	-0,49	0,05	0,44
20	1,719	0,9979	2,052	2,048+	0,14	-0,07	0,07
21	1,730	0,9916	2,056	2,039	0.34	-0,51	-0,17
22	1,712	1.0020	2,047+	2,051	-0,10	0,10	±0,00
23	1,681	1,0205	2,054	2,096	0,24	2,29	-2,05
24	1,696	1,0144	2,036	2,059	-0,64	0,50	0,14
25	1.713	1,0014	2,042	2,045	-0,35	-0,21	0,14
26	1,709	1,0037	2,046	2,054	-0,15	0,22	-0,07
27	-	-	-	-	-	-	-
28	1.568	1,0940	1,884	2,061	-8,06	0,59	7,47
29	-	-	-	-	-	-	-
30	1,728	0,9927	2,071	2,056	1,07	0,33	0,74
31	-	-	-	-	-	-	-
REF.[d]	71		68				

[a] AGREED CERTIFIED VALUE R-SOLUTION $C^* = 1,7154 \pm 0,0017$ MG U/G SOL.

[b] VALUES WITHIN THE UNCERTAINTY RANGE OF THE CERTIFIED VALUE ARE MARKED BY '+'

[c] AGREED CERTIFIED VALUE B-SOLUTION $2,0491 \pm 0,0019$ MG U/G SOL.

[d] INDICATES THE EVALUATION SHEET NUMBER IN VOL. III /10/

IDA-80/TAB XL: USE OF COMMON REFERENCE MATERIAL FOR CALIBRATION OF LABORATORY OWN SPIKE SOLUTIONS (LOS) FOR PLUTONIUM

1	2	3	4	5	6	7	8
LAB. CODE	CONC. (RU/2.1) (AT.PU-239 / G SOL.)	'CORR.' FACTOR[a]	CONCENTRATION[b] x10^{16} (AT.PU-239 / G SOL.)		REL.DEV.(%) FROM CERTIFIED VALUE[c]		
	Cx10^{-16}	K_L= C*/C	C_{BU}	C'_{BU}= K_LxC_{BU}	ΔC_{BU}	$\Delta C'_{BU}$	$\lvert\Delta C_{BU}\rvert - \lvert\Delta C'_{BU}\rvert$
1	1.536	1.0035	1.252$^+$	1.256	0.13	0.48	-0.35
2	1.541	1.0003	1.253$^+$	1.253$^+$	0.21	0.24	-0.03
3	1.551	0.9938	1.261	1.253$^+$	0.85	0.22	0.63
4	1.531	1.0068	1.260	1.269	0.77	1.45	-0.68
5	1.531	1.0068	1.264	1.273	1.09	1.78	-0.69
6	1.542	0.9996	1.250$^+$	1.250$^+$	-0.03	-0.07	-0.04
7	1.561	0.9874	1.265	1.249$^+$	1.17	-0.10	1.07
8	1.601	0.9628	1.298	1.250$^+$	3.81	-0.06	3.75
9	-	-	-	-	-	-	-
10	1.540	1.0004	1.253$^+$	1.254$^+$	0.21	0.30	-0.09
11	1.532	1.0061	1.250$^+$	1.258	-0.03	0.58	-0.55
12	1.551	0.9938	1.257	1.249$^+$	0.53	-0.09	0.44
13	1.368	1.1268	1.242	1.399	-0.67	11.92	-11.25
14	1.559	0.9887	1.256	1.242	0.45	-0.69	-0.24
15	1.543	0.9990	1.251$^+$	1.250$^+$	0.05	-0.06	-0.01
16	1.541	1.0003	1.251$^+$	1.251$^+$	0.07	0.05	0.02
17	1.387	1.1113	1.152	1.280	-7.87	2.39	5.48
18	1.573	0.9799	1.265	1.240	1.17	-0.86	0.31
19	1.506	1.0235	1.230	1.259	-1.63	0.68	0.95
20	1.532	1.0061	1.241	1.249$^+$	-0.75	-0.14	0.61
21	-	-	-	-	-	-	-
22	1.548	0.9957	1.237	1.232	-1.07	-1.49	-0.42
23	1.509	1.0215	1.225	1.251$^+$	-2.03	0.07	1.96
24	1.526	1.0101	1.243	1.256	-0.59	0.41	0.18
25	1.532	1.0061	1.243	1.251$^+$	-0.59	0.02	0.57
26	1.544	0.9983	1.252$^+$	1.250$^+$	0.13	-0.04	0.09
27	-	-	-	-	-	-	-
28	-	-	-	-	-	-	-
29	-	-	-	-	-	-	-
30	1.532	1.0061	1.248$^+$	1.256	-0.19	0.42	-0.23
31	-	-	-	-	-	-	-
REFERENCE[d]	82		76				

a) AGREED CERTIFIED VALUE R-SOLUTION C*=1.5414 ±0.0037x10^{16} AT.PU-239/G SOL.

b) VALUES WITHIN THE UNCERTAINTY RANGE OF THE CERTIFIED VALUE ARE MARKED BY '+'

c) AGREED CERTIFIED VALUE B-SOLUTION 1.2504 ±0.0030x10^{16} AT.PU-239/G SOL.

d) INDICATES THE EVALUATION SHEET NUMBER IN VOL.III /10/

concentration values from the agreed certified values are also listed (columns 6 and 7) as well as the differences of the absolute values of these deviations (column 8). Those concentration values which lie within the uncertainty ranges of the certified values are marked by '+'. In Tab. XLI, the interlaboratory spreads of the sets of 'corrected' and 'uncorrected' values are presented. They were calculated after the exclusion of extreme values according to the Bartsch criterion /14/. These calculations were additionally made for the maximum common laboratory groups.

Observations:

a) Application of the K_L-factor changes the concentration values by more than 0.5 % for 11 laboratories (41 %) in the case of uranium and for 17 laboratories (68 %) in the case of plutonium (Tabs. XXXIX and XL, column 3).

IDA-80/TAB. XLI: INFLUENCE OF LABORATORY OWN SPIKE SOLUTION (LOS) CALIBRATION WITH A COMMON REFERENCE MATERIAL ON THE INTERLABORATORY SPREADS OF CONCENTRATION VALUES

	1	2	3	4	5	6	7
1	ELEMENT	DATA BASIS	REFERENCE TABLE/ COLUMN	LABORATORY EXCLUDED BECAUSE OF INCOMPLETE DATA	 EXTREME VALUE	NUMBER OF CONTRIBUTING LABS[a]	INTERLAB SPREAD[a] (%)
2	URANIUM	C_{BU}	XXXIX/4	9, 27, 29, 31	17, 18, 28 30	23 (21)	0,38 (0,38)
3		C'_{BU}	XXXIX/5		13, 17, 23	24 (21)	0,37 (0,35)
4	PLUTONIUM	C_{BU}	XL/4	9, 21, 27, 28, 29, 31	8, 17	23 (22)	0,84 (0,81)
5		C'_{BU}	XL/5		13	24 (22)	0,80 (0,69)

[a] THE VALUES FOR THE MAXIMUM COMMON LABORATORY GROUP OF 'CORRECTED' AND 'UNCORRECTED' DATA ARE GIVEN IN BRACKETS

b) For uranium as well as for plutonium, these 'corrections' cause - as judged by the agreed certified values - approximately as many improvements as changes for the worse (Tabs. XXXIX and XL, column 8). However, there are more values entering the uncertainty ranges of the agreed certified values than leaving them: the ratios are 4:2 for uranium and 7:3 for plutonium (columns 4 and 5). This indicates that for some laboratories the original spike solution calibrations involved errors (see Chapt. 7.9).

c) For the data groups considered, application of the K_L-factor has nearly no effect on the interlaboratory spreads of uranium concentration determinations. For plutonium, a slight improvement is indicated[1] (Tab. XLI, column 7).

7.9 Use of separate spike solutions

It was observed already in the IDA-72 programme /1/ that U-233 spike material may contain small impurities of the Pu-239 isotope which may remain unrecognized. If U-233 and Pu-242 spike solutions are calibrated separately but added to the same aliquot of sample solution, this Pu-239 impurity causes the plutonium determination to be too high[2].

In the IDA-80 programme, 10 laboratories used separate spike solutions for uranium and plutonium and reported in total 18 plutonium concentration determinations of BU and RU samples (programme parts 1.11 and 2.1). 5 of them are within the stated uncertainty ranges of the agreed certified values, but 9 out of the remaining 13 values (70 %) are higher than the upper limitations. Three laboratories exceed these upper limitations of the uncertainty ranges in the analysis of both samples, BU and RU. However, calibrating their spike solutions with the reference solution R (see Chapt. 7.6), brings the values for the BU-samples back into the uncertainty range (for the RU sample, this test is not possible). At least for these three laboratories (about 10 % of the participants), unrecognized Pu-239 impurities of the spike

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[1] Refer in this context to Chapt. 7.9.

[2] Of course, the same effect occurs if mixed spike solutions are blended from separately calibrated U-233 and Pu-242 spike materials without rechecking of the Pu-239 content.

material may be a significant contribution to their plutonium measurement uncertainties.

7.10 Measurement of minor isotopes

For application of isotope correlation technique in practical safeguards, the accuracy of minor isotope abundances is of particular interest. According to a general (but also disputed) opinion, the use of multiple stage mass spectrometer is required for this purpose.

With this in mind, it seemed to be of interest to compare the results obtained by four laboratories using multiple stage instruments with those obtained by the other participants. In Tab. XLII, the data are listed for the three uranium isotopes with abundances below 0.1 %: 35 % of the results are within the uncertainty ranges of the agreed certified values for single stage mass spectrometers and 42 % for multiple stage instruments, indicating no difference of high significance.

IDA-80/TAB. XLII: DETERMINATION OF MINOR ISOTOPES BY DIFFERENT TYPES OF MASS SPECTROMETERS

	1	2	3	4	5	6
1	SOLUTION/ ISOTOPE	AGREED CERTIFIED VALUE[a] (WT.%)	NUMBER OF DETERMINATIONS BY		NUMBER OF VALUES WITHIN CERT. RANGE	
			SINGLE STAGE	MULTIPLE STAGE	SINGLE STAGE	MULTIPLE STAGE
			MASS SPECTROMETERS		MASS SPECTROMETERS	
2	B U-234	0.0087 ± .0001	25	4	10 (40 %)	2 (50 %)
3	R U-234	0.0089 ± .0001	22	4	9 (41 %)	2 (50 %)
4	R U-236	0.0067 ± .0001	21	4	5 (24 %)	1 (25 %)
5	TOTAL		68	12	24 (35 %)	5 (42 %)

a) SEE TAB. IV

7.11 Man-power spent by the participating laboratories

A survey on the work load for each of the participating laboratories is given in Tab. XLIII.

Approximately 50 % of the laboratories completed the whole programme as requested. The others did not perform and/or report measurements of some programme parts for various administrative or technical reasons. These incomplete data sets complicated and delayed data treatment, but did not adversely affect the information value of the IDA-80 programme: the more than 60,000 reported data represent about 90 % of the maximum information which could be expected (Fig. 30). This yield certainly is very satisfactory with regard to the rather high requirements of this programme on the participants.

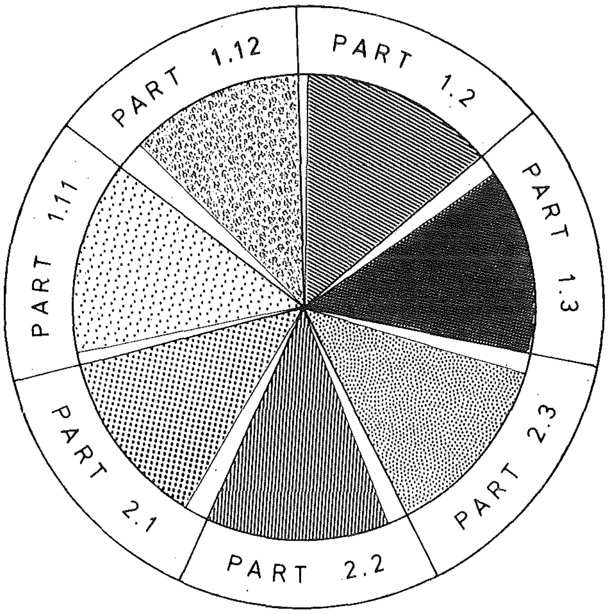
Fig. 31 shows the information on the man-power spent by the laboratories which completed the full programme. The man-power required for the analytical

IDA-80/TAB. XLIII: ANALYTICAL EFFORTS PER LABORATORY

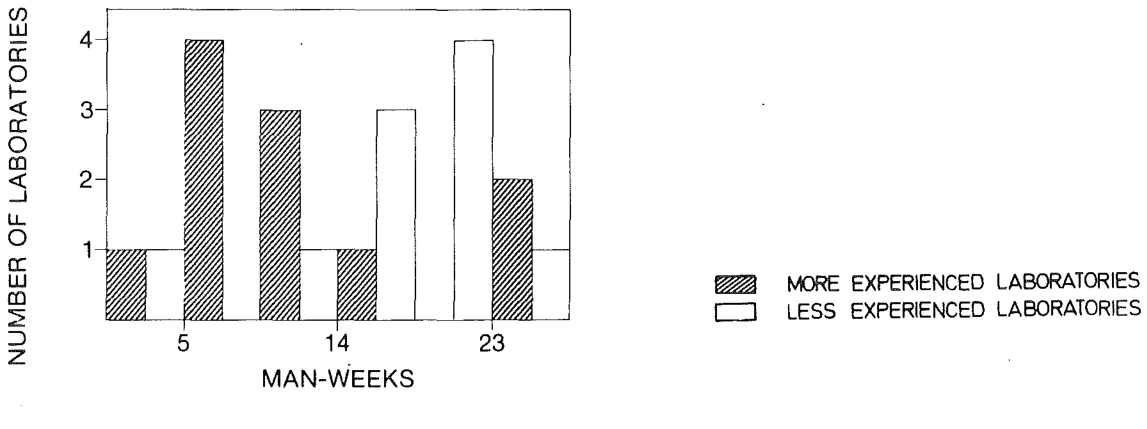
ANALYTICAL STEP	PART 1	PART 2	IN TOTAL
SPIKING	6	6	12
REDISSOLUTIONS OF DRIED SOLUTION IN VIALS	6	-	6
REDOX STEPS	13	10	23
SEPARATIONS OF ELEMENTS	13	10	23
MS-FILAMENT LOADINGS AND U MEASUREMENTS (8 SCANS EACH)	18	15	33
MS-FILAMENT LOADINGS AND PU MEASUREMENTS (8 SCANS EACH)	18	15	33

work varies by a factor of approximately six, the mean value being 14 man-weeks. The 'more experienced' laboratories needed on the average about 11, the 'less experienced' laboratories about 18 man-weeks.

The additional man-power necessary for reporting the extended data material on the 79 data sheet forms (see Fig. 3, page 17) was approximately 2.5 man-weeks. Hence, the total contribution of all participants to IDA-80 amounts to about 470 man-weeks.



IDA-80/Fig. 30: Programme accomplishment (shaded sectors indicate completion of subtasks)



IDA-80/Fig. 31: Man-power spent by the laboratories

8. Comparison with the IDA-72 interlaboratory experiment

The IDA-72 interlaboratory experiment /1/ was carried out about 8 years before the performance of the IDA-80 programme and applied itself to the same task. 22 laboratories had taken part; 11 of them participated also in the IDA-80 programme.

In the IDA-72 experiment, two diluted input solutions 'A' and 'B' as well as a synthetic reference solution 'R' free of fission products had been analyzed. They were similar in composition to the diluted input solution 'B' and the synthetic reference solution 'R' used in IDA-80 (see Tab. XLIV).

In contrast to IDA-80 the main part of IDA-72 was directed to the analysis of prespiked sample material, as at that time it was the opinion of many analysts that unspiked liquid sample material might be unsuitable for such an intercomparison programme because of 'ageing effects' of plutonium in fission product containing samples. The layout of this so-called 'Standard Experiment' was the same as used in parts 1.2 and 2.2 of IDA-80 (see Fig. 1, page 7). Information obtained from such studies is restricted to the measurement uncertainties of chemical sample preparation and mass-spectrometric measurement: no information can be gained about the spiking procedure or the spike-solution calibration.

About one half of the IDA-72 participants also analyzed (in the so-called 'Self-spike Experiment') unspiked liquid samples of the fission-product-free reference solution R using their own spike materials, analogous to the studies in part 2.1 of IDA-80. However, as opposed to IDA-80, these samples were not shipped in sealed glass ampoules but in vials with screw caps. For this reason, evaporation losses during transportation could not be excluded as an additional source of error.

The evaluation methods were essentially similar in both programmes: in particular, estimates of the relative standard deviations of the uncertainty components related to the levels 'SCAN', 'RUN', and 'BETWEEN LABs' in the case of isotope ratio measurements were calculated by variance analyses; in the case of isotope abundances and element concentration determinations estimates were calculated for the 'RUN' and 'BETWEEN LABs' component[1].

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[1] For the 'BETWEEN LABs' uncertainty component the expression 'INTERLABORATORY DEVIATION' was used in IDA-72.

IDA-80/TAB. XLIV: COMPOSITION OF SAMPLE SOLUTIONS IN IDA-80 AND IDA-72

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	PROGRAMME	SAMPLE SOLUTION	ELEMENT CONCENTRATION		ISOTOPIC COMPOSITIONS (WEIGHT-%)								
			U	PU	URANIUM				PLUTONIUM				
			MG/G SOL.	µG/G SOL.	234	235	236	238	238	239	240	241	242
2	IDA-72	A	1.19	9.47	0.02	2.14	0.38	97.46	1.05	71.54	16.57	9.18	1.66
3		B	1.13	9.02	0.02	2.13	0.38	97.47	1.04	71.59	16.53	9.17	1.67
4		R	1.11	8.60	0.01	0.71	-	99.28	-	97.36	2.57	0.07	< 0.01
5	IDA-80	B	2.05	7.19	0.01	0.56	0.18	99.25	0.21	69.06	25.67	3.33	1.73
6		R	1.72	7.98	0.01	1.20	0.01	98.78	0.12	76.65	19.89	2.74	0.60

In the IDA-72 evaluation the Dixon criterion /15/ ($\alpha = 1$ %) was applied for the rejection of extreme laboratory mean values. Therefore, in order to improve the comparability of results the data of the IDA-72 programme had to be recalculated using the Bartsch criterion /14/ as it was applied in the IDA-80 programme (see Chapt. 2.4). This is the reason for some differences between the data given in the IDA-72 report /1/ and the data given in this chapter.

The isotope ratios of uranium and plutonium in IDA-72 were measured on unspiked and prespiked samples of the diluted input solutions, of the reference solution (see Table XLIV) and of the U-233/Pu-242 mixed spike solution used. The evaluation of isotope ratio determinations considered in this chapter is based on a total of about 1500 laboratory mean values[1], each one being based in most cases on the measurement of three filament loadings ('runs'). In IDA-72, the percentage of excluded laboratory mean values was 5.4 for uranium and 9.3 % for plutonium. For IDA-80, the corresponding figures were 12.1 % and 8.8 %. In Figs. 32 to 37 the curves averaging the estimates calculated in IDA-72 for each of the three error components 'SCAN', 'RUN'

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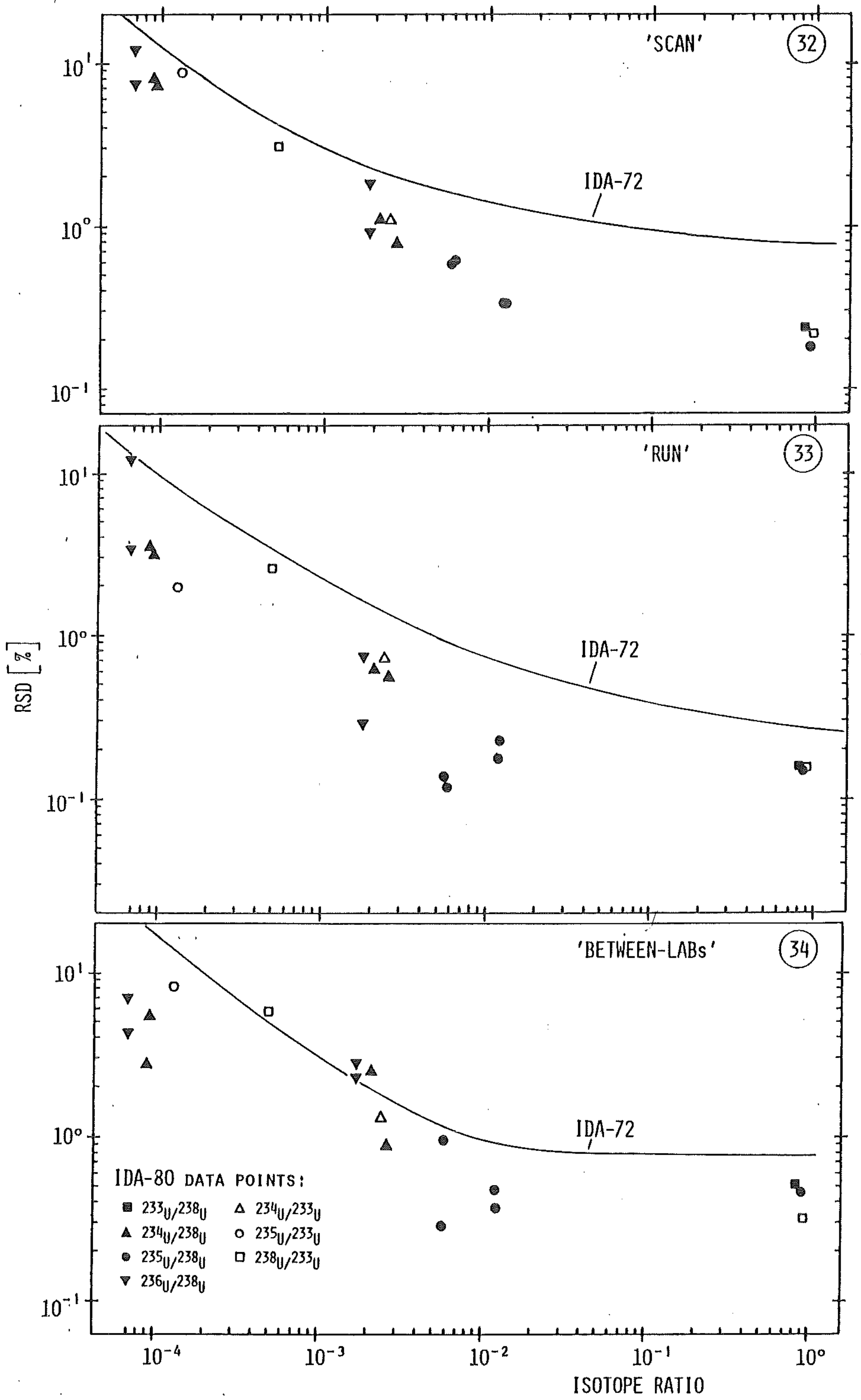
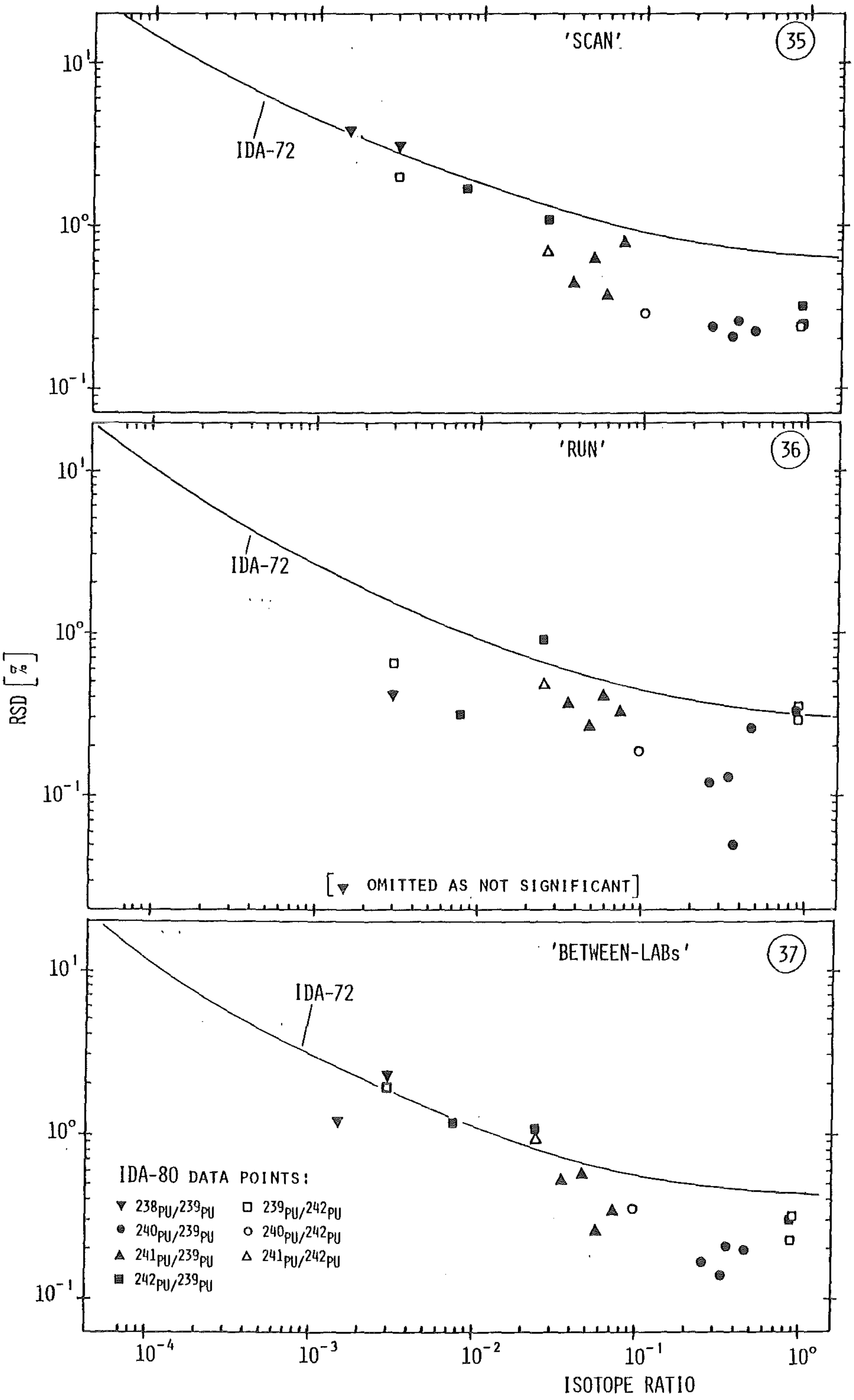
[1] The IDA-72 evaluation is based on 315 sets of data for uranium and 322 for plutonium, the IDA-80 evaluation on 430 for uranium and 415 for plutonium.



IDA-80/Fig. 32 to 34:

Uncertainty components of uranium isotope ratio determinations estimated from IDA-72 and IDA-80 data



IDA-80/Fig. 35 to 37:

Uncertainty components of plutonium isotope ratio determinations estimated from IDA-72 and IDA-80 data and 'BETWEEN LABs' for uranium and plutonium[1] are compared to the corresponding results of the IDA-80 programme.

From this data basis of isotope ratios, the isotope abundances were derived for the unspiked diluted input solutions and the reference solutions in both programmes[2]. The rates of extreme values excluded are 3.7 % and 11.1 % for uranium and 5.4 % and 6.6 % for plutonium for the IDA-72 and IDA-80 data. In order to compare the results for each isotope abundance the relative standard deviations of the spread of the laboratory mean values ('interlaboratory spreads') were calculated. The data are presented in Figs. 38 and 39.

The uranium element and Pu-239 concentrations of the prespiked A, B and R solutions were determined in the 'Standard Experiment' of IDA-72 by 18 and 17 laboratories, respectively. In IDA-80 corresponding concentration determinations were performed on the prespiked B and R samples (parts 1.2 and 2.2) for uranium by 30 and 28 laboratories, for plutonium by 29 and 27 laboratories (see Chap. 5.4). In both programmes the results were obtained as laboratory means of three run means (filament loadings). From these data estimates were calculated for the RSDs of the 'RUN' and 'BETWEEN LABS' uncertainty component. They are compiled in Tab. XLV for both programmes. The data calculated on the basis of the group of 11 laboratories which participated in IDA-72 as well as in IDA-80 are given in brackets.

As mentioned above, 10 IDA-72 participants determined the element concentrations in the unspiked R samples using their own spike solutions. Estimates calculated for the RSDs of uncertainty components on that data are presented in Tab. XLVI together with the corresponding ones obtained in parts 1.11 and 2.1 of IDA-80.

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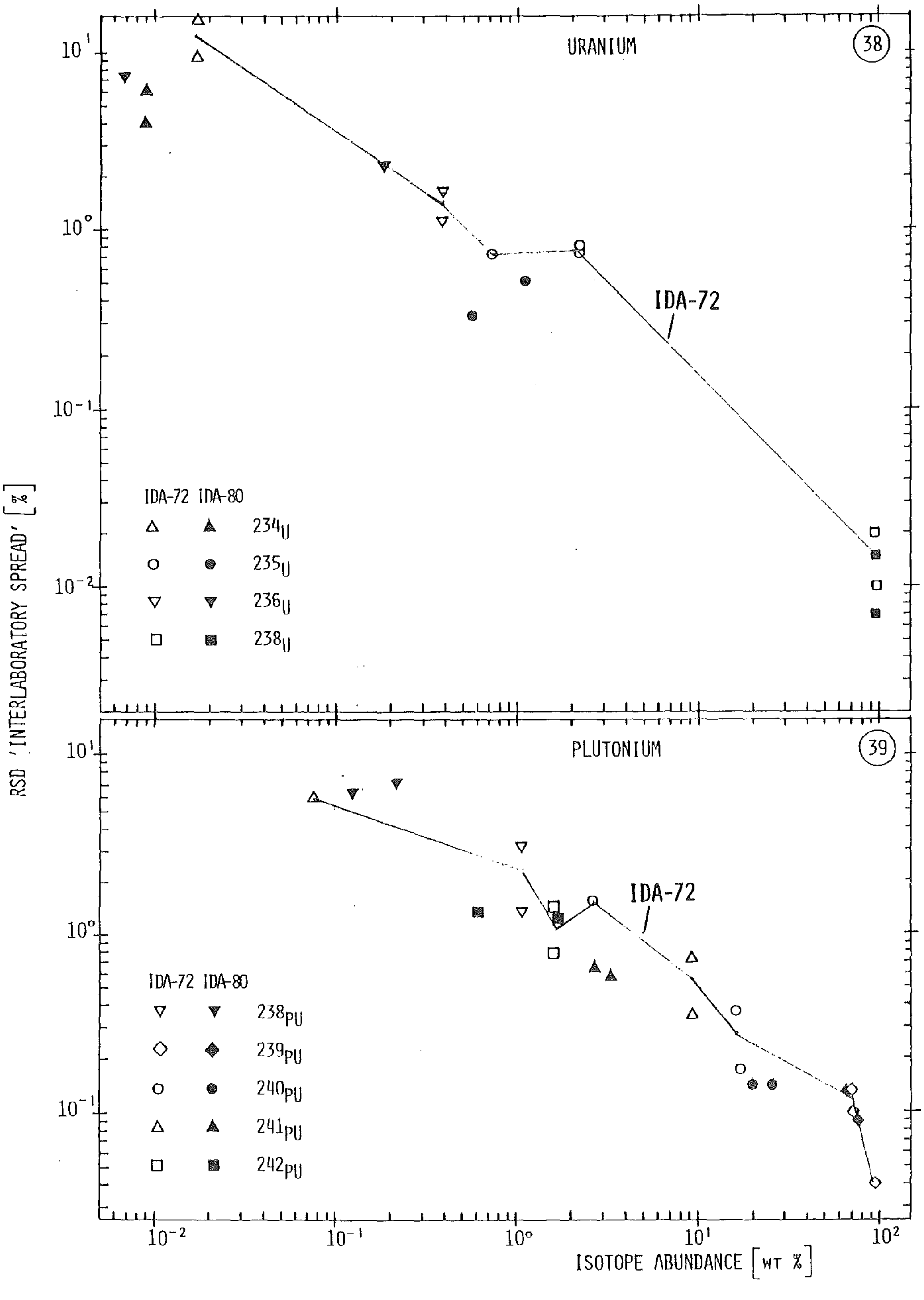
[1] For uranium, these curves are taken from /1/ Fig. 3-28, for plutonium, they were derived from the data points shown in /1/ Fig. 3-29.

[2] The IDA-72 report represents these abundances for uranium in Tabs. 3-11 to 3-13 and for plutonium in Tabs. 3-14 to 3-16.



IDA-80/Figs. 38 to 39:

Interlaboratory spreads of uranium and plutonium abundance determinations estimated from IDA-72 and IDA-80 data

IDA-80/TAB. XLV: COMPARISON OF ESTIMATED UNCERTAINTY COMPONENTS OF CONCENTRATION DETERMINATIONS ON PRESPIKED SAMPLES IN IDA-72 AND IDA-80

	1	2	3	4	5	6	7	8	9
1	ELEMENT OR ISOTOPE	PROGRAMME	TEST-SOLUTION	ESTIMATES OF RSD (%)			NUMBER OF CONTRIBUTING LABS	EXCLUDED EXTREME VALUES (%)	REFERENCE[b]
				RUN	BETWEEN LABS	INTERLAB. SPREAD			
2	URANIUM	IDA-72	A	0.57 (0.60)	0.79 (0.76)	0.86 (0.84)	18	0	3-18
3			B	0.45 (0.33)	0.84 (0.81)	0.88 (0.84)	18	0	
4			R	0.29 (0.31)	0.75 (0.87)	0.77 (0.88)	18	0	
5		IDA-80	B	0.18 (0.18)	0.52 (0.52)	0.53 (0.53)	30	17	70
6			R	0.18 (0.14)	0.32 (0.40)	0.34 (0.41)	28	14	72
7	PU-239	IDA-72	A	0.52 (0.60)	0.45 (0.00)	0.54 (0.20)	17	18	3-19
8			B	0.66 (0.46)	0.48 (0.50)	0.61 (0.56)	17	24	
9			R	1.79 (0.63)	2.59 (1.72)	2.79 (1.76)	17	12	
10		IDA-80	B	0.31 (0.20)	0.24 (0.38)	0.30 (0.40)	29	21	80
11			R	0.36 (0.60)	0.31 (0.15)	0.37 (0.38)	27	11	84

a) VALUES IN BRACKETS ARE BASED ON THE DATA OF 11 LABORATORIES PARTICIPATING IN BOTH PROGRAMMES

b) FOR IDA-72 DATA, TABLE NUMBERS IN /1/ ARE GIVEN, FOR IDA-80 DATA EVALUATION SHEET NUMBERS IN VOL. III /10/

IDA-80/TAB. XLVI: COMPARISON OF ESTIMATED UNCERTAINTY COMPONENTS OF CONCENTRATION DETERMINATIONS ON UNSPIKED SAMPLES IN IDA-72 AND IDA-80

	1	2	3	4	5	6	7	8	9
1	ELEMENT OR ISOTOPE	PROGRAMME	TEST SOLUTION	ESTIMATES OF RSD (%)			SUCCESSFUL PARTICIPANTS	PERCENTAGE OF EXTREME VALUES EXCLUDED	REFERENCE[b]
				RUN	BETWEEN LABS.	INTERLAB. SPREAD	FRACTION/PERCENTAGE[a]		
2	URANIUM	IDA-72	R	0.41	0.81	0.84	10 OUT OF 22 / 45	0.0	4-4
3		IDA-80	R	0.26	0.46	0.48	22 OUT OF 31 / 71	21.4	71
4			B	0.37	0.69	0.72	28 OUT OF 31 / 90	6.7	68
5	PU-239	IDA-72	R	1.75	5.82	5.91	9 OUT OF 22 / 41	10.0	4-5
6		IDA-80	R	0.28	1.27	1.28	23 OUT OF 31 / 74	11.5	82
7			B	0.38	0.75	0.79	26 OUT OF 31 / 84	7.1	76

a) CALCULATED ON THE BASIS OF ALL 22 AND 31 PARTICIPANTS IN IDA-72 AND IDA-80, RESPECTIVELY

b) FOR IDA-72 DATA, TABLE NUMBERS IN /1/ ARE GIVEN, FOR IDA-80 DATA EVALUATION SHEET NUMBERS IN VOL. III /10/

Observations:

a) All IDA-80 data points of the 'SCAN' and 'RUN' uncertainty components are below the IDA-72 curves for isotope ratio determinations of uranium, demonstrating clearly a reduction of these uncertainties by - roughly - a factor of 2 (Figs. 32 and 33). For the 'BETWEEN LABs' component (see Fig. 34), 78 % of the data points are below the IDA-72 curve, also indicating an improvement.

b) For plutonium isotope ratio determinations, 83 % of the IDA-80 data points of the three uncertainty components considered are below the IDA-72 curves, indicating considerable improvement also for the measurement of this element (Figs. 35 to 38).

c) Also for isotope abundance determinations, the majority of IDA-80 data points are below the interconnection lines of the IDA-72 data points for uranium as well as for plutonium indicating a general reduction of measurement uncertainties (Figs. 38 and 39).

d) Smaller estimated uncertainties were calculated for the concentration determinations of prespiked sample materials, for both uranium and plutonium from data obtained in IDA-80 (roughly 50 %) (Tab. XLV). For plutonium, where no reduction of the 'BETWEEN LABs' uncertainty component was observed for the isotope ratio measurements (see Fig. 37) this improvement in the element concentration determination may indicate that the redox treatment of the prespiked samples was performed more satisfactorily than in IDA-72.

The percentage of extreme values for plutonium is approximately equal in both experiments. For uranium, however, about 16 % had to be eliminated in IDA-80 but none in IDA-72 (see column 8).

e) The decreased measurement uncertainties in IDA-80 as compared to the results of IDA-72 for the analysis of unspiked samples are evident (see Tab. XLVI, columns 4 to 6)[1]. The percentages of rejected extreme values for uranium and plutonium (column 8) are similar to those observed for the analysis of prespiked samples (see Par. d).

f) The improvement of the overall measurement capability is in particular obvious from the data compiled in column 7 of Tab. XLVI representing the increased number of laboratories which performed the analysis of unspiked sample material 'successfully', which means that they produced no outlier values.

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[1] The improvement for plutonium may be overestimated due to a particular outlier situation.

9. Summary of main observations

9.1 Overall performance data

9.1.1 About one third of the values reported by the participants for the element concentrations and isotope abundances are within the uncertainty ranges of the agreed certified values for both uranium and plutonium. Negative deviations predominate for Pu-241 abundance values indicating unsatisfactory decay corrections (Chapt. 4).

9.1.2 Comparison with the IDA-72 programme shows that the number of laboratories capable of performing isotope dilution analysis of uranium and plutonium sucessfully has about doubled during the last decade, whereas the spread of their results decreased - very roughly - to about one half. Improved instrumentation and increased experience in sample preparation techniques are obviously the main reasons for this positive development (Chapt. 8).

9.1.3 About 70 % of the medians of isotope ratio, isotope abundance and concentration values are within the uncertainty ranges of the agreed certified values (Chapt. 7.5).

9.1.4 For the isotope ratio and abundance determinations there is a tendency for all uncertainty components considered to increase with decreasing value of the ratio/abundance. Exceptions are the measurement uncertainties of uranium isotope ratios between 0.01 and 1 which seem to be constant. The total measurement uncertainty is mainly governed by the between-laboratory-uncertainty component. Influences of the 'SCAN' uncertainty component ('internal' reproducibility of mass spectrometric measurement) show up at the measurement of low abundant isotopes only (below 0.1 %) (Chapts. 5.2 and 5.3).

9.1.5 From all data, overall measurement uncertainties can be estimated for element concentration determinations as: ±0.6 % for uranium and ±1.0 % for plutonium (Chapt. 6.2). They are mainly determined by laboratory biases (Chapt. 5.4).

9.1.6 The determination of minor isotope abundances (<0.01 %) yields the observation that for both single and multiple stage mass spectrometers about the same fraction of the results are within the uncertainty ranges of the agreed certified values: 35 % and 42 % respectively (Chapt. 7.10).

9.1.7 Good results for the measurements on liquid samples containing fission products (as opposed to dried and fission-product-free sample material), even after storage times of more than one year, are not in accordance with any hypothesis of 'ageing' (Chapts. 6.1 and 6.2).

9.1.8 No part of the programme indicates any detrimental effect of fission products on the measurement uncertainties of uranium and plutonium (Chapts. 5, 6.2). (On the contrary more care applied in the preparation of samples to remove fission products leads to better measurements.)

9.1.9 Abundance and concentration values reported by the laboratories deviate surprisingly often from those calculated by the evaluation team on the basis of the reported isotope ratio data; in some cases the differences are larger than 1 %.

The interlaboratory spreads of the reported data are in most cases higher than for those calculated by the evaluation team. The medians of the evaluation team data deviate generally by the same amount or even less from the agreed values.

Possible reasons are
- use of different basic data sets
- use of different physical constants (half-life values etc.)
- insufficient decay corrections
- transcription and calculation errors
- rounding errors

(Chapt. 7.3).

9.1.10 The FeII/$NaNO_2$ and the $NH_2OH \cdot HCl/HNO_3$ methods are most often applied as redox procedures and about 80 % of the participants use anion exchange for element separation. From the information available, no statistically significant correlation can be derived between the application of specific sample preparation methods and the analytical performance achieved (Chapt. 3.2).

9.1.11 More than 60 % of the mass spectrometers used were brought into operation after the IDA-72 programme. The majority of all instruments are equipped with electron multipliers or ion counting systems for ion detection. About 50 % of the laboratories reported fully computerized systems, about 30 % semi-computerized ones (Chap. 3.3).

9.2 Uncertainty sources

9.2.1 For isotope ratios below 10^{-1} the quality of Pu isotope ratio data is poorer than those achieved on similarly sized U ratios. Possible reasons are:

- smaller samples
- the use of ion multipliers
- the unavailability of suitable reference materials.

One laboratory could show that up to 0.4 % errors can be made with the Daly detector (Chapt. 5.2 and App.A).

9.2.2 In the correction for Pu-241 decay, the date of mass spectrometric measurement yields more reliable results than the date of the americium separation. However the time interval between both should be kept below one week (Chapt. 7.2).

9.2.3 The uncertainty components of the concentration determination of uranium are of the same size. In the case of plutonium, spike calibration is apparently a major source of error.
Possible reasons for this are:

- lack of control of the isotope fractionation
- incomplete redox procedure
- incomplete dissolution of samples
- lack of appropriate reference material

(Chapt. 6.2).

9.2.4 Several evaluation results indicate the presence of measurement uncertainties due to mass-dependent error sources such as e.g. isotope fractionation in the ion source (Chapt. 7.6).

Only 60 % of the laboratories calibrate with isotopic reference materials to correct for mass dependent bias effects (Chapt. 3.4).

9.2.5 Isotopic contamination of samples and spikes during element separations is likely to be a possible source of error (App.A).

9.2.6 When using externally calibrated spikes, measurement uncertainties may be introduced due to non-compensation of isotope fractionation effects (Chapt. 7.6).

9.2.7 Traces of Pu-239 in U-233 spike material cause errors when separate uranium and plutonium spikes are added to the same sample aliquot or when they are mixed without recalibration (Chapt. 7.8).

9.3 Specific techniques

9.3.1 Dried sample aliquotes proved to be successfully. Some laboratories, however, encountered difficulties in quantitative redissolution of the sample material (Chapt. 6.1).

9.3.2 The performance data obtained for the metal spike technique are comparable to those of spiking with solutions of dissolved spike material. Application for verification purposes shows advantages (Chapt. 6.3 and App.A).

9.3.3 The percentage of extreme values in the metal spike technique is considerably smaller than for spiking with solutions of dissolved spike material. Possible reasons are the complete chemical reduction of plutonium by the uranium metal and the absence of a dilution step of the unknown sample. There is also no evidence for incomplete dissolution of the metal spike (Chapt. 6.3 and App.A).

9.3.4 Both mass and α-spectrometry have been applied successfully for the determination of Pu-238 abundances in the investigated abundance range (a few tenths of a percent). The majority of laboratories used α-spectrometry (Chapt. 3.5).

9.4 Data handling

9.4.1 During generation and transfer of the data from the laboratories to the evaluation site an error rate of 0.15 % was observed. In punching data for computer input, an error rate of 0.07 % relative to the number of punched digits was noted (Chapt. 7.1).

9.4.2 Two thirds of the laboratories reported the application of outlier criteria to their measurement data; 50 % of them used the Dixon criterion (Chapt. 3.4).

9.4.3 Applying the criteria of this programme, 12 % of the uranium measurements and 9 % of the plutonium measurements had to be rejected as outliers. They were observed with 71 % of the participating laboratories. These rates were smaller (but not zero) for 'more experienced' laboratories. (Chapt. 7.4)

9.4.4 A standard format of data collection is required to make a meaningful data analysis possible. However, the collection format used in IDA-80 may not be appropriate for use with current instrumentation operating under computer control, since the programmes may be different for different instruments (some of the discrepancies between the participants' reported values and those calculated by the evaluation team, may have their origine here; see 9.1.9).

10. Recommendations

10.1 Safeguards and general aspects

10.1.1 A continuous quality control programme for isotope dilution analysis, open to international participation, should be established.

10.1.2 It is proposed to the ESARDA-WGDA[1]

- that the results of IDA-80 be used to work out optimized procedures for sample preparation, spiking, chemical separation and mass-spectrometric measurements,
- that its conclusions from IDA-80 be presented to ISO[2] and that comments be made on an ISO-procedure, presently undergoing approval.

10.1.3 Certified tracers, including mixed U- and Pu-tracers, in solution and metal alloy form, should remain or become available, and their use as 'common spike' is recommended.

10.1.4 Isotopic reference materials, in particular for plutonium, should urgently be made available to correct for isotope fractionation and non-linearity of measurement systems.

The following proposals were made:

- Isotope mixture of Pu-239/Pu-244 or Pu-239/Pu-242 1:1
- Pu-isotopic reference materials:

Pu-239		Pu-242		Pu-244
1	:	1	:	1
10	:	1	:	1
100	:	1	:	1
1000	:	1	:	1

- Isotopic mixture of U-233 : U-235 : U-238

  1 : 1 : 1

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[1] Working Group on Destructive Analysis of the European Safeguards Research and Development Association.

[2] International Standards Organization

10.1.5 Certified unspiked reference materials similar to the 'R'-solution should be made available.

10.1.6 CBNM should prepare and characterize metallic spikes with plutonium contents accurate to 0.1 %.

10.1.7 To further improve mass spectrometric measurements special attention should be paid to the ongoing developments in internal calibration techniques.

10.1.8 Any isotopic analysis involving radioactive nuclides should carry the date of measurement. When comparing data a correction for radioactive decay must be made.

10.1.9 When preparations for a next IDA programme are initiated, a survey should be made of participants' data collection formats to see if the required data can be taken under the same conditions or, at least under conditions close to those normally used.

10.2 Analytical aspects

10.2.1 The isotopic contamination of samples and spikes during chemical preparation of samples for isotopic measurements should be rigorously avoided. Work under controlled conditions and use large samples.

10.2.2 Treat systematic errors individually and not 'piled up'.

10.2.3 Use a calibrated common spike; however, be careful that no measurement uncertainties are introduced due to uncompensated isotope fractionation effects (see 10.2.5).

10.2.4 Use a U/Pu spike solution which has been calibrated as mixture or, if separate U and Pu spike solutions are used, proceed with different spikings, chemical treatments and measurements for each element.

10.2.5 Make careful determinations of the mass fractionation at regular intervals using isotopic reference materials of the same elements. This calibration should be done on isotope ratios and not abundances. Linearity of the isotope fractionation effect versus mass difference is not fully established by experiment. Consequently use a reference material with the same mass difference as in your sample to avoid unprecise extrapolation (or interpolation).

10.2.6 Determine the non-linearity of the measurement system.

10.2.7 Plutonium isotopic measurements should be done within a week after the Pu/Am separation. The use of the date of mass spectrometric measurement is preferable to the date of Am-separation as reference date. For Pu-241 decay corrections, the IAEA half life value of 14.4 ± 0.2 a can be used. However, CBNM uses 14.33 ± 0.02 a and NBS uses 14.34 ± 0.04 a.

10.2.8 If quantitative redissolution of dried sample materials is required, the following procedure is recommended:

a) Dry samples at $\leq 90^{o}C$ from a solution of $HNO_3 \geq 3$ M.

b) To redissolve: simmer under reflux with a mixture of $HNO_3 \geq 7$ M HF 0.05 M at $100-115^{o}C$, possibly not in glass.

10.2.9 In the measurement of low-abundant isotopes (below 0.1 %), special consideration should be given to the shape of the baseline and in particular to the selection of suitable points to measure this baseline. Measurement system linearity, time constant effects, isobaric interferences and ion-multiplier discrimination are also important sources of error.

10.2.10 Buoyancy corrections: usually errors due to the lack of buoyancy correction will cancel when a laboratory does its own spike calibration. This does not happen with a common spike. Therefore, correct in this case for air buoyancy and for the errors in any own spike calibration.

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Appendix A

Documents of the IDA-80 Participants' Meeting held at Karlsruhe on March 27/30, 1984

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A-1

CBNM/Geel KfK/Karlsruhe

IDA-80 Interlaboratory Measurement Evaluation Programme
Participants' Meeting

Kernforschungszentrum Karlsruhe, March 27-30, 1984

AGENDA

Tuesday, March 27

8.15 - 8.30	Bus from hotels	
9.00	Registration	
9.30	Welcome addresses	D. Gupta, KfK R. Lesser, CBNM
10.00	General introduction	W. Beyrich, KfK P. De Bièvre, CBNM
10.30	Break, registration (cont'd)	
11.00	Session I: Determination of isotope ratios and abundances as well as associated problems (e.g. corrections for decay)	
	Chairman:	J. Dalton, BNFL
	Co-Chairman:	P. De Bièvre, CBNM
	Secretaries:	G. Spannagel, KfK M. Gallet, CBNM
	Introduction:	G. Spannagel, KfK
12.30	Lunch	
13.30	Session I (cont'd)	
15.00	Break	
15.30	Session I (cont'd)	
17.00	Adjourn	
17.30	Cocktails	
	(Bus to hotels at 19.30h)	

Wednesday, March 28

8.15 - 8.30	Bus from hotels	
9.00	Session II: Concentration determinations of solutions R and B; liquid spiking procedure, dried sample technique and associated problems	
	Chairman:	R. Berg, WAK
	Co-Chairman:	M. Lucas, CEN (Saclay)
	Secretaries:	R. Wellum, TUI B. Stojanik, WAK
	Introduction:	W. Golly, KfK
10.30	Break	
11.00	Session II (cont'd)	
12.30	Lunch	
13.30	Session II (cont'd)	
	Chairman:	L. Koch, TUI
	Co-Chairman:	D. Thiele, BAM
	Secretaries:	R. Wellum, TUI K. Henn, WAK
15.00	Break	
15.30	Session II (cont'd)	
17.00	Adjourn	
17.15	Bus to hotels	

Thursday, March 29

8.15 - 8.30	Bus from hotels	
9.00	Session III: Concentration determinations of solution A; metal spike technique and associated problems	
	Chairman:	P. Doutreluingne COGEMA (Marcoule)
	Co-Chairman:	S. Deron, IAEA
	Secretaries:	G. Spannagel, KfK H. Wertenbach, KfK
	Introduction:	W. Golly, KfK
10.30	Break	
11.00	Session III (cont'd)	
12.30	Lunch	
13.30	Session IV: Characterization, preparation and transport of samples and formalities; special topics (e.g. calculation of isotope abundances, errors in calculating and data transfer, open questions etc.)	
	Chairman:	P. De Regge, SCK/CEN
	Co-Chairman:	W. Lycke, CBNM
	Secretaries:	E. Foster, AERE K. Henn, WAK
	Introduction:	W. Wolters, CBNM
15.00	Break	
15.30	Session IV (cont'd)	
17.00	Adjourn	
17.15	Bus to hotels	
19.30	Dinner	

Friday, March 30

8.15 - 8.30	Bus from hotels	
9.00	Session V: IDA-80 compared to IDA-72	
	Chairman:	J. Van Raaphorst, ECN
	Co-Chairman:	E. Mainka, KfK
	Secretaries:	W. Golly, KfK G. Spannagel, KfK
	Introduction:	W. Beyrich, KfK
10.30	Break	
11.00	Session VI: Summary of conclusions prepared in the foregoing sessions, recommendations	
	Chairman:	P. De Bièvre, CBNM
	Co-Chairman:	W. Beyrich, KfK
	Secretaries:	W. Golly, KfK G. Spannagel, KfK
12.30	Closing remarks	D. Gupta, KfK
13.00	Lunch; end of the meeting	
14.00	Bus to main railway station and to hotels	
14.00 - 17.00	Possibility of visits to WAK, KfK, TUI	
17.00	Bus to main railway station and to hotels	

List of persons attending

ADACHI, T.	JAERI, Tokai-Mura, Japan
BAUMANN, S.	NUKEM, Hanau, F.R. Germany
BERG, R.	WAK, Karlsruhe, F.R. Germany
BEYRICH, W.	KfK, Karlsruhe, F.R. Germany
BODEN, R.	SCK/CEN, Mol, Belgium
CALLIS, E.L.	ANL, Argonne, Il., USA
CESARIO, J.	CEN, Saclay, France
CRAWFORD, D.W.	NBL, Argonne, Il., USA
DALTON, J.C.	BNFL, Windscale, UK
DE BIEVRE, P.	CBNM, Geel, Belgium
DE REGGE, P.	SCK/CEN, Mol, Belgium
DENIAUD, S., Ms.	CEA/SCQ, Montrouge, France
DERON, St.	IAEA, Wien, Austria
DEURLOO, P.A.	ECN, Petten, Netherlands
DOUTRELUINGNE, P.	COGEMA, Marcoule, France
FALTA, G.	ÖFZ, Seibersdorf, Austria
FOSTER, E.	AERE, Harwell, UK
GALLET, M.	CBNM, Geel, Belgium
GOLLY, W.	KfK, Karlsruhe, F.R. Germany
GRAMLICH, J.W.	NBS, Washington, D.C., USA
GUPTA, D.	KfK, Karlsruhe, F.R. Germany

HAREMAKER, H., Ms.	ECN, Petten, Netherlands
HENN, K.H.	WAK, Karlsruhe, F.R. Germany
KIRCHNER, H.	KFA,Jülich, F.R. Germany
KOCH, L.	TUI, Karlsruhe, F.R. Germany
KUHN, E.	IAEA, Wien, Austria
LAFON, H., Ms.	COGEMA, Marcoule, France
LARSEN, E.	RNL, Roskilde, Denmark
LAUG, M.T.	ANL, Idaho Falls, USA
LESSER, R.	CBNM, Geel, Belgium
LUCAS, M., Ms.	CEN, Saclay, France
LYCKE, W.	CBNM, Geel, Belgium
MAINKA, E., Ms.	KfK, Karlsruhe, F.R. Germany
MOGENSEN, M.	RNL, Roskilde, Denmark
NÄGELE, G.	KfK, Karlsruhe, F.R. Germany
OKAZAKI, S.	JAERI, Tokai-Mura, Japan
PICHLMAYER, F.	OFZ, Seibersdorf, Austria
RAMSDEN, C.N.	BNFL, Windscale, UK
ROSMAN, K.*	CBNM, Geel, Belgium
RUST, W.	KfK, Karlsruhe, F.R. Germany

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*on leave at CBNM from the Australian Institute of Technology

SANTNER, E.	BAM, Berlin, F.R. Germany
SPANNAGEL, G.	KfK, Karlsruhe, F.R. Germany
STOJANIK, B.	WAK, Karlsruhe, F.R. Germany
THIELE, D.	BAM, Berlin, F.R. Germany
TYRELL, A.C.	AWRE, Aldermaston, UK
VAN RAAPHORST, J.G.	ECN, Petten, Netherlands
WELLUM, R.	TUI, Karlsruhe, F.R. Germany
WERTENBACH, H.	KfK, Karlsruhe, F.R. Germany
WOLTERS, W.	CBNM, Geel, Belgium

A-9

Minutes of the Meeting

The minutes of the sessions are presented as a list of topics with comments made on them by the evaluation team (ET) and the participants (P).

Session I

Tuesday, March 27, 1984

Topic: Determination of ratios and abundances

Chairman:	J. Dalton, BNFL, Windscale
Co-Chairman:	P. De Bièvre, CBNM, Geel
Secretaries:	M. Gallet, CBNM, Geel G. Spannagel, KfK, Karlsruhe

1. Data collection format:

   ET. This format was chosen to place the data from the different laboratories on the same basis so that comparable evaluation would be possible.

   P. The choice of format did not take into account the existence of automated equipment.

   ET. Some of the discrepancies observed between the reported values and those calculated by the evaluation team may be due to the use of this format.

2. The high U-234/U-238 ratio(Fig. C-6)[1]:

   ET. Abundance sensitivity (baseline)
   P. Data collection measurement sequence (...238/234..., i.e. time constant)

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[1] This corresponds to Evaluation Sheet 4 in Vol. III /10/.

P. Difficulties with small signals

P. Problems with filament material (e.g. recycling of Re containing U, isobaric interferences (K_6 ?))

3. The U-235/U-238 measurements in the BU and BS solutions: the interlaboratory spread of this ratio is large compared to the measurement precisions. (Figs. C-7 and C-17[1]).

ET. Isotope fractionation

P. 235-contamination during the processing of the sample.

4. Determination of Pu-238 by α- and mass spectrometry:

ET. Similar accuracies can be attained by both methods.

P. The certified value is significantly lower than the participants' values (α- and mass spectrometry) for the RU-samples.

5. The quality of Pu isotope ratio data: The Pu data showed greater inaccuracies than similarly sized U-ratios.

ET. Smaller samples were being measured yielding smaller ion currents.

P. Use of ion multipliers for the smaller ion currents.

P. Lack of suitable reference materials for Pu, i.e. bias correction factors could not be determined.

6. Systematic bias for U-235/U-238 and Pu-242/Pu-239 ratios:

ET. The U-235/U-238 ratio is high and the Pu-242/Pu-239 ratio is low compared to the corresponding certified value, which is consistent with lack of control of the isotope fractionation.

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[1] These correspond to Evaluation Sheets 5 and 9 in Vol. III /10/.

7. Decay corrections for Pu.

ET. Participants had been requested to report their isotope ...

(a) ratios corrected for known systematic errors but not corrected for radioactive decay,

(b) abundances valid for general reference date of February 9, 1980.

A consistent set of half life data for Pu nuclides was not supplied by the organizers (on purpose) so that each laboratory had to choose its own values.

P. Pu-238-isotope ratios should be back-corrected to the date of the measurements. Pu-241-measurements should be made less than one week after the chemical separation because of the production of interfering Am-241 from the decay of Pu-241 ($T_{1/2}$ = 14.4a).

All results should be corrected for radioactive decay in the isotope ratios rather than in the abundances.

8. Graphical presentation of pure spike (SUP) isotopic data:

ET. Only with a strong recommendation from the meeting could consideration be given to this request[1].

9. Evaluation of sources of systematic error by the ET.

The participants requested that specific sources of systematic errors in participants' calculations and measurements be identified.
ET. Same answer as 8.[2]

10. Sample preparation.

Accurate mass-spectrometry requires careful chemical processing of the samples.

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[1] see Chapt. 5.2 of this Report

[2] Some contributions are given in Chapt. 7 of this report.

Session II

Wednesday, March 28, 1984
(morning)

Topic: Concentration determination of solutions R and B

Chairman: R. Berg, WAK, Karlsruhe
Co-Chairman: M. Lucas, CEN Saclay
Secretaries: B. Stojanik, WAK, Karlsruhe
R. Wellum, TUI, Karlsruhe

U-Concentrations

1. Large differences exist between some results reported by the participants and the corresponding values calculated by ET.

   - computational errors (rounding)
   - transcription errors
   - use of wrong nuclear constants or not using them at all. (ET described the double punching method used to minimise the likelihood of errors).

2. Larger deviations from the certified values were found for dried samples than for liquid samples.
   A bias towards lower concentrations (negative bias) occurs which could be due to incomplete dissolution of the sample.

3. Measurements were poorer for the R-solution than for the B-solution. This could result, from better chemical preparation of the B-samples for isotopic measurements because of their fission products. Most of the represented laboratories indicated that chemical separation was performed$^{1)}$.

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1) A written inquiry to all laboratories after the Participants' Meeting was answered by 20 laboratories. 4 of them did not confirm sample purification in the case of the R samples.

4. Poorer results were obtained on pre-spiked samples with a negative bias for U and a positive bias for Pu. This may be caused by isotope fractionation effects which do not fully cancel when supplied spike is used (vs own calibration).

5. Uncertainty components of U-determination have similar size. To achieve a significant improvement it will be necessary to reduce all uncertainty components.

6. It was proposed that lab-orientated criteria be applied to outlier selection.
   ET. Not possible for principle reasons (decoding danger!).

Plutonium concentrations

7. The experience of one laboratory showed that sources of systematic errors of ≈0.4 % could be attributed to a Daly multiplier. This was identified using synthetic mixtures of Pu-isotopes.

8. Reference materials are needed for Pu-calibration.
   Pu-239/Pu-242 1:1 being prepared this year (NBL)
   Pu-239/Pu-244 1:1 available from CBNM in limited supply.

   Availability of such reference materials is vital to the mass-spectrometry community.

9. Statistical analysis of B-sample for Pu showed inhomogeneities (3 groups were observed)[1].
   - certain labs consistently experienced difficulties with Pu.

10. Analysis using CBNM spike gave a negative bias of ≈0.2 % for U and a positive bias of ≈0.1% for Pu.

11. Isotope fractionation effects are much more ubiquitous than is generally accepted. These are not dependant on concentration or abundances but only on mass. Systematic effects must be individually identified and corrected for.

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[1] see Ref. /16/ of this Report.

Session II

Wednesday, March 28, 1984
(afternoon)

Topic: Concentration determination of solutions R and B

Chairman: L. Koch, TUI, Karlsruhe
Co-Chairman: D. Thiele, BAM, Berlin
Secretaries: R. Wellum, TUI, Karlsruhe
K. Henn, WAK, Karlsruhe

Comparison of B and R solutions

1. Interlab errors were greater for the R than the B solution.
   - may be due to more intensive chemical treatment of B solutions because of the presence of fission products and the necessity to clean them[1].

2. Is the physical state of the R and B solutions different?
   - Pu for R solution was dissolved in HNO_3/HF
   - filtering was done on B solution, not on R which was clear.
   - however residues on filters were very small.
   - influence of outliers? To be checked by ET.[2]

Comparison of liquid and dried samples

3. Certain laboratories achieved low values for Pu in the dried samples.
   - dissolution problems due to lack of heating. Recognition of these problems is important in the transmission of dried spikes/samples. A recommendation for dissolution method is wanted for Friday (see page A-30, par. 6.2).

4. Are deviations from certified values for Pu in dried B-samples due to instrumental effects for the "good" labs?

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[1] A written inquiry to all laboratories after the Participants' Meeting was answered by 20 laboratories. 4 of them did not confirm sample purification in the case of the R samples.

[2] Cannot be explained by outliers only. See Evaluation Sheets 77 and 83 in Vol.III /10/.

5. The fact that results for liquid B samples (1.11) are at least as good as for dried samples (1.12) eliminates reasons to look for 'ageing' effects of Pu-solution.

Reference solution R

6. Interlaboratory spread for Pu-concentrations in the R-solution using own spike was unexpectedly high.
   The spread was lower when using CBNM spike.

7. Calibration of the labs' own Pu-spikes is apparently a major source of error.
   - isotope fractionation
   - systematic errors in spike calibration
   - incomplete redox for spike calibration
   - Pu metal reference material NBS 949e is widely used. It is known to better than 0.1 %.

8. Why can the U-spike be calibrated better than Pu-spike?
   - problems in dilution and standardisation.
   - different calculation procedures by different labs?
   - Pu traces in U-spike interferes when mixed spikes are used.
   - use of common spike is advised in order to identify sources of systematic errors in laboratories.

9. The contamination of samples or spikes during chemical preparation work prior to isotopic measurements was also discussed as a possible source of error.

10. A procedure to check/confirm LOS spike values should be worked out[1].

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[1] see Chapt. 7.8 of this Report.

A-16

Session III

Thursday, March 29, 1984
(morning)

Topic: Concentration determination of solution A

Chairman: P. Doutreluingne, COGEMA
Co-Chairman: S. Deron, IAEA
Secretaries: G. Spannagel, KfK
H. Wertenbach, KfK

1. The higher Pu-concentrations observed in the case of metal spiked samples.
   - The chemical purity of the Pu-242 was not as high as expected; this would alter the certified value slightly.
   - Homogeneity; the contribution from this effect is considered negligible.
   - isotope fractionation
   - incomplete digestion of the metallic spike (cannot be maintained as cause).
   - incomplete isotopic homogenisation of the spike with the sample (idem).

2. Time needed for the dissolution of the metal spike:
   - IDA-80 organizers used 4 hours but one hour was considered sufficient for complete dissolution.
   - Some participants expressed concern regarding the formation of gelatinous precipitates during the dissolution of the spike. Other participants never observed such precipitates when using metal spiked samples.

3. Extent of use of the metal spike technique.
   Its use is not as extensive as might be expected because of erroneous but wide spread opinions that
   (a) U-233 gives better accuracy,
   (b) the higher the isotopic enrichment the greater the accuracy of measurement.

4. The nature of the precipitate formed during digestion of the metal spike. Some participants had determined the composition of the precipitate (U and Pu content was negligible).

5. Isotope fractionation.
   The consistency between errors for Pu- and U-concentrations indicated that isotope fractionation could be an important factor.

6. Participants agreed that interlaboratory spreads were of similar magnitude for U and Pu in the case of B-, R- and A-solutions.

7. Extensive discussions ensued regarding the best method for determining U and Pu in practice.

8. Advantages and disadvantages of the metal spike procedure are given in the attached table1).

9. Sources of error in the redox step can be avoided by the metal spike procedure. The excess uranium reduces all plutonium to the same valency state.

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1) see page A-30, par. 6.1

Session IV　　　　　　　　Thursday, March 29, 1984

Topics: Characterisation, preparation and transport of samples and formalities; special topics

Chairman:	P. De Regge, SCK/CEN, Mol
Co-Chairman:	W. Lycke, CBNM, Geel
Secretaries:	E. Foster, AERE, Harwell
	K. Henn, WAK, Karlsruhe

1. Characterisation of samples

   Six samples of the input solution were taken for the characterisation. Discussion between characterisation laboratories were lengthy and values for the samples were established over a period of time. There were no significant differences except for rounding errors. Agreements between the laboratories was 0.15 % or better. Only one jointly agreed value was released by the characterizing laboratories. Each characterizing laboratory calculated its uncertainties by normal propagation methods.

   The meeting recommended that the uncertainty calculations used by the two characterizing laboratories should be published in the final report together with the magnitude of each uncertainty component[1].

   The reproducibility of the two certifying laboratories was more than ten times better than the interlaboratory spread of results in all cases except for Pu-238.

2. Transportation of samples

   An account of the transportation of the samples was given by representatives of TRANSNUBEL (TNB), Belgium.

   IAEA 1973 revised regulations were adhered to. Member states' own regulations also had to be met.

   Type B containers were used for the IDA-80 samples.

   These were transported by land, sea and air including a type B container to Japan by air.

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[1] see Vol. II /9/.

3. Special topics

3.1 Comparison of results from participating laboratories for the dried samples AS I, II, IV and VI with individual results obtained on these by the characterizing laboratories will be included in the final report[1].

3.2 Analysis of the residue from fuel dissolution showed it to contain more than 50% zirconium compound (but of this only 2% was fission product-zirconium). Other components were 20% $(Cs,Rb)_3\ P(Mo_{17}O_{40})$, 10% H_3BO_3, 2% Te,Tc, 2% Ru,Pb and 15% chemical loss, but very little plutonium, uranium and americium from the high burn up.
The particle size was mostly 10-25 microns and was hence removed by the 0.4 micron filter used.

3.3 Some of the residue in the metal spike experiment may be due to HF attack on glass. The final solution contained approximately 0.1 M HF.
No other anions which would complex plutonium, other than nitrate, phosphate or borate are present in the fuel solution.
Inhomogeneity is extremely unlikely in the IDA-80 solution because of the good reproducibility of the many aliquots used by the characterizing laboratories.
Equilibration of sample and tracer solutions appears to work very well, whether oxidation or reduction steps were or were not used in chemical preparation by participants.
A number of laboratories have analyzed solutions that have been stored several years after the first analysis and found no 'ageing' effects.
The spiking followed by equilibration, if carried out as soon as possible after dissolution of the sample, will ensure 'freezing' of the sample/spike ratio despite solution changes thereafter. Metallic spikes have been used 'in field' at Marcoule from 1979 to 1983. The solution was filtered with a 0.4 micron filter. It was dissolved in concentrated nitric acid and hydrofluoric acid at 90° C. The volume was 6-8 ml, sputtering losses were not observed and no residue was seen.

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1) see Chapt. 6.3 of this Report.

Session V   Friday, March 30, 1984

Topic: IDA-80 compared to IDA-72

Chairman:	J. Van Raaphorst, ECN
Co-Chairman:	E. Mainka, KfK
Secretaries:	W. Golly, KfK G. Spannagel, KfK

1. The summary of the preliminary evaluation report, part F was accepted. This reads as follows: "According to the information gained with the two measurement evaluation programmes IDA-72 and IDA-80, the number of laboratories capable of performing isotope dilution analysis of uranium and plutonium successfully has about doubled world wide during the last decade. The spread of their results decreased - very roughly - to about one half. Improved instrumentation and increased experience in sample preparation techniques are obviously the main reasons for this positive development. The spiking procedure remains as one of the critical steps, in particular spike-solution calibration and redox for plutonium analysis."

2. Isotope ratio measurement:
   - In order to improve measurement precision, an improvement in the control of isotope fractionation will be necessary.
   - In order to extend the precision plateau to lower isotope ratios, an improvement in the instrumentation and procedures used will be necessary[1].

3. Isotope ratios of 1:1 are not essential for a good isotope dilution measurement. Care must be taken when this ratio comes into the range of 1:100.

4. The use of a double spike has the potential of improving the measurement precision of U isotope ratios by a factor of 5 to 10.

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[1] See Fig. 20, Chapt. 5.2 of this Report

Session VI Friday, March 30, 1984

Topic: Summarizing observations and recommendations

Chairman: P. De Bièvre, CBNM, Geel
Co-Chairman: W. Beyrich, KfK, Karlsruhe
Secretaries: W. Golly, KfK, Karlsruhe
G. Spannagel, KfK, Karlsruhe

1. Mass Spectrometry

1.1 Data acquisition format

The present data collection format may not be appropriate to current instrumentation which operates under computer control: the computer programmes are different for different instruments.

RECOM: At the time of preparation of a next IDA interlaboratory programme, a survey should be made of participants' data collection formats to see if the required data can be taken under conditions close to those normally used.

1.2 The U-234/U-238 ratio

The values reported for this ratio are generally higher than the certified one. Effects which could lead to these results have been identified as -

- limitations from lack of abundance sensitivity
- general difficulties associated with the measurement of small signals
- interferences from isobaric ions.

RECOM: Consideration should be given to the principal sources of error in the measurement of small ratios. For instance, the shape of the baseline and the selection of suitable points to measure the baseline for the U-234 isotope. Other factors to be considered are measurement system linearity, time constant effects, interferences and ion multiplier discrimination.

1.3 U and Pu isotope ratios

The isotope ratios in general show precisions which are high compared to the interlaboratory spread, while the bias for the U-235/U-238 and Pu-242/Pu-239 is in opposite directions. These results are consistent with problems caused by isotope fractionation.

RECOM: Careful determinations of the isotope fractionation should be made at regular intervals using isotopic reference materials of the same elements.

1.4 The quality of Pu-isotope ratio data is poorer than that achieved on U-ratios of the same size. Reasons given are:

- smaller samples
- the use of ion multipliers
- the lack of suitable reference materials.

RECOM: Pu isotopic reference materials must be made available which would be suitable for determining mass fractionation and measurement system non-linearity.

1.5 The different uncertainty components of U are now approximately of the same size.

1.6 One laboratory could show that up to 0.4 % errors can be made with the Daly multiplier due to its non-linearity.

RECOM: Determine the (non-)linearity of the measurement system.

1.7 A Pu-239/Pu-244 1:1 IRM is vitally needed by the mass spectrometry community.

- CBNM has limited supply of such an IRM.
- NBL announced availability by the end of 1984 of a Pu-239/Pu-242 1:1 reference material.

1.8 Measurements using CBNM spike gave a bias of -0.2% for U and +0.1% for Pu. This may result from residual isotope fractionation errors.

RECOM: Calibration for isotope fractionation should be done on ratios and not abundances, since it is dependent upon mass and not on concentration or abundance.

1.9 Systematic errors.

RECOM: Systematic errors should be individually treated and not 'piled up' and globally corrected.

1.10 Calibration of Pu spike by participants is apparently a major source of error (unsuitable corrections for isotope fractionation, incomplete redox, incomplete dissolution of reference materials).

RECOM: Use a common certified spike (but keep corrections for isotope fractionation in mind).

1.11 Calibrations of U-spikes are apparently better than those of Pu-spikes. Possible reasons:

- traces of U in Pu-spike cause errors when separate U and Pu spikes are mixed by the laboratories and the values of the mixed spike are calculated from the values of the components
- non-availability of 1:1 isotopic reference materials.

1.12 Spike calibration

RECOM: Procedure to check/confirm a laboratory's own spike values should be established1). (PRIORITY 1)

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1) see Chapt. 7.8 of this Report.

1.13 An observation was made that consistency between uncertainties of Pu- and U-concentration values (AS) point to isotope fractionation as a possible error source.

1.14 Participants agree that interlaboratory spreads for uranium as well as for plutonium were of similar magnitudes for R, B and A solutions. Advantages and disadvantages of metallic spike were given as per attached table (see 6.1, page A-30).

1.15 The isotopic composition of a sample is changed by the process of measurement.

RECOM: To further improve mass spectrometry measurements, special attention should be given to the development and utilization of internal calibration techniques.

2. Chemistry

2.1 Dried samples showed accurate medians but larger spreads in the results than the liquids since some laboratories had obviously difficulties in redissolving the dried samples.

RECOM: Pay special care to the dissolution of dried samples; quantitative dissolution is difficult to achieve. A recipe is recommended in par. 6.2, page A-30.

2.2 Mass spectrometrists should have control over the chemical treatment of the samples prior to the isotopic measurement because this treatment contributes to the reproducibility of the isotope fractionation.

2.3 Very careful chemical preparation must be carried out prior to isotopic measurements in order to achieve good precision and accuracy.

2.4 The measurement results for the synthetic R-solution were poorer than for the B-solution (containing fission products)[1).

[1)] A written inquiry to all laboratories after the Participants' Meeting was answered by 20 laboratories. 4 of them did not confirm sample purification in the case of the R-samples.

2.5 Differences between certified and median values were observed on prespiked samples with a negative bias for U and a positive one for Pu.

RECOM: Correct adequately for isotope fractionation.

2.6 The fact that results for liquid B-samples (1.11) are as good as for dried samples (1.12) eliminates the need for hypotheses on 'ageing'.

None of the participants, especially the processing plants' laboratories, could present evidence for inhomogeneities (with respect to U and Pu) of analytical input samples.

RECOM: Where there is evidence of 'ageing' effects or inhomogeneities in samples it should be clearly demonstrated and brought to the attention of the organizers.

2.7 Isotopic contamination of samples and spikes during separations is likely to be a possible source of error.

RECOM: Work under controlled conditions and use big samples.

2.8 Metallic spike characterisation for Pu is not as good as for U.

RECOM: CBNM to prepare and characterize metallic spikes with Pu good to 0.1%.

2.9 There was no evidence for incomplete digestion of metallic spike. Much simpler recipe for successful valency homogeneisation was presented than the traditional procedures.

2.10 Evidence was presented for easy and complete dissolution of metallic spike (1 hour).

2.11 Use of long published metallic spike technique has not been as extensive as expected because of erroneous but widespread opinions such as:

(a) U-233 gives better accuracy

(b) the higher the isotopic enrichment of the spike material the better the accuracy of measurement

(c) metallic spike would be difficult to dissolve (analytical nuclear laboratories have been dissolving U and Pu metal reference material without apparent problems for many years).

(d) sludge in input solutions would contain significant amounts of U and Pu (evidence was presented that this was not the case).

Note: The use of U-233 spike removes the necessity for analyzing an unspiked sample.

2.12 Certified tracers, including mixed U and Pu-tracers, in solution and metal alloy form, should remain or become available and their use as 'common spike' should be recommended.

2.13 A continuous quality control programme for isotope dilution analysis, open to international participation, should be established.

2.14 The IDA-80 results should be used to work out optimum procedures for sample preparation, spiking, chemical preparation and mass spectrometry.

2.15 R-solutions:

RECOM: Certified unspiked materials should be made available with uranium and plutonium compositions similar to reprocessing input solutions.

2.16 Buoyancy corrections: usually errors due to the lack of buoyancy correction will cancel when a laboratory does its own spike calibration. This will not be the case with a common spike.

RECOM: Correct for air buoyancy if externally weighed aliquots are implied.

2.17 Uncertainty ranges of agreed certified values:

RECOM: The method of error calculation used by the two characterizing laboratories should be published in the final report together with the magnitude of each uncertainty component[1].

2.18 The reproducibility of the two certifying laboratories was more than ten times better than the interlaboratory spread of results in all cases except for Pu-238.

2.19 Isotope dilution mass spectrometry is a physical method of measurement and not a chemical method. It derives its powerful potential from that character. However the potential of isotope dilution mass spectrometry does not obviate the need for careful execution of each step in the procedure.

2.20 The introduction of calibrated spikes will make tracer calibration unnecessary and significantly reduce the analysis time.

RECOM: See par. 2.12, page A-26

3. Other topics

3.1 SUP-isotope ratio data

RECOM: A strong recommendation is made to ET for graphical presentation of spike (SUP) isotopic data[2].

3.2 Outlier selection

RECOM: The ET is recommended to apply laboratory-oriented criteria rather than statistics generated criteria on outlier selection[3].

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[1] see Vol. II /9/

[2] see Chapt. 5.2 of this Report

[3] for principle reasons not possible

3.3 Correction for Pu-241 decay

Some participants have not made appropriate corrections for Pu-241 decay. Different values for half lives have been used.

RECOM: Pu 241 decay corrections should use the IAEA value for half life of 14.4 ±0.2 a (CBNM uses 14.33 ± .02 a; NBS uses 14.34 ±0.04 a.)

Pu isotopic measurements should be done within a week after Pu/Am separation.

3.4 Correction for radioactive decay in general

RECOM: Any isotopic analysis involving radioactive nuclides should carry the date of the measurement. When comparing data a correction for radioactive decay must be made.

3.5 Pu-241 evaluation in IDA-80

RECOM: The ET should correct the 241 data to the day of the measurement (PRIORITY 2)[1].

3.6 Determination of Pu-238

With both mass and alpha spectrometry similar accuracies can be attained for the determination of Pu-238 abundances.

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[1] see Chapt. 7.2 of this Report

Specific Contributions of Meeting Participants*

1. R. BERG, WAK

Recommendations:

- Use of certified spike Pu-242 or Pu-244
- Pu-isotopic reference materials wanted:

Pu-239		Pu-242		Pu-244
1	:	1	:	1
10	:	1	:	1
100	:	1	:	1
1000	:	1	:	1

- Metal spike supply
- Certified unspiked R-solutions
- Further studies on
    - . isotope fractionation
    - . instrument linearity
    - . mass discrimination

      i.e. detection, control and identification of origin (source, detector)
- Supply of desirable, certified spike solutions for U and Pu.

2. J. CESARIO, CEA

Linearity of the isotope fractionation effect versus mass difference is not fully established by experiment. Consequently use, each time available, a reference material with the same mass difference as in the sample, to avoid unprecise extrapolation (or interpolation).

3. D. CRAWFORD, NBL

The upcoming meeting of the SALE Programme Steering Committee will be addressing the need for participation samples of U/Pu containing fission products for participants involved in reprocessing analyses.

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*These contributions were made available to the organizers of the meeting in a written form.

4. P. DE BIÈVRE, CBNM

Use of long published metallic spike technique is not as extensive as expected because of erroneous but widely accepted opinions that

- U-233 gives better accuracy
- the higher the isotopic enrichment the better the accuracy of measurement
- metallic spike would be difficult to dissolve
- sludge in input solutions would contain significant amounts of uranium and plutonium.

5. P. DE REGGE, SCK/CEN

There is a need for 1:1 Pu IRM's similar to the NBS 500 for uranium.

6. S. DERON, IAEA

6.1 Advantages and disadvantages of the metal spike procedure for verification purposes

Advantages:

- Verification of dilution is not needed
- Witnessing is possible
- Use of common spike by both operators and inspectors
- Chemical equilibrium
- Simple sample preparation
- Simplified shipment

Difficulties:

- Availability of tracer
- Time of preparation
- Cost of hot cell operation

6.2 Recommended recipe for dried samples:

a) Dry samples at $\leq 90^{\circ}C$ from a solution of $HNO_3 \geq 3$ M.

b) To redissolve: simmer under reflux with a mixture of $HNO_3 \geq 7$ M HF 0.05 M at $\simeq 100-115^{\circ}C$, possibly not in glass.

7. S. DERON, E. KUHN

   Proposals for recommendations:

   a) It is proposed to the ESARDA-WGDA
      - to use the results of IDA-80 to work out optimized procedures for sample preparation, spiking, chemical treatment and the final mass-spectrometric measurement,
      - to present its conclusions from IDA-80 to ISO and to also comment on an ISO-procedure, presently undergoing approval.
   b) Certified tracers, including mixed U- and Pu-tracers, in solution and metal alloy form, should remain or become available, and their use as 'common spike' is recommended.
   c) A certified isotope mixture of Pu-239/Pu-244 or Pu-239/Pu-242 should be available.
   d) A continuous quality control programme for isotope dilution analysis, open to international participation, should be established.
   e) To further improve mass spectrometry measurements special attention should be paid to the ongoing developments in internal calibration techniques.

8. H. KIRCHNER, KFA Jülich

   There is a need for an IRM with U-233 : U-235 : U-238 ratio 1:1:1.

9. C.N. RAMSDEN, BNFL

   Recommendation: isotope fractionation control must be improved, if external tracers are to be used.

Appendix B

IDA-80 Comments

by

R. Boden and P. De Regge
SCK/CEN Mol, Belgium

IDA 80 - COMMENTS BY R. BODEN AND P. DE REGGE*

1. Remarks concerning the own experience of S.C.K./C.E.N. in the programme

The following experience is a perfect illustration of the usefulness of interlaboratory measurement evaluation programmes for identifying error sources in the measurement procedures of the participating laboratories. Our results for the isotopic analyses of the samples BU and RU and also the measurement of the ratios 240/239 and 241/239 in the samples BS and RS show an average deviation of ± 0.13 % with a maximum of 0.39 %. The measurement of the ratio 242/239 in the samples BS, RS and AS was off by about 0.61 to 0.75 % or more than five times the expected error on this measurement. Careful investigation of the data and additional calibration measurements on the mass spectrometer permitted to understand the causes of the discrepancy observed.

The calibration of the mass spectrometer was formerly carried out using the NBS IRM 947. The results can be expressed as follows :

it was observed that the true ratio (certified by NBS) was obtained by multiplication of the measured ratio by a mass discrimination factor such that

$$({}^{240}/_{239})_{\text{true}} = ({}^{240}/_{239})_{\text{measured}} \times 1.00093$$

$$({}^{241}/_{239})_{\text{true}} = ({}^{241}/_{239})_{\text{measured}} \times 1.00186$$

and it was concluded that a mass discrimination factor of 0.00093/amu could be used for the measurements made with the DALY detector.

In reality however this observed factor was the result of a combination of the true mass discrimination factor with an amplifier non-linearity correction which is dependent on the ratio measured. This was discovered during our investigations to identify the source of the discrepancies observed in IDA-80, using carefully blended batches of 239, 240 and 242 enriched isotopes. The true mass discrimination factor was 0.0026/amu and the non-linearity correction was $(1.0017)^{-1}$ for a ratio of about 0.24 and $(1.0028)^{-1}$ for a ratio of about 0.05. In fact a better interpretation of

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*Received October 24, 1984

our measurements on the NBS IRM-947 is as follows :

$$({}^{240}/_{239})\text{true} = ({}^{240}/_{239})\text{measured} \times \frac{1.0026}{1.0017}$$

and

$$({}^{241}/_{239})\text{true} = ({}^{241}/_{239})\text{measured} \times \frac{1.0052}{1.0028}$$

Because most of the plutonium batches currently measured have isotopic compositions similar to NBS IRM-947 this was not noticed even by participating in interlaboratory exercices. This remained also unnoticed when comparing isotopic dilution measurement with other techniques as long as the ^{242}Pu spike was calibrated in our laboratory, because the exact reciprocity of the errors made in the spike calibration and the isotopic dilution analysis. In IDA-80 however we used ^{242}Pu spike solution certified by another laboratory (CBNM) and the unknown systematic errors did not cancel anymore. The results however did not identify the source of the error. Only a systematic investigation using blended isotopes was able to show its exact nature. Simultaneously careful measurements of the DALY detector linearity using the NBS uranium series of isotopic reference materials confirmed the results found for the plutonium. Recalculating our measurements for the IDA-80 samples with due corrections for non-linearity and mass discrimination results in a decrease of the differences with respect to the certified values from the range 0.61-0.75 % to a fair 0.18 % for BS, 0.11 % for RS and 0.24 % for AS. The major contribution to the discrepancy has thus been identified and corrected for. The remaining difference is still worth some further investigation but falls within the expected performance. For the samples AS other considerations are to be taken into account (see section 2).

2. Remarks concerning the certified values

It is expected that the U/Pu ratio in the samples BU, BS and AS remains constant. The same is true for the samples RU and RS. It can be seen from Table I that this is not the case when those ratios are computed from the certified values, particularly the sample AS is different from BU and BS. This should be further investigated and reported in the final document.

Table II shows the plutonium results for the BU, BS, RU and RS samples and their respective standard deviations. It can be seen that the single standard deviations on the value for BU and RU do not include the corresponding certified values for BS and RS and vice versa. This is very surprising. Apart from the systematic effect in the two groups (BU, BS) and (RU, RS), the single standard deviation seems to be underestimated and should preferably include both values since no reason exists for any difference in Pu concentration between RS and RU or between BU and BS. The differences however are small and insignificant with respect to the requirements put on the certified values.

It can be remembered that the requirement for the certified value was defined as such that its uncertainty should be smaller by a factor of five to ten than the observed interlaboratory spread in the exercise. The Tables III and IV show that they conform to this characteristic in most cases.

P. DE REGGE

Table I Uranium/Plutonium Ratios as calculated from the characterisation values

Sample	Ratio	Difference with respect to sample BU
BU	284.87	0
BS	285.10	+0.08 %
AS	284.04	-0.29 %
		Difference with respect to sample RU
RU	214.91	0
RS	215.28	+0.17 %

Reply from the organizers to point 2 Table I:

The uncertainties of the U/Pu ratios are the following:

BU : ±0.27%　BS : ±0.25%　AS : ±0.31%
RU : ±0.26%　RS : ±0.25%

Consequently all U/Pu ratios are within the uncertainty ranges.

Table II Comparison of certified Plutonium Results

BU 3.0042 +- 0.0075 RU 3.3354 +- 0.0081

BS 3.0013 +- 0.0070 RS 3.3312 +- 0.0078

Units are E-8 molar with 3 sigma intervals

However when looking at 1 sigma intervals the following is observed

BU	BS	RU	RS
3.0067		3.3381	
3.0042		3.3354	
	3.0036		3.3338
3.0017		3.3327	
	3.0013		3.3312
	2.9987		3.3286

The 1 sigma intervals on BU and RU do not include the certified value of BS as is normally expected .

Reply from the organizers to point 2 Table II:

One should not compare 1$\overline{s}$ values (3$\overline{s}$ was given), but 1s. The latter are 2.45 times larger than those displayed in the graph.

Table III Comparison of Interlaboratory Spread with the Uncertainty on the Certified Value

Ratio Determinations (values given in percent)

Sample	Uranium			Plutonium		
		Spread	3sigma		Spread	3sigma
BU	234/238	3.93	1.12	238/239	2.60	0.83
	235/238	0.43	0.087	240/239	0.22	0.11
	236/238	2.26	0.72	241/239	0.61	0.17
				242/239	1.25	0.27
RU	234/238	6.07	1.09	238/239	1.42	2.45
	235/238	0.50	0.089	240/239	0.21	0.085
	236/238	8.26	1.47	241/239	0.70	0.35
				242/239	1.32	0.21

Table IV Comparison of Interlaboratory Spread with the Uncertainty on the Certified Values

Isotopic Dilutions (values in percent)

Sample	Uranium		Plutonium		
	Spread	3sigma		Spread	3sigma
BU conc	0.72	0.093	conc	0.83	0.25
BS 33/38	0.55	0.067	42/39	0.29	0.12
RU conc	0.48	0.10	conc	1.25	0.24
RS 33/38	0.34	0.084	42/39	0.37	0.11
AS conc	0.47	0.071	conc	0.54	0.30
AS I 5/8	0.58	0.026	42/39	0.37	0.099
AS II 5/8	0.51	0.049	42/39	0.74	0.21
AS IV 5/8	0.67	0.047	42/39	0.39	0.13
AS VI 5/8	0.27	0.037	42/39	0.21	0.13

Reply from the organizers to point 2 Tables III - IV: correct